PHYSICAL REVIEW VOLUME 171, NUMBER 3 15 JULY 1968

Photothermal Ionization and Photon-Induced Tunneling in the Acceptor Photoconductivity Spectrum of Semiconducting Diamond

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(Received 21 February 1968)

Structure has been observed in the photoconductivity spectrum of semiconducting diamond at energies *below* the ionization threshold. Photoconductivity maxima in this spectral region have been found to coincide exactly with maxima in the absorption spectrum associated with transitions to excited states of the aluminum acceptor center (ionization energy=0.373 eV). In general, the acceptor spectrum is better resolved in these photoconductivity measurements than in absorption measurements on the same specimen, and this is particularly true for synthetic semiconducting diamonds in which the acceptor concentration is very high. Measurements in the temperature range 4 to 150°K have shown that a two-stage process is predominantly responsible for the appearance of the excited-states spectrum in photoconductivity: optical excitation of holes from the ground state to these excited states, followed by thermal excitation into the valence band. This process is referred to as "photothermal ionization." An investigation of the electric field dependence of this process has shown that the only effect is a broadening of the spectrum at high fields which are comparable in magnitude with the binding field experienced by a hole in an excited state. At temperatures close to 4°K, where the thermal contribution is negligible, residual structure can still be observed which is specimen-dependent, and the features may appear as either minima or maxima superimposed on the low-energy tail of the photo-ionization continuum. This low-energy tail is presumably due to direct photoexcitation of slightly perturbed acceptor centers, and minima can appear on this tail because of the strong competitive absorption to the excited states. However, in many specimens, tunneling from the excited states appears to be possible, and the features are then observed as maxima. This picture is further substantiated by the fact that in those diamonds for which tunneling does not normally occur, it can be induced by simultaneously illuminating the crystal with radiation of energy lying within the photoconductivity continuum. This increases the number of ionized centers present, and so increases the probability of tunneling.

I. INTRODUCTION

MEASUREMENTS on the photoconductivity associated with donor and acceptor impurities in Si, Ge, and the II-VI binary compounds have been widely reported in the literature, and the photoconductive properties of these semiconductors are reviewed, for example, by Bube[1] and by Moss.[2] The photoconductivity spectra are characterized by a threshold close to the ionization energy of the impurity, and a continuum at higher energies. The activation energies of Group-III and Group-V impurities in Ge are typically around 10 to 15 meV and in Si around 40 to 60 meV, and the corresponding photoconductivity thresholds are in the far infrared, around 100 μ for Ge and 25 μ for Si. Because the thermal ionization of the impurity centers must be relatively small in order to investigate the photo-ionization, it is necessary to work at temperatures below 20°K for Si and below 5°K for Ge, and in fact, most measurements have been made at liquid-helium temperatures. Naturally occurring p-type diamond is the widest band-gap semiconductor currently available and contains virtually no dispersed impurities except the aluminum acceptors (typically 5×10^{16} cm^{-3}) and deep lying nitrogen donor centers.[3] Because of its large band gap (5.49 eV), the energy levels produced in the forbidden gap by the various defects are also very large, and the associated phenomena occur at easily accessible temperatures and at optical wavelengths where relatively intense sources and sensitive detectors are available.

Hardy, Smith, and Taylor[4] have measured the infrared photoconductivity of a natural semiconducting diamond at 80°K. They show that the photoconductive response is zero for energies less than 330 meV, then rises rapidly to a continuum extending well beyond 0.9 eV. The threshold energy agrees fairly well with the ionization energy of ~0.37 eV determined by earlier workers from electrical-conductivity measurements.[5,6] Minima were observed on the photoconductivity continuum corresponding to the phonon-assisted maxima observed in absorption,[7] and were considered to be due to the phonon-assisted capture of holes in the valence band to bound states of the acceptor center.

In a recent series of investigations, some of the optical and electrical properties of synthetic semiconducting diamond have been measured on specimens having a large range of neutral acceptor concentrations (10^{17} to 10^{19} cm^{-3}). The infrared absorption was shown to be very similar to that for natural semiconducting diamond although the perturbing effect of the high con-

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[1] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., London, 1960).

[2] T. S. Moss, Rept. Progr. Phys. **28**, 15 (1965).

[3] P. J. Dean, E. C. Lightowlers, and D. R. Wight, Phys. Rev. **140**, A352 (1965).

[4] J. R. Hardy, S. D. Smith, and W. Taylor, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962*, edited by A. C. Stickland (The Institute of Physics and The Physical Society, London, 1962), p. 521.

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

[6] P. T. Wedepohl, Proc. Phys. Soc. (London) **B70**, 177 (1956).

[7] S. D. Smith and W. Taylor, Proc. Phys. Soc. (London) **79**, 1142 (1962).

centration of acceptor centers in the synthetic material resulted in much larger spectral line widths.[8] The ionization energy of ~ 0.35 eV determined electrically for synthetic specimens with low neutral acceptor concentrations was very close to the value 0.373 eV obtained for a natural diamond, but for much higher concentrations electrical transport became dominated by impurity conduction (hopping transport).[9]

Photoconductivity measurements on the same set of diamonds yielded two unexpected results. Firstly, with the exception of slight broadening of the fine structure associated with the phonon-assisted transitions, the photoconductive response was virtually the same over the whole range of neutral acceptor concentrations available, and practically identical with that previously observed for natural diamond.[4] Secondly, photoconductivity maxima were observed in the spectrum at energies *less* than the ionization energy which corresponded exactly with the maxima in the absorption spectrum. These maxima in the absorption spectrum are due to transitions from the ground state to excited states of the acceptor center, and such transitions cannot directly contribute to the photoconductivity. A repeat of Hardy, Smith, and Taylors's measurements showed that these features below the ionization energy are also present in the photoconductivity spectrum of natural diamond, and so the phenomenon is not one which is peculiar to synthetic diamond.

A similar behavior has recently been reported by Lifshitz and Nad',[10] for germanium doped with Group-III impurities. These authors conclude that a two-stage process is responsible for the appearance of structure below the ionization energy: optical excitation to an excited state of the impurity center followed by either (i) electric field induced tunneling into the valence band or (ii) thermal excitation into the valence band.

The low ionization energies involved necessitated cooling the specimen to near-helium temperatures and an investigation of the temperature dependence was not attempted. In a later investigation Sidorov and Lifshitz[11] observed that the intensities of different peaks, and also the ratio of these intensities, were dependent on both temperature and electric field, but they considered, because of the very low impurity concentration employed (3×10^{14} cm^{-3}), that substantial hopping transport was unlikely. From theoretical considerations Kogan and Sedunov[12] conclude that thermal excitation is the most likely process to explain the results of Lifshitz and Nad', and introduce the terminology "photothermal ionization."

Because of the much higher ionization energy this phenomenon is much more easily studied in diamond, and following the detailed series of measurements on both natural and synthetic semiconducting diamond to be reported in this paper we are able to reach the following conclusions. The appearance of structure below the ionization energy is indeed due to the two-stage process photothermal ionization. At low temperatures, when there is no contribution from photothermal ionization, the excited-state structure can be displayed by simultaneously irradiating the specimen with "bias light," the energy of which lies within the photoionization continuum. This is attributed to a tunneling photocurrent due to the hopping of holes between adjacent neutral and ionized centers. This process is much more likely in the excited states where the wavefunction overlap is much larger than in the ground state, and is substantially enhanced when the number of ionized centers is increased by the action of the bias light. Finally, because the photothermal ionization is a selective process, the excited-states spectrum is generally better defined in photoconductivity than in absorption. It is felt, therefore, that the techniques of photothermal ionization and photon-induced tunneling to be described may well represent the most satisfactory method of investigating new semiconductors.

II. EXPERIMENTAL

All the semiconducting diamonds synthesized by General Electric (G.E.) that have been made available at the present time contain about 150 ppm of aluminum[9] and the neutral aluminum acceptor concentration varies from about 10^{17} cm^{-3} in the very pale blue specimens to 10^{19} cm^{-3} in the dark blue crystals.[8,9] The linear dimensions of the various synthetic diamonds available were between 0.3 and 1.0 mm. Each specimen was mounted in a thin filament of Araldite epoxy resin on a fused silica disk $\frac{5}{8}$ in. in diameter. Two electrical pressure contacts consisting of 0.2-mm-diam tungsten wires etched to a fine point were arranged on the diamond using a jig under a binocular microscope, and the tungsten leads were finally cemented to the silica disk using Saureisen No. 29 low-expansion ceramic cement. This assembly was then screwed to the copper nose piece of the optical cryostat. The much larger natural diamonds were fastened directly to the cryostat using G.E. low-temperature varnish and a thin piece of mica or cigarette paper for insulation, and the surface of the diamond was coated with silver paint except for a small strip 0.5 mm wide between the probles. Alternatively, contacts were electron-beam welded on to the diamond using a gold-tantalum-aluminum alloy (90% Au, 9% Ta, 1% Al) supplied by Westinghouse Research Laboratories. These contacts were near-Ohmic and more electrically stable than the silver-paint contacts, and so were less noisy

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[8] A. T. Collins, P. J. Dean, E. C. Lightowlers, and W. F. Sherman, Phys. Rev. **140**, A1272 (1965).

[9] E. C. Lightowlers and A. T. Collins, Phys. Rev. **151**, 685 (1966).

[10] T. M. Lifshitz and F. Ya. Nad', Dokl. Akad. Nauk SSSR **162**, 801 (1965) [English transl.: Soviet Phys.—Doklady **10**, 532 (1965)].

[11] V. I. Sidorov and T. M. Lifshitz, Fiz. Tverd. Tela **8**, 2498 (1966) [English transl.: Soviet Phys.—Solid State **8**, 2000 (1967)].

[12] Sh. M. Kogan and B. I. Sedunov, Fiz. Tverd. Tela **8**, 2382 (1966) [English transl.: Soviet Phys.—Solid State **8**, 1898 (1967)].

at higher temperatures. In all cases the electrical insulation between the diamond and the cold finger was $>10^{12}\ \Omega$.

A conventional helium cryostat was used for the majority of the measurements; the external window was CaF_2 and an intermediate window of quartz, cooled to liquid-nitrogen temperature, absorbed wavelengths above 4.3 μ. With liquid nitrogen in the radiation shield a wide range of specimen temperatures, all of which could be maintained for many hours at a time, was obtained using liquid helium, oxygen, and nitrogen solidified by pumping liquid nitrogen and oxygen, and various organic liquids held at their melting points (e.g., *n*-pentane; 143°K). At temperatures above 150°K the increasing dark conductivity of the sample makes photoconductivity measurements impossible. For a more rapid investigation of the temperature dependence of various phenomena, an Air Products and Chemicals "Cryotip" refrigerator was used in which the cooling is obtained by a Joule-Thomson expansion of various gases, generally helium, hydrogen, and nitrogen. Temperatures in both cryostats were measured using copper-Constantan or chromel-Constantan thermocouples with the reference junction at ice temperature, and monitored on a digital voltmeter. For greater accuracy the thermoelectric emf was measured to $\pm 1\ \mu V$ on a Cambridge Instruments 5-decade potentiometer.

All the measurements reported here have been made using either a modified Grubb-Parsons S3 monochromator with double pass through a 6-in. 60° LiF prism or a modified Grubb-Parsons GM2 grating monochromator with a 7500 lines per inch grating blazed at 3.5 μ. Unwanted orders were suppressed using either a Ge filter (1.8–3.5 μ) or a 2.4-μ long-wavelength-pass interference filter. Radiation from the monochromator was focused onto the diamond using a 4:1 image reduction. When investigating the photon-induced tunneling, a split-beam arrangement enabled radiation from two monochromators to be focused onto the diamond simultaneously. For this measurement the GM2 was used to supply the exciting radiation and the "bias light" was provided by a Perkin-Elmer model 99 monochromator with double pass through a NaCl prism. In all cases a light modulation frequency of either 12 or 13 Hz was used and the signal from the diamond amplified using a Perkin-Elmer model 107 amplifier, rectified by a mercury-wetted relay switching in phase with the light chopper, and displayed on a Honeywell chart recorder. The resistance of a natural diamond is extremely high ($>10^{10}\ \Omega$) at temperatures below 150°K; the electric field is therefore applied to the diamond via a 100-MΩ resistor across which the photoconductivity signal is detected. An electrometer valve cathode follower mounted as close to the specimen as possible is used to transform the impedance to a value suitable for the main amplifier.

Because of the problems associated with normalizing the photoconductivity spectrum against the source spectrum, especially in the regions of atmospheric water vapor absorption, the GM2 monochromator has recently been converted to split-beam output. Half the radiation from the exit slits is directed onto a thermocouple and half onto the diamond, the signals are amplified separately, and the signal in the thermocouple channel is used to servo-control the gain of the sample channel. The output is therefore the ratio of the two signals, and, since the thermocouple has approximately uniform sensitivity throughout the spectral region, represents the photoconductivity response independent of source, filter, and monochromator characteristics or atmospheric absorption. This method of compensation is preferred to that used by Ruffino and Charette[13] who directed the (unchopped) radiation from the monochromator *alternately* onto the sample and the thermocouple, since for this latter method it is necessary to provide a constant-temperature reference source for the thermocouple to avoid random fluctuations of the signal.

III. RESULTS AND DISCUSSION

Some of the spectra presented in this section have been normalized, either electronically as described or manually, point by point. For these diagrams the ordinate axis is labeled "photoresponse." Other data have been obtained using single beam detection and the results taken directly from the chart recorder trace; for these diagrams the ordinate axis is labeled "photocurrent."

A. Photothermal Ionization

A low-resolution spectrum, recorded at 120°K, of the structure below the ionization energy for natural diamond SA65C is shown in Fig. 1. Close examination of the structure shows that the maxima in the photoconductivity coincide exactly with maxima in the absorption spectrum. This is illustrated in Fig. 2 where the estimated underlying continuum of Fig. 1 (shown dotted) has been subtracted, and the replotted spectrum is compared with the absorption spectrum in this same spectral region for another natural diamond, A100. In addition, it should be noted that the closer the peak position to the photo-ionization continuum, that is the smaller the amount of thermal energy required to complete the ionization process, the greater is the peak intensity in the photoconductivity spectrum relative to that observed in the absorption spectrum. This is exactly what would be expected for the two-stage photothermal ionization process.

In order to show more clearly that the photothermal process is the correct mechanism to explain the observed phenomena, the structure below the ionization energy has been investigated in the temperature range 5 to 150°K. Figure 3 shows this spectral region at four

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[13] G. Ruffino and J. J. Charette, Ric. Sci. **36**, 526 (1966).

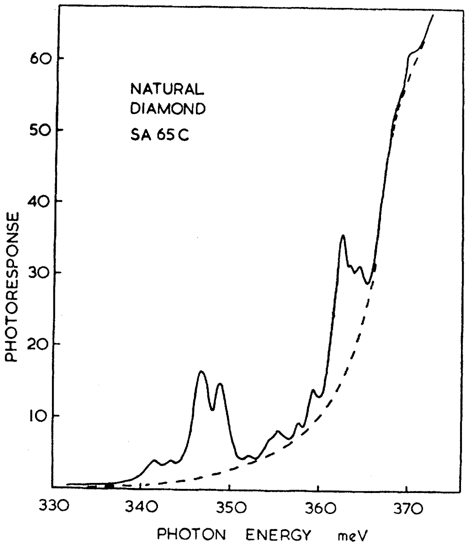

FIG. 1. Low-resolution spectrum of the photoconductivity response of a natural type-IIb diamond SA65C at energies below the ionization energy, recorded at ∼120°K. The dashed line is an estimate of the underlying continuum.

representative temperatures, 55, 63, 90, and 143°K, and the marked temperature dependence of the structure is quite clearly visible. For convenience and conciseness of discussion, attention is particularly drawn to the dominant features in both the absorption and the photoconductivity spectra, namely the multicomponent bands centered around 0.348 eV and 0.364 eV which we will call the 0.348-eV band and the 0.364-eV band. The behavior of these excited-state features in the photoconductivity spectra below 55°K is, at first, rather surprising. For some specimens, on reducing the temperature the 0.348-eV band first disappears at about 45°K and then inverts, the components appearing as *minima* on the background continuum. This is shown in Fig. 4(A) where the spectra at ∼0.348 eV are compared at 13 and 66°K. To understand this phenomenon it is first necessary to consider the origin of the background continuum. In an "ideal" semiconductor at low temperatures the absorption, and therefore the photoconductivity, at energies below the ionization energy of the acceptor center should be zero, and should cut on sharply as soon as the activation energy is exceeded. In practice the thresholds are quite diffuse due, presumably, to the existence of nontypical centers, and although the photoconductive response drops off quite quickly for energies below the ionization energy, some photocurrent is still measurable at much

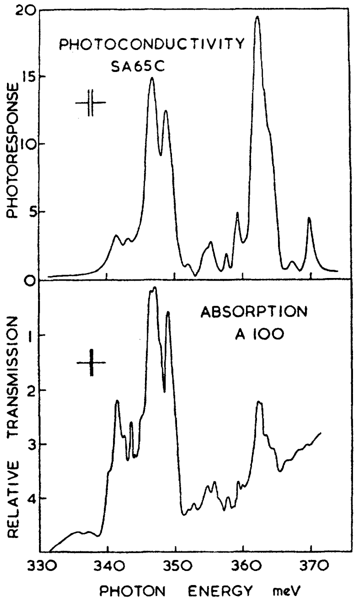

FIG. 2. Comparison of the photoconductivity structure for natural type-IIb diamond SA65C at ∼120°K with the transmission spectrum of another natural type-IIb diamond A100 at ∼80°K. The structure in the photoconductivity spectrum has been obtained by subtracting the underlying background as indicated in Fig. 1.

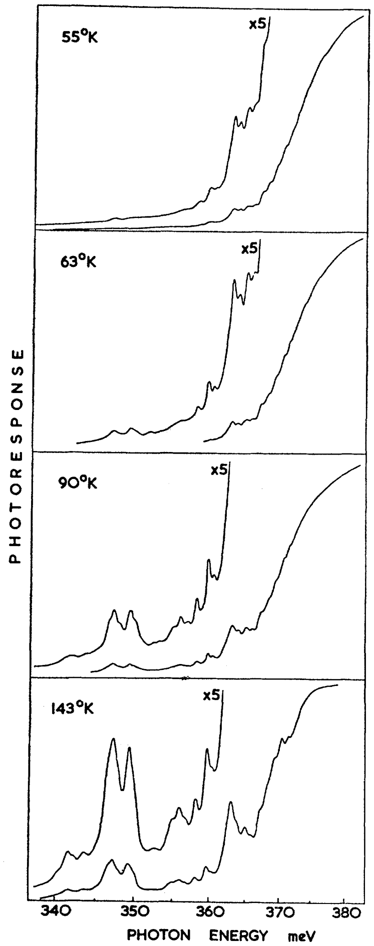

FIG. 3. Photoconductivity response of a natural type-IIb diamond SA65C at energies below the ionization energy, recorded at four different temperatures (effective slit width ∼0.4 meV).

lower energies. For many semiconductors it is found that the best agreement between the ionization energy deduced from photoconductivity measurements and from other data is obtained if the energy is taken, not at some arbitrary threshold, but at the point where the photoresponse has risen to 50% of the maximum.[14] Because the edge is diffuse, in the absence of any photothermal effects strong absorption systems of the sample (e.g., excited-state transitions) will appear as minima on this subionization energy background continuum. Thus, on cooling, the excited-state features will invert when their photothermal contribution is frozen out. This occurs at about 45°K for the 0.348-eV band which is ~25 meV from the valence band edge and at about 15°K for the 0.364-eV band which is ~9 meV from the band edge.

This inversion of the excited-state features is not observed in all diamonds, nor indeed for all parts of the same diamond. In some crystals, notably strongly absorbing synthetic diamonds in which both the neutral and ionized acceptor concentrations are high, the 0.348-eV band appears as a broad positive hump on the background continuum even at temperatures as low as 4°K. For some natural diamonds a combined effect is observed with sharp minima at 0.347 and 0.349 eV superimposed on the broad positive peak centered at 0.348 eV. These two different effects are illustrated in Fig. 4(B), alongside the third possibility of complete inversion shown in Fig. 4(A). The positive contribution to the excited-states photoconductivity at low temperatures is thought to be chiefly due to tunneling of holes from the excited states of acceptor centers to neighboring ionized centers, and is most likely to occur in heavily doped synthetic crystals, and at localized regions of high impurity concentration in natural diamond. It is also possible that in some cases free holes could be produced by transitions to perturbed valence-band states within the forbidden gap in regions of high impurity concentrations or lattice defects. In either case, the acceptor centers contributing to the positive photoresponse are likely to be perturbed and the resulting structure would not be expected to be well resolved. In natural diamond there is also a large proportion of unperturbed centers which cause the competitive absorption in this region just like that observed in the absence of tunneling [Fig. 4(A), 13°K] and so the *absorption* of the *unperturbed* centers is seen superimposed as minima on the positive hump in the spectrum due to *tunneling* from *perturbed* centers. For synthetic diamond, on the other hand, the perturbed centers predominate and only the positive hump is observed. Tunneling from the excited states of unperturbed centers can be observed if the ionized acceptor concentration is sufficiently increased by simultaneously illuminating the specimen with radiation which has an energy lying within the photo-ionization continuum, and this phenomenon is further discussed in Sec. III D.

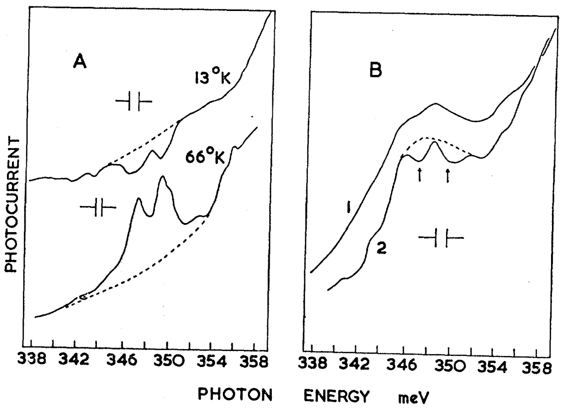

Fig. 4. Photoconductivity response in the neighborhood of the 0.348-eV band demonstrating the behavior of different specimens at low temperature. (A) (diamond SA65C) demonstrates that when there is no tunneling from the excited states the peaks appear as *minima* at low temperatures (e.g., 13°K). The 66°K spectrum in which the excited-state features appear as maxima is included for comparison. (B) curve 1 shows the behavior for a synthetic semiconducting diamond GE67AL1 at 4°K which contains mainly perturbed centers and the excited-state structure appears as a broad positive hump due to tunneling from the excited state; curve 2 is for a natural IIb diamond SA65E which exhibits some tunneling giving rise to a broad positive hump with the features due to competitive absorption by unperturbed centers superimposed as sharp minima (indicated by arrows). The zeros of the spectra have been displaced for the sake of clarity.

At higher temperatures the structure that appears in the excited-state region is predominated by the photothermal contribution. In Fig. 5 the areas of the 0.348- and 0.364-eV bands, measured on two different areas of diamond SA65C, are plotted as a function of temperature. For one part of the diamond complete inversion of the spectrum is obtained at low temperatures, but for the second arrangement of the contacts the alternative response described earlier is evident. Because the photoconductive sensitivity of the diamond also varies with temperature the areas have, in all cases, been measured relative to the continuum photoconductivity at 560 meV. If one applies Fermi-Dirac statistics to the photothermal ionization process, treating the excited states as further shallow levels, then a straightforward calculation yields the temperature dependence of the effect as

$$\sigma(T)=A+B/(C+\exp\Delta E/kT).$$

In the derivation of this expression the constant A has been included to take into account the fact that $\sigma(0)\neq 0$, and the constants B and C involve geometry, light intensity, absorption cross section, number of acceptors, and hole lifetimes in the excited state and the valence band, and cannot be explicitly calculated. The energy ΔE in the exponential factor is the distance between the excited state and the valence-band edge.

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[14] T. M. Lifshitz, F. Ya Nad', and V. I. Sidorov, Fiz. Tverd. Tela. 8, 3208 (1966) [English transl.: Soviet Phys.—Solid State 8, 2567 (1967)].

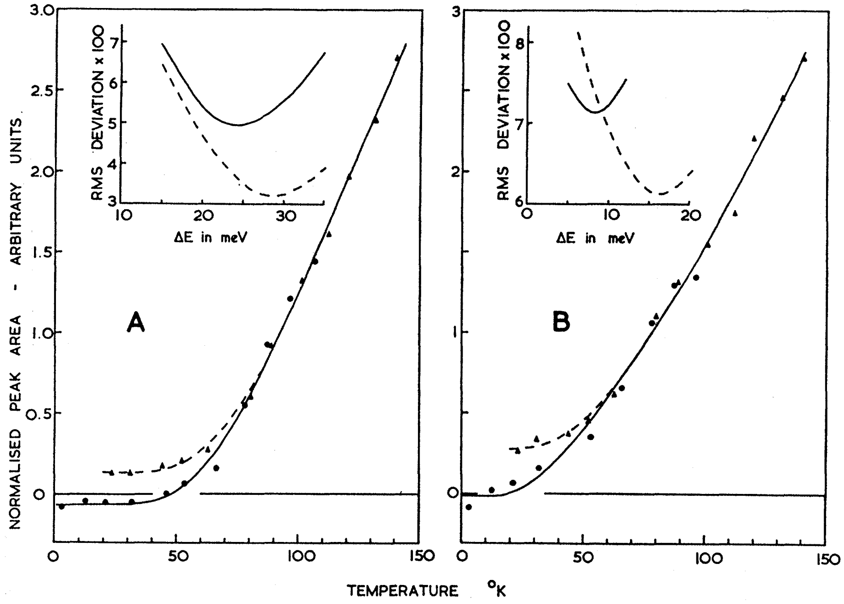

FIG. 5. Temperature dependence of the photothermal ionization of (A) the 0.348-eV band and (B) the 0.364-eV band for diamond SA65C with two different contact arrangements. The measured areas under the excited-state peaks are denoted by circles for the case when there is no tunneling and by triangles when there is a contribution from tunneling. The computed best fits to these data are represented by the continuous and dashed curves, respectively. The insets in each diagram show the rms deviations between the computed curves and experimental points plotted as functions of energy ΔE, the continuous curves being for the nontunneling case, as before. The value of ΔE for which the rms deviation is a minimum is used to calculate the best fit in the main diagram.

Values of $\sigma(T)$ have been measured for the 0.348- and 0.364-eV bands as a function of temperature between 5 and 150°K. At higher temperatures the noise due to the increasing dark conductivity of the specimens makes further measurements impossible. After drawing in the estimated underlying continuum, the areas of the 0.348- and 0.364-eV complexes (each consists of at least four components) were taken as a measure of $\sigma(T)$ and were determined for several different temperatures. This was investigated for two different contact arrangements of diamond SA65C, one which exhibited tunneling at low temperatures [and so $\sigma(T)$ stayed positive] and the other which did not exhibit tunneling [and so the sign of $\sigma(T)$ reversed at low temperatures].

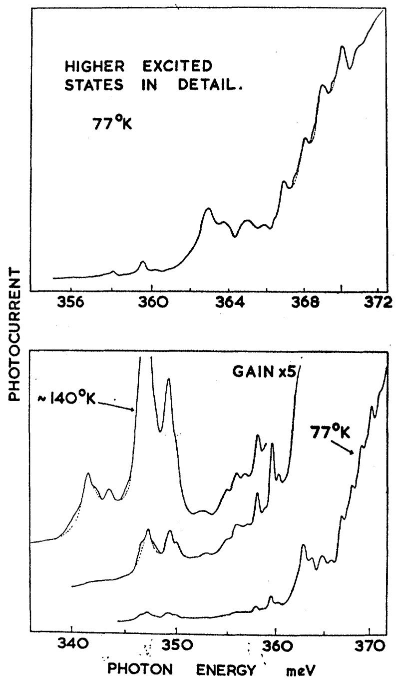

FIG. 6. High-resolution spectra (effective slit width ~0.3 meV) of the photoconductivity in the photothermal-ionization region at 77 and 140°K for a natural type-IIb diamond SA65C.

The curves through the experimental points in Fig. 5 have been computed using a least-squares fit by adjusting the values of A, B, and C in the above expression for different values of ΔE. The root-mean-square (rms) deviations between the calculated and experimental values of $\sigma(T)$, plotted as functions of ΔE, are shown in the insets in Fig. 5. The appropriate value of ΔE to obtain the best possible curves through the experimental points is obviously that for which the rms deviation is a minimum. When tunneling contributions are present (the dashed curves in Fig. 5) the term A in the above expression is no longer constant, but is also a function of temperature, and under these conditions the true significance of the value obtained for ΔE is not clear. However, when there is no tunneling at low temperatures, the value of ΔE which gives the best fit to the data is expected to be the energy difference between the valence-band edge and the mean energy of the excited-state complex in question. It can be seen from the insets in Fig. 5 that the appropriate values of ΔE for these excited-state complexes are, respectively, 24.5 and 8.5 meV. The mean energies of these excited states are, respectively, 348 and 364 meV above the acceptor ground state. Summing the two appropriate energies leads to the value 372.5 meV, in each case, for the ionization energy of the acceptor center. This value is seen to be in excellent agreement with the value of 373 meV determined by electrical conductivity measurements.[9]

When tunneling occurs the best fits to the data are obtained by using the values $\Delta E = 29$ meV for the 0.348-eV band and $\Delta E = 16.5$ meV for the 0.364-eV band. It can be seen from Fig. 5 that, using the four quoted values of ΔE for the relevant sections of the data, the calculated curves are in close agreement with the experimental points in all cases. Thus it is felt that the proposed mechanism of photothermal ionization is conclusively established.

Figure 6 shows the photothermal-ionization region in more detail and at high resolution. This method of studying the acceptor spectrum has the advantage that the relatively weak transitions to bound states close to the valence band are far more prominent in photoconductivity than in absorption. The complete spectrum from 335 to 373 meV, and also the region 356 to 373 meV shown on an expanded scale in the top diagram, were obtained at liquid-nitrogen temperature. The low-energy section of the spectrum in the bottom diagram was obtained at ~140°K to emphasize the features in the neighborhood of the 0.348-eV band. For reasons to be discussed later, the electric field used for this run was ~1.25 kV/cm. It can be seen from Fig. 6 that there are several more features in the acceptor spectrum than have previously been reported in the absorption spectrum. However, we have recently remeasured the absorption spectra at 5 and 77°K in a natural diamond SA67F of exceptional optical quality and these results are shown in Fig. 7. The diamond had two quite distinct regions, one very much more strongly absorbing than the other. The inset at ~350 meV in the 80°K spectrum was measured through the weaker section of the crystal; the insets at ~363 meV in each spectrum were obtained using another natural diamond SA65B with an absorption coefficient intermediate between the weak and strong regions of SA67F. A comparison of the energies derived from this precision absorption study and the photoconductivity results shows that there is an exact correlation between the features observed in each spectrum.

The improvement in resolution using photoconductivity rather than optical absorption is very much more marked in the case of synthetic semiconducting diamond. With increasing neutral acceptor concentrations in doped synthetic diamonds, the sharp structure in the absorption spectrum becomes progressively broadened until at concentrations $>10^{18}$ cm^{-3} the absorption lines are no longer discernible.[8] Even at much lower neutral acceptor concentrations similar to those found in natural semiconducting diamond there is sufficient interaction between neighboring centers to produce considerable line broadening, since the *total* aluminum concentration is generally $\sim 10^{19}$ cm^{-3} with ~99.5% compensation by nitrogen donors. A comparison between the photoconductivity and absorption spectra

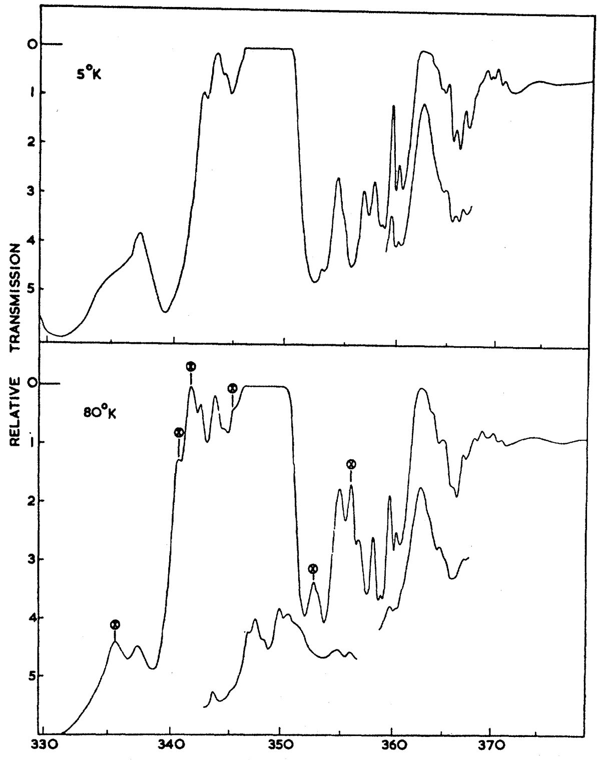

FIG. 7. Transmission spectra at 5 and 80°K for a natural IIb diamond SA67F of exceptional optical quality (effective slit width ~0.2 meV). The symbol ⊗ indicates absorption peaks in the 80°K spectrum which disappear at 5°K. The inset at ~350 meV in the 80°K spectrum represents transmission measurements through a less optically dense region of the same diamond, and the insets at ~363 meV in each spectrum were obtained with a second natural IIb diamond SA65B. These insets illustrate the features in spectral regions of high absorption.

for two aluminum-doped synthetic diamonds of similar neutral and ionized acceptor concentration ($\sim 10^{17}$ and 10^{19} cm^{-3}, respectively) is shown in Fig. 8. The photoconductivity curve has been obtained in the same way as for Fig. 2, i.e., subtracting an estimated background from the actual spectrum and replotting. It can be seen that although the absorption spectrum shows quite considerable broadening compared with a natural diamond, the photoconductivity spectrum is still quite well resolved. The photoconductivity spectrum for an extreme case of a completely opaque synthetic diamond D1002Cl is shown in Fig. 9. The resolution is very poor, but the major 0.348- and 0.364-eV peaks are still observable in photoconductivity whereas optical-absorption measurements on such a specimen are completely impossible.

The fact that corresponding features are far better defined in photoconductivity than in absorption can be explained as follows. Since the photothermal ionization is a two-stage process, the probability of a transition from an excited state into the valence band will depend, among other factors, on the lifetime of the hole in the

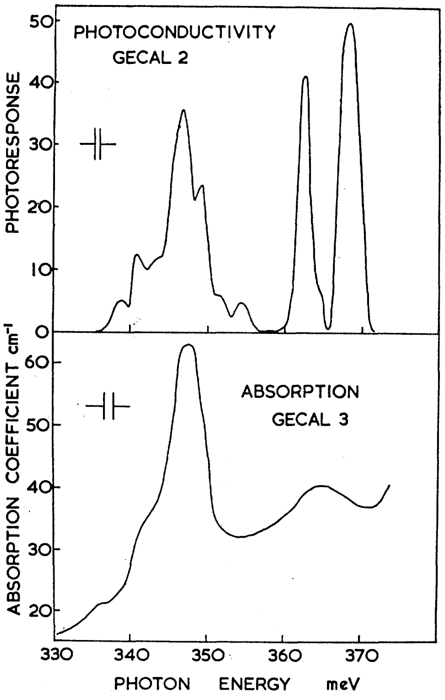

FIG. 8. Comparison of the photoconductivity structure in the photothermal-ionization region with the absorption spectrum for two almost identical aluminum-doped synthetic semiconducting diamonds GECAL 2 and 3. Both measurements were made at ~120°K.

excited state. The broad absorption spectrum in the heavily doped synthetic diamonds is attributed to a large concentration of acceptor centers perturbed by interaction with closely adjacent centers. However, because of the extremely inhomogeneous distribution of acceptor centers in synthetic semiconducting diamond it is not unreasonable to suppose that some relatively unperturbed centers will be present. The lifetime in the excited state is very much larger for a relatively isolated center than for a perturbed center, and therefore the photothermal ionization will preferentially select those centers which are least perturbed. On the other hand, absorption is a bulk effect and an average over all perturbed and unperturbed centers is obtained.

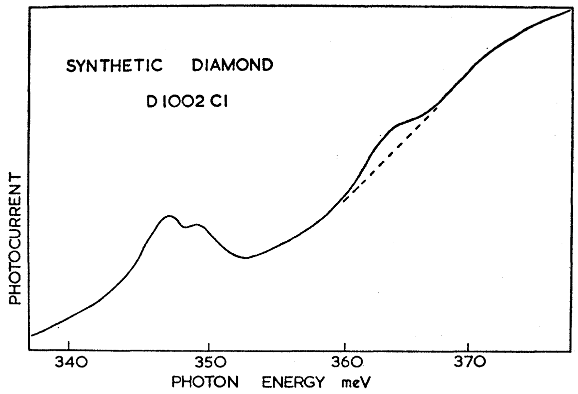

FIG. 9. Photoconductivity spectrum in the photothermal-ionization region for a very heavily doped synthetic semiconducting diamond D1002Cl, measured at 120°K. This specimen is virtually opaque to visible light.

B. Phonon-Assisted Transitions

Before considering the photon-induced tunneling effects it is of interest to examine the photoresponse at energies above the ionization energy. This region up to 650 meV is shown for diamond SA65C at 131°K in Fig. 10. Several minima are observed on the continuum, and of particular interest is the detailed sharp structure between 490 and 550 meV. This region is shown at 5 and 77°K at higher resolution in Fig. 11. Hardy *et al.*[4] suggested that these minima are due to phonon-assisted capture of holes from the valence band to bound states of the acceptor center, and showed that if the energy of the zero wave-vector phonon, 165 meV, is subtracted from the energies of the sharp minima in the one-phonon-assisted region (peaks A to P) the resulting energies coincide exactly with sharp maxima in the absorption spectrum associated with the excited states of the acceptor. Since the energy is so well defined, these features represent recoiless transitions from the valence band to the excited states of the acceptor center with the emission of the zero-momentum phonon. We have recently extended the measurements of Hardy *et al.* to about 2.2 eV and shown that phonon-assisted transitions involving ten or more phonons are readily observable. Similar measurements have been reported by Ruffino and Charette.[13] We have observed from our measurements that the phonon energy involved is not that of the Raman (zero-momentum) phonon, but has an average value, taken over ten transitions, of about 161 meV. A detailed interpretation of these phonon-assisted transitions will be published shortly in another paper.

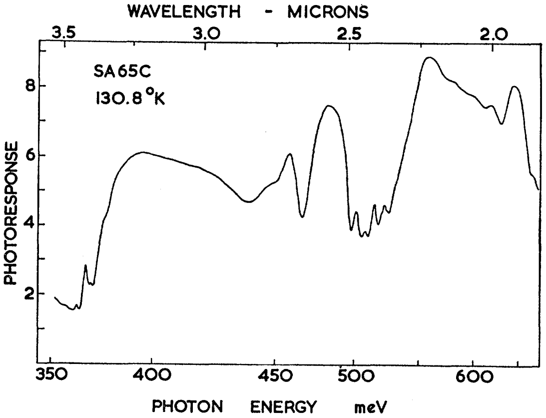

FIG. 10. An electronically normalized spectrum on a linear wavelength scale of the photoconductivity in the one- and two-phonon-assisted region for natural diamond SA65C at 130.8°K.

C. Electric Field Effects

When measuring the photoresponse for the heavily doped synthetic diamond D1002Cl it was observed that the structure in the one-phonon-assisted region was dependent on electric fields of quite low values. The structure is very poorly resolved compared with that for a natural diamond even at low fields and, as can be seen in Fig. 12, only 140 V/cm is necessary to cause some broadening of the spectrum, and at 2000 V/cm the minimum is only just visible. There is a similar, though much less marked, effect with electric field for natural diamond in this same spectral region. The results are shown in Fig. 13 for diamond SA65C at 77°K at six different electric fields between 0.5 and 5.0 kV/cm. It can be seen that for electric fields above 1 kV/cm the fine structure at high energies becomes progressively distorted as the field is increased. Since this fine structure is coupled to the excited-states region by the Raman phonon, then the behavior in the one-phonon-assisted region is simply mirroring that of the primary excited states. Figure 14 shows the effect of electric field in this latter region, measured at high resolution. The fields used are 1.5 and 4.0 kV/cm, since at both extremes of field available the signal-to-noise ratio decreases markedly and obscures the effect being investigated. However, the spectra obtained at these two values of applied field adequately demonstrate the expected behavior; at the higher field features corresponding to those transitions to states closest to the valence band are severely affected and, in addition, the whole of the spectrum is broadened slightly. This emphasizes the necessity for carefully choosing the electric field before attempting high-resolution studies, and indicates why a field of 1.25 kV/cm was used for the measurements described in Sec. III A. It can be shown quite simply, using a simple Bohr model for the acceptor center, that the total energy ϵ of an electron in an orbit of radius r can be expressed in terms of the electric field E due to the nucleus to give

$$E=4K\epsilon^2/e^3,$$

where K is the static dielectric constant of the medium

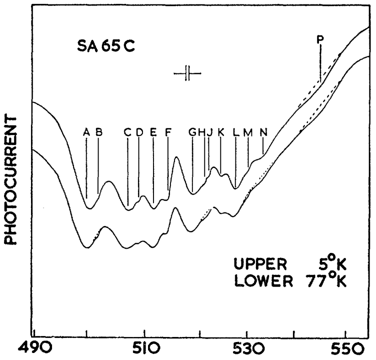

Fig. 11. High-resolution photoconductivity spectra in the one-phonon-assisted region for a natural diamond SA65C at 5 and 77°K. The zeros of the spectra have been displaced for convenience.

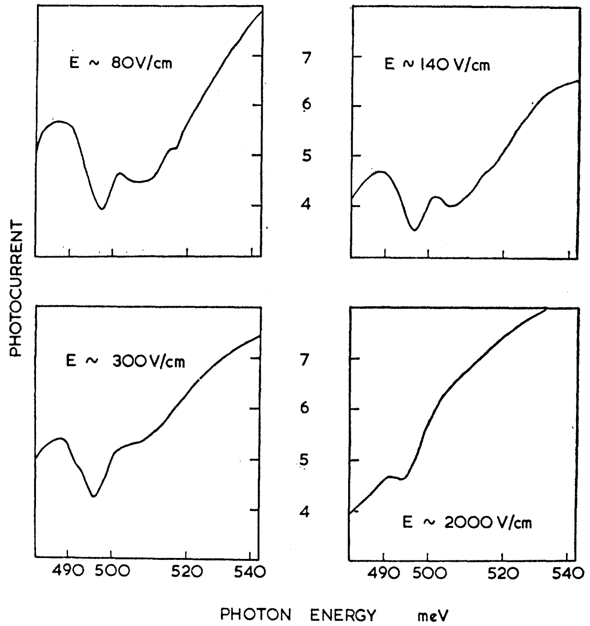

Fig. 12. Electric field broadening in the one-phonon-assisted region for semiconducting synthetic diamond D1002Cl recorded at 120°K for four different values of the applied field E.

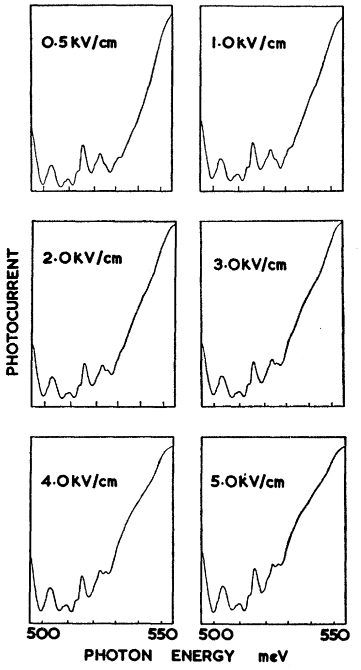

Fig. 13. Electric field broadening in the one-phonon-assisted region for natural semiconducting diamond SA65C, recorded at 77°K. For fields above 1 kV/cm the spectrum becomes progressively distorted at energies around 530 meV.

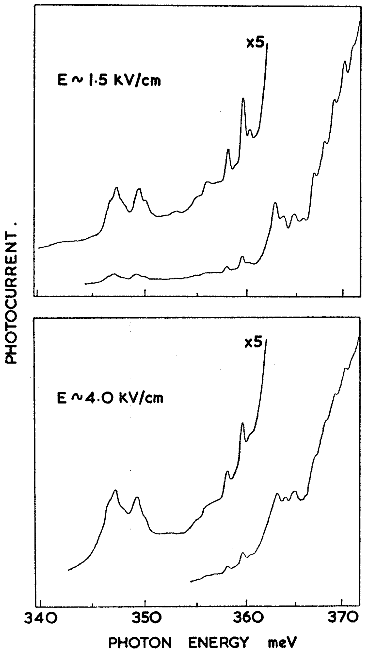

FIG. 14. Electric field broadening in the photothermal-ionization region for natural IIb diamond SA65C recorded at 77°K. Note that at the higher field, features at energies higher than ~360 meV are severely distorted, and that the rest of the spectrum is broadened.

and e is the electronic charge. It seems reasonable to expect that this orbit will become severely disturbed when the external applied field is comparable with this central field. If we consider the excited-state transitions close to the valence band for which a typical value is $\epsilon = 4$ meV, then using the value $K = 5.7$ we obtain

$$E = 2.5 \text{ kV/cm}.$$

This is seen to be in excellent agreement with the external field required to completely broaden these features close to the valence band.

The reason why the synthetic diamond D1002Cl exhibits such a marked electric field dependence in the one-phonon-assisted region is thought to be as follows. The over-all neutral acceptor concentration is extremely high ($\sim 10^{18}$ cm^{-3}), but since these synthetic diamonds show marked inhomogeneity in the distribution of acceptors, there are probably small regions of the crystal where the acceptor concentration is much lower than average. The bulk of the diamond will be fairly low resistance even at 77°K because of conduction by hopping transport, and the major part of the applied field will be developed across the regions of low concentration which may only be a few hundred Angstroms in extent. It is these regions of the crystal which contain the relatively unperturbed centers which contribute to the structure in the photoconductivity continuum.

D. Photon-Induced Tunneling

The residual structure at low temperature in the photothermal-ionization region has already been discussed in Sec. II A. During the course of the measurements at liquid-helium temperature it was accidently observed that the photoconductivity in this region was strongly affected by stray light falling on the diamond. For specimens with a fairly homogeneous distribution of acceptor centers, and in the absence of stray light, the strongest excited-state features are just visible as shallow minima on the background continuum. When the specimen is simultaneously illuminated with radiation from a tungsten filament lamp these minima invert, and the whole of the acceptor spectrum appears as a series of maxima. By using two monochromators it has been found that the only radiation effective in producing this reversal is that with quantum energy lying within the photoconductivity continuum (i.e., >0.37 eV), and we refer to this as "bias light." The effect of this bias light on the 5°K spectrum is shown in Fig. 15, which is recorded at relatively low resolution, and the reversal and enhancement of the excited-states structure relative to the continuum photoconductivity is quite apparent. A very-high-resolution spectrum in the vicinity of the 0.348-eV band is shown with and without bias light in Fig. 16 from which it can be seen that with this bias light the various subcomponents are far better resolved than in either the photothermal-ionization spectrum or the absorption spectrum obtained at 77°K. Preliminary measurements had established that only bias light of energy greater than 0.37 eV was effective in producing any change in the low-temperature spectra. The relative efficiency of bias light of different energies has been found by *setting* the primary monochromator (using chopped radiation) on a prominent feature in the spectrum and scanning the energy from the monochromator supplying the bias light (which is not chopped). The resulting spectrum is shown in Fig. 17 and it can be seen that this bias-light

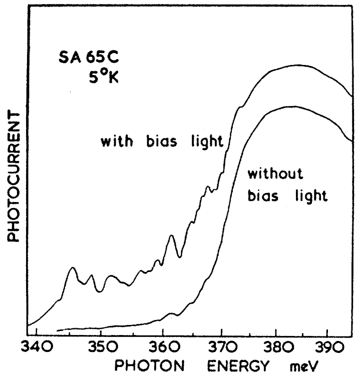

FIG. 15. Low-resolution spectra of the photoconductivity response in the photothermal-ionization region for a natural IIb diamond SA65C, recorded at 5°K, with and without bias light of photon energy >0.37 eV simultaneously incident on the crystal.

versus energy-response curve is virtually identical with the normal photoresponse spectrum shown in Fig. 10, including the phonon-assisted features. The reason for the negative change for energies immediately below the ionization energy is not understood at the moment.

These bias-light experiments further substantiate the picture put forward in Sec. II A. The appearance of the excited-state features as maxima in the 5°K photoconductivity spectrum is due to tunneling from the excited states of the acceptor center to neighboring ionized centers. The effect would be expected to be much more pronounced in the excited states because the degree of wave-function overlap is much greater than in the ground state. For specimens in which this tunneling does not normally occur the bias-light experiments show that it can be *induced* by simultaneously illuminating the diamond with radiation of energy falling within the photo-ionization continuum. This increases the number of ionized centers present and so enhances the probability of tunneling. Consequently it would be expected that the degree of enhancement with bias light, determined as a function of the bias-light energy, would follow the normal photo-ionization continuum. This is clearly seen to be the case from Fig. 17.

At first sight it is perhaps surprising that the tunneling photocurrent in synthetic diamonds is not very much higher than in natural diamond in view of the much higher acceptor concentrations. Our photoconductivity measurements on synthetic diamond at liquid-helium temperatures are not very extensive, but they do indicate that although photoconductivity minima have never been observed the contribution from tunneling is quite small. We can only conclude, therefore, that although the tunneling probability in these synthetic diamonds is probably much higher than in natural diamonds, the lifetimes in the excited states are smaller for the majority of the centers present. Hence the tunneling-transition probability (i.e., the product of tunneling probability and lifetime) differs only slightly from that for natural diamond.

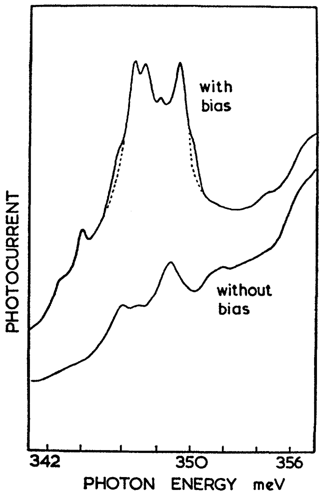

FIG. 16. High-resolution spectrum (effective slit width ~0.3 meV) of the photoconductivity response of a natural semiconducting diamond SA65C at 5°K in the neighborhood of the 0.348-eV band, with and without bias light. Without bias light the excited-state features are observed as shallow minima on the background continuum with bias light all the components appear as sharply defined maxima.

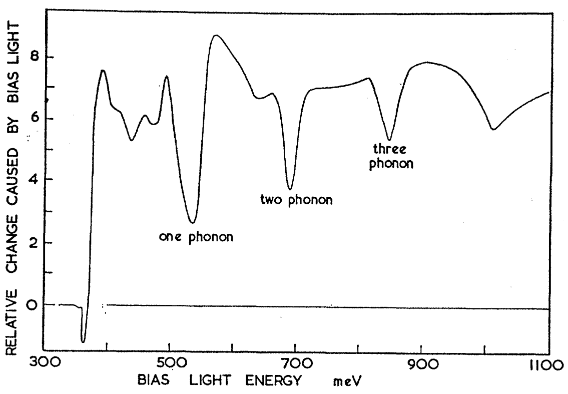

FIG. 17. Relative change in the magnitude of the 0.348-eV band displayed by means of bias light plotted as a function of bias-light energy for diamond SA65C at 5°K.

IV. SUMMARY AND CONCLUSIONS

The measurements reported in the previous section demonstrate that the appearance of structure below the ionization energy in semiconducting diamond is primarily due to the two-stage ionization of the aluminum acceptor center, i.e., photothermal ionization. At low temperatures where the thermal contribution is negligible the acceptor spectrum is still visible in some specimens (particularly synthetic diamonds) because of tunneling from the excited states of highly perturbed centers. In more perfect diamonds, which do not normally show this tunneling effect, photon-induced tunneling can be exhibited by optically ionizing a large number of other acceptor centers simultaneously. The acceptor spectrum displayed in this way is typical of unperturbed centers and is often more detailed and informative than the best absorption spectra obtained from the same crystal. In general, and particularly for poor quality diamonds which contain a large number of perturbed acceptor centers, the photothermal spectrum is better defined than the absorption spectrum since the photothermal-ionization process preferentially selects the unperturbed centers. The investigation of electric field dependence has shown that there is no impact or field ionization, but has demonstrated the need to use fields low compared with the internal fields experienced by holes in the excited states if undistorted spectra of the highest resolution are required. The simultaneous electric field broadening of the acceptor spectrum and fine structure in the one-phonon-assisted region further confirms the origin of the structure in this latter region. The energies of the various excited states, obtained by the several methods described in this paper, are listed in Table I. It can be seen that for the 36 features detected in the acceptor spectrum the energy agreement between the different methods of observation is consistently excellent. Finally it is particularly gratifying that the energy differences between the valence-band edge and the 0.348-eV and 0.364-eV bands, as deduced from the temperature dependence of the photothermal ionization, are in exact agreement with our previous electrical data.[9]

Note added in manuscript. During the preparation of this manuscript, our attention has been drawn to a recent paper by Krumme and Leivo[15] which is chiefly concerned with phonon-assisted structure on the photoconductivity continuum associated with the acceptor center in natural semiconducting diamond. Although the present paper is primarily concerned with structure below the ionization energy and the process of photothermal ionization and photon-assisted tunneling, we feel that some comment should be made on their work since the interpretation presented seriously conflicts with the model of the acceptor center in semiconducting diamond which we have used and which has been firmly established by a large number of authors in the last 12 years.[16] Confusion chiefly arises from the fact that Krumme and Leivo have based their analysis on misleading conclusions reached by Halperin and Nahum[17] from infrared absorption, thermoluminescence, and two-probe electrical-conductivity measurements, but abandoned in later work by Halperin and Chen.[18]

Halperin and Nahum[17] measured the infrared absorption of natural semiconducting diamond and found absorption maxima at 0.20, 0.206, 0.305, 0.345, 0.364, 0.51, 0.53, and 0.67 eV. Thermoluminescence-glow curves gave activation energies of 0.21, 0.30, 0.37, 0.52, and 0.7 eV, and dark-conductivity measurements yielded activation energies of 0.21, 0.30, and 0.37 eV. From these data, Halperin and Nahum concluded that there are discrete levels lying at about 0.2, 0.3, 0.37, 0.52, and 0.7 eV above the valence band from which holes can be released by either thermal or optical excitation. However, both Austin and Wolfe[5] and Wedepohl[6] had previously shown that all the infrared absorption peaks, except the ones near 0.2 eV which only Halperin and Nahum have observed, together with the absorption continuum commencing at ~0.37 eV were associated with one center, and suggested that the features below 0.37 eV were probably due to transitions of bound holes between the ground state and various excited states of the acceptor center. This was confirmed in more detailed measurements by Smith and Taylor,[7] and the peaks superimposed on the absorption continuum at 0.462, 0.508, 0.625, and 0.670 eV were considered to be bound hole transitions of the acceptor center with the emission of one or more lattice phonons of energy 0.159 eV. This latter process is peculiar to semiconductors like diamond in which the impurity-activation energy is substantially larger than the Raman energy.[19] Smith and Taylor were unable to detect any absorption at ~0.2 eV, but pointed out that there are strong water-vapor absorption bands in this region. The electrical-conductivity results of Halperin and Nahum have been refuted in a report by Leef,

TABLE I. The table lists all the features in the diamond acceptor spectrum which have been detected by the various techniques. The results are tabulated with energies in meV in five columns as follows: A. Absorption at 5°K; diamonds SA67F and SA65B (from Fig. 7). B. Absorption at 80°K; diamonds SA67F and SA65B (from Fig. 7). C. Photon-induced tunneling at 5°K; diamond SA65C (Fig. 16). D. Photothermal ionization at 77°K and, for peaks with energies less than 346 meV, ~140°K; diamond SA65C (Fig. 6). E. One-phonon-assisted photoconductivity features less the energy of the Raman phonon (165 meV) 5 or 77°K; diamond SA65C (Fig. 11). (The letters in parentheses in this column refer to the letters on Fig. 11.)

A	B	C	D	E
370.9	370.9	[a]	370.9	[b]
370.0	370.0	[a]	370.1	[b]
369.5	[b]	[a]	369.5	[b]
368.9	368.8	[a]	368.9	368.8 (N)
368.1	[b]	[a]	368.5	[b]
367.7	367.9	[a]	368.0	[b]
[b]	[b]	[a]	367.5	[b]
366.7	366.8	[a]	366.9	[b]
365.9	366.0	[a]	365.9	[b]
365.1	365.0	[a]	364.9	365.2 (M)
364.5	[b]	[a]	[b]	[b]
363.8	363.9	[a]	363.9	[b]
362.7	362.7	[a]	362.9	362.4 (L)
360.2	360.2	[a]	360.3	[b]
359.5	359.3	[a]	359.7	359.6 (K)
358.6	358.7	[a]	358.8	[b]
357.9	357.9	[a]	358.1	357.4 (J)
356.7	356.7	[a]	356.8	[b]
355.0 (?)	355.8[c]	[a]	355.9	355.4 (H)
354.1	354.7	[a]	354.9	354.1 (G)
353.0	352.9	[a]	[b]	[b]
[b]	352.4[c]	[a]	352.5	[b]
[a]	351.1	[b]	[b]	[b]
[a]	350.1	350.1	350.2	[b]
[a]	349.2	349.3	349.4	349.4 (F)
[a]	348.0	348.2	348.1	[b]
[a]	347.1	347.3	347.2	347.5 (?)
[a]	346.5	346.7	346.5	346.7 (E)
[b]	345.0[c]	345.8	345.2	[b]
344.3 343.6	$\left.\begin{matrix}344.4\\343.5\end{matrix}\right\}$	343.9	343.8	344.0 (*D*)
342.3	342.3	342.6	342.4	342.1 (?)
[b]	341.5[c]	[a]	341.6	341.4 (C)
[b]	340.2[c]	[a]	340.5	[b]
337.4	337.2	[a]	[b]	336.5 (B)
334.4 (?)	335.3[c]	[a]	[b]	334.0 (A)

[a] Measurements not made in this region.
[b] No feature was detected at this energy.
[c] Absorption peaks at 80°K that disappear at 5°K (see Fig. 7).

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

[18] A. Halperin and R. Chen, Phys. Rev. **148**, 839 (1966).

[19] J. R. Hardy, Proc. Phys. Soc. (London) **79**, 1154 (1962).

Seeley, and Nordlin,[20] who measured the dark conductivity as a function of temperature using a four-probe method, and obtained 100 experimental points in the region covered by Halperin and Nahum which lie on a single straight line plot yielding on activation energy of ~0.35 eV.

The thermoluminescence peak at ~0.2 eV has recently been investigated in this laboratory using a considerable number of natural and synthetic semiconducting and insulating diamonds.[21] It is concluded that this peak is probably due to boron acceptors which are normally completely compensated by deep-lying donors, but can be metastably neutralized in the thermoluminescence measurements when the crystal is excited by suitable radiation at low temperatures. Certainly, it has not been possible to detect any optical absorption in this region in any diamond, which would arise if the boron acceptors were only partially compensated.

It is generally accepted that the semiconducting properties of natural type-IIb diamond can be explained in terms of one invariant acceptor center, namely, aluminum with an ionization energy of 0.373 eV. Hall-effect measurements indicate that the acceptors are partially compensated by deep-lying donors, and the donor center is considered to be nitrogen with an ionization energy of ~4 eV.[22] It seems likely that there is also a boron acceptor present with an activation energy of ~0.2 eV, but this is invariably completely compensated. With the exception of the thermoluminescence measurements, where this center can be metastably neutralized, it will not be detected either optically or electrically. It follows, therefore, that in the analysis presented by Krumme and Leivo any correlation with the five activation energies of Halperin and Nahum must be regarded as largely fortuitous. Oscillations in the photoconductivity spectrum of diamond have been previously observed by Hardy *et al.*[4] and by Ruffino and Charette,[13] and these authors show that the energies of the minima are given approximately by

$$h\nu = E + n\hbar\omega_0 ,$$

where E is the energy of an excited state of the acceptor measured from the ground state, and $\hbar\omega_0$ is the energy of the zero wave-vector optical phonon. We feel that this is something of an over simplification and hope to comment further in a subsequent paper, but this interpretation is substantially nearer the true situation than that given by Krumme and Leivo based on five activation energies and three discrete phonon energies.

Finally, we are puzzled by the structure obtained by Krumme and Leivo (their Fig. 1) in the wavelength region 3.45 to 4.6 μ (0.27 to 0.36 eV). Of all the authors who have reported measurements on semiconducting diamond, none has observed any extrinsic continuum absorption in this region, and no continuum photoconductivity would be expected of the form reported by Krumme and Leivo. We have only observed the very weak continuum and the photothermal-ionization features described in this paper. However, we have reproduced a spectrum similar to that reported by Krumme and Leivo by using the grating monochromator with a germanium filter instead of a long-wavelength-pass filter; for apparent energies less than ~330 meV the diamond is then detecting the second-order reflection from the grating.

ACKNOWLEDGMENTS

We are particularly indebted to Dr. W. F. Sherman for the loan of his S3 monochromator during the early part of this work, and for his assistance with the absorption measurements. We would also like to thank Dr. P. J. Dean for helpful discussions and G. Davis for preparing the computer programs. The natural semiconducting diamonds were supplied by Dr. F. A. Raal and Dr. L. du Preez of the Diamond Research Laboratory, Johannesburg, and the synthetic semiconducting diamonds by Dr. P. Cannon, Dr. R. H. Wentorf, and Dr. H. M. Strong of the General Electric Research Laboratories, Schenectady. We are grateful for their cooperation and their continued interest in this work. We are also indebted to Dr. W. J. Choyke of Westinghouse Research Laboratories for providing the Au-Ta-Al alloy used for welding p-type contacts to the natural semiconducting diamonds. The project was partially financed by equipment grants from Industrial Distributors Ltd., the Science Research Council, and the Royal Society.

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