case $a_A = a_D$ are

$$J' = (e^2/\kappa)[(e^{-2\rho}/R)(-4-\tfrac{5}{2}\rho+3\rho^2+\tfrac{2}{3}\rho^3) + (e^{-2\sqrt{2}\rho}/R)(\sqrt{2}+5/4\rho-3/\sqrt{2}\rho^2-\tfrac{2}{3}\rho^3)]. \qquad (13)$$

The exchange integrals are given here in a form valid for $\rho \geq 2$:

$$K' \approx -(e^2/\kappa)(\Delta/R)[4e^{-\sqrt{2}\rho}(\rho+\sqrt{2}\rho^2)-4e^{-2\rho}(3-\rho) + 9\sqrt{2}S\,\mathrm{Ei}(-y)+(12\sqrt{2}/5)S\,\mathrm{Ei}(-2.828\rho)] + (e^2/\kappa)(\Delta^2/R)[4.841+1.698\ln\sqrt{2}\rho+12.726\,\mathrm{Ei}(-x)] - (e^2/\kappa)(e^{-2\sqrt{2}\rho}/R)(-5\rho/4+2.3\sqrt{2}\rho^2+12\rho^3/5 + 4\sqrt{2}\rho^4/5)+O(\rho^5\,e^{-4.8\rho}/R), \qquad (14)$$

where $\Delta = e^{-\sqrt{2}\rho}(1+\sqrt{2}\rho+\tfrac{2}{3}\rho^2)$. The $\mathcal{E}_d{}^2$ are tabulated in Table I from the full eigenvalue equation, for s-type $F(r)$ with the κ, $m_e{}^*$, and $m_h{}^*$ as previously noted. Again, we find the electronic energy per electron and hole less negative than for the pair: $\mathcal{E}_p \leq \mathcal{E}_d{}^2 - \mathcal{E}_d{}^1$.

The equality applies in the limit of no overlap at large R and is evident from Eqs. (8) and (12) combined with the corresponding expression for pairs.[3] In other words, the D-A states are perturbed more towards their respective band edges for both singly and doubly excited dipairs than for pairs. From Table I it is evident that the second electron and hole are more tightly bound than are the first: $\mathcal{E}_d{}^2 - \mathcal{E}_d{}^1 \leq \mathcal{E}_d{}^1$.

Although the electron and hole are not bound more tightly to symmetrical dipairs than to pairs for either state of excitation and for any interimpurity distance, dipairs do have their own distinct energy-level structure [Eq. (8)] and also have an energy-level structure for double excitation [Eq. (12)]. We recognize that unsymmetrical dipairs $R \neq R'$ are more probable at the lower concentration range for dipairs. These will be discussed elsewhere, as will even higher associates.

A property which can be predicted for dipairs, and not for pairs, is two-step optical excitation to yield radiative deexcitation with approximately twice the energy of recombination at pairs. The radiation would be observable only if the photon energy is less than the bandgap E_g. This condition for the proposed mechanism is satisfied if $E_A + E_D > \tfrac{1}{2}E_g$, which is the case for ZnS:Cu,In where $E_D = 0.7$ eV, $E_A = 1.3$ eV, and $E_g = 3.7$ eV. It has been observed that the D-A pairs in this material can be excited to metastable states.[5] The proposed two-step excitation of anti-Stokes emission of dipairs may be more feasible experimentally by direct optical excitation of the dipair or by energy transfer from D-A pairs. The inverse process, creation of a doubly excited dipair by a single photon of energy $2E_g - \mathcal{E}_d{}^2$, should also be considered. It is not yet clear which process would be easier to detect.

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Stark Effect on Impurity Levels in Diamond*

E. ANASTASSAKIS†

Physics Department and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104

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In this article we present our experimental results on the Stark effect of the shallow impurity levels of p-type semiconducting diamond (IIb). The shift of the levels is found to be quadratic in the applied electric field, and to tend towards the ground state. No splitting of the fourfold degenerate levels was observed; instead, a broadening of the levels, quadratic in the field, is attributed to an unresolved splitting. The over-all behavior of the spectrum agrees with the group-theoretical predictions, and the estimated Stark coefficients are in reasonable relation with those of silicon and germanium.

1. INTRODUCTION

It is well known that the presence of substitutional impurity atoms in the pure crystal lattice of an insulator or semiconductor is of great importance in determining the electrical properties of the system. The impurity atoms introduce discrete energy levels into the otherwise energetically forbidden energy gap, which can then be occupied by charge carriers loosely bound to the impurity center. Depending on the nature of the impurity and host atoms, the discrete levels may be either close to the edge of the conduction or valence band (shallow levels), or far away from the bands and deep in the energy gap (deep levels). For the shallow levels which we are concerned with, the interaction of the electron or hole with the impurity center is determined by a Coulomb-type potential

$$U = \pm e/Kr \qquad (1)$$

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† Present address: Physics Department, Northeastern University, Boston, Mass. 02115.

superimposed on the crystal potential. (K is the static dielectric constant of the crystal. The quantum-mechanical treatment of the shallow levels, based on (1) and a model analogous to the hydrogen atom, have been made in the so-called effective-mass approximation (EMA). The spectrum of the shallow levels therefore includes a series of excited states analogous to the hydrogenlike atom spectrum. Such spectra have been observed experimentally by a number of workers.[1–6]

In recent years, the nature and symmetry of the shallow levels has been investigated in some materials by applying an external perturbation, such as uniaxial stress, magnetic or electric field. Useful information has been obtained in this way concerning the character and multiplicity (degeneracy) of the ground and excited states.

In the present work we will present a discussion and experimental results of the effect of an electric field on the shallow acceptor levels in diamond. We will first briefly discuss the theory of acceptor levels in the EMA, together with a number of related experimental facts. A detailed review on this subject has been presented by Kohn[7] and by the references therein.

2. SHALLOW ACCEPTOR LEVELS

The theoretical treatment of the shallow acceptor levels, even in the EMA, is a difficult problem because it involves the structure at the top of the valence band, which in general is more complicated than the bottom of the conduction band. In diamond-type crystals, the top of the valence band lies at the center of the zone ($\mathbf{k}=0$) and has a threefold orbital degeneracy which becomes sixfold if spin is included. However, if one considers a perturbation arising from the spin-orbit coupling, the sixfold degenerate band at $\mathbf{k}=0$, splits into one fourfold band and one twofold band of lower energy, the split-off band, separated by a splitting λ known as spin-orbit splitting. The fourfold state belongs to the Γ_8 irreducible representation of the tetrahedral double group T_d^2. It is built up from $P_{3/2}$ atomic functions on each atom. The twofold band belongs to the Γ_7 representation of the same group, and is made of $P_{1/2}$ atomic functions.

The total wave function of an acceptor state in the EMA can be written as

$$\psi(\mathbf{r})=\sum_{j=1}^{6} F_j(\mathbf{r})\varphi_j(\mathbf{r})\,, \tag{2}$$

where j refers to the sixfold degeneracy, i.e., $j=1\cdots 6$, $\varphi_j(\mathbf{r})$ are Bloch waves normalized in the unit cell, and going to P atomic functions in the vicinity of the atoms. Otherwise, they are periodic and rapidly varying, with four of them being fourfold degenerate at $\mathbf{k}=0$ and the other two being twofold degenerate at $\mathbf{k}=0$ and with an energy λ below the top of the valence band. Finally, it can be shown[8,9] that $F_j(\mathbf{r})$ are the solutions of a system of six partial differential equations rather than one, as is the case in the shallow donor states. This is the main reason why the situation is more complicated for acceptor states than for donor states. Since the functions $F_j(\mathbf{r})$ form a basis for the T_d^2 irreducible representations Γ_8 (fourfold) Γ_7(twofold) and Γ_6(twofold), we expect them to be either fourfold or twofold degenerate for any level. A twofold degeneracy is always left, because of the Kramers theorem on time reversal symmetry.

In Ge where the ionization energies of the acceptor states ($\sim$0.013 eV) is much smaller than λ($\sim$0.3 eV), one can neglect the two split-off functions and solve a system of four equations instead of six. Of the calculations based on the EMA and variational methods, those of Mendelson and James[10] seem to be the most complete ones for group-III impurities in Ge. The experimental results[11] are in very good agreement with theory for the p-type excited states, which appear to be independent of the impurity atom. But, as expected, they show a considerable difference for the impurity-dependent ground state where the EMA fails.

In the case of Si the acceptor ionization energies ($\sim$0.04 eV) are of the same order of magnitude as the spin-orbit splitting λ($\sim$0.035 eV), and the same approximation of ignoring the two split-off functions is not good any more. Thus, one has to face the difficulty of finding exact solutions for the fourfold and twofold degenerate functions $F_j(\mathbf{r})$. This makes the EMA less successful in describing not only the ground state of the shallow acceptors in Si, but also the excited states. In fact, the most recent and complete theoretical results for ground state and excited shallow acceptor states in Si [12] are not in good agreement with the available experimental results.[13] The value of λ for Si has been established by Zwerdling *et al.*[14]

Several investigators have experimentally studied the structure, linewidth, and degeneracy of these levels in Si. A fourfold degeneracy has been assigned to the lowest two excited states of Si:Al by examining the Zeeman splittings.[14] Also, by applying a uniaxial stress on Si:B the lowest four excited states have been identified as

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fourfold degenerate,[13,15] on the basis of a fourfold ground state. Similar conclusions have been reached by examining the Stark effect of these levels.[16]

The structure of the valence band of diamond is similar to that of Si. A spin-orbit coupling of 0.006 eV[17,18] is rather small as compared with the ionization energy, so that a theoretical approach of the problem in the EMA is fairly complicated. No complete theoretical calculations for the wave functions exist, although several attempts have been made to assign a symmetry and a multiplicity (degeneracy) to the observed bands.[19–21] The most complete presentation, based on group-theoretical and experimental facts, has been reported by Crowther, Dean, and Sherman,[21] (CDS). Their assignments are in partial agreement with the conclusions of Bagguley *et al.*[20] based on Zeeman splittings of the acceptor levels, but they are perfectly consistent with their own stress data and our electric field data.

3. SYMMETRY OF SHALLOW ACCEPTOR LEVELS IN DIAMOND

Following the arguments given by CDS[21] one starts with Bloch functions $\varphi_j(\mathbf{r})$ taken from the top ($\mathbf{k}=0$) of the threefold (spinless) degenerate valence band, and mixes them with the hydrogenlike envelope functions $\varphi_j(\mathbf{r})$ to obtain spinless wave functions like those of Eq. (2). Then the spin-orbit coupling is added as a further fine splitting of the spinless states.

In group-theoretical language, the same approach can be expressed as follows: The spinless top of the valence band of diamond belongs to the Γ_{5+} irreducible representation of the $O_h{}^7$ space group.[22] Since the tetrahedral point group T_d is a subgroup of O_h, it can be shown that Γ_{5+} reduces to the Γ_5 irreducible representation of both T_d and T_d.^{2} Therefore the corresponding Bloch functions φ belong to the threefold Γ_5, as well. On the other hand, since the ground state and first excited states of the impurity system are 1*s* and 2*p* hydrogenlike states, the envelope functions for the 1*s* and 2*p* states belong to the onefold and threefold irreducible representations of the full rotation group, i.e., D_0 and D_1, respectively. In turn, D_0 and D_1 can be reduced to the Γ_1 and Γ_5 irreducible representations, respectively, of the double tetrahedral group of the impurity site $T_d{}^2$. The envelope functions F_{1s} and F_{2p} are of even and odd parity, respectively. Also, the twofold degenerate representation $D_{1/2}$ of the full rotation group reduces to Γ_6, since its functions are of even parity.[23] It is clear that the nine degenerate functions φF_{2p} (without spin) belong to the $\Gamma_{5+}\times D_1$ representation of the direct-product group $O_h\times$(rotation group), or equivalently to the $\Gamma_5\times\Gamma_5$ representation of $T_d{}^2$ (or T_d). But,

$$\Gamma_5\times\Gamma_5=\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5\,, \tag{3a}$$

and, similarly, for the ground state

$$\Gamma_5\times\Gamma_1=\Gamma_5(g)\,. \tag{3b}$$

Thus, before including any spin effects and only by considering the band-envelope splitting, we find that the ground state remains threefold degenerate, but the 2*p* state splits into one singlet (Γ_1), one doublet (Γ_3), and two triplets (Γ_4 and Γ_5). The expectation energies for the four, according to the EMA, can be shown to be as $E_4<E_3<E_5<E_1$ when measured from the ground state. So far we have neglected the spin-orbit coupling, and the above scheme is entirely due to the band-envelope interaction, which originates from the nonspherical symmetry of the inverse-mass tensor. (A spherical inverse-mass tensor would lead to $E_4=E_3=E_5=E_1$ according to the EMA.[7])

If the spin is now included, each of the above levels is split in accordance with the reduction of the products $\Gamma_i\times D_{1/2}[i=1,\,3,\,4,\,5,\,5(g)]$, i.e.,

$$\begin{aligned}\Gamma_1\times\Gamma_6&=\Gamma_6(1)\,,\\ \Gamma_3\times\Gamma_6&=\Gamma_8(3)\,,\\ \Gamma_4\times\Gamma_6&=\Gamma_6(4)+\Gamma_8(4)\,,\\ \Gamma_5\times\Gamma_6&=\Gamma_7(5)+\Gamma_8(5)\,,\\ \Gamma_5(g)\times\Gamma_6&=\Gamma_7(g)+\Gamma_8(g)\,.\end{aligned} \tag{4}$$

Useful tables for all these arguments can be found in the CDS paper. The numbers in parentheses indicate the spinless parent representation. The energy scheme up to 0.35 eV, based on the above analysis, and our data is shown in Fig. 1 (first and second column). To establish agreement with thermal and stress experimental results, CDS have made the following assumptions: (i) The twofold ground level $\Gamma_7(g)$ lies above $\Gamma_8(g)$ with a separation of ~2 meV due to the spin-orbit coupling of the ground state. This value for the separation is not accidental; in the spectrum there are several pairs of bands with the same separation. Each pair therefore can be considered as a transition from the $\Gamma_8(g)$ and $\Gamma_7(g)$ to the same excited state. That the spin-orbit coupling is only 2 meV, instead of 6 meV reported for the free valence band, could be attributed to the presence of a *d*-like envelope function in the ground-state wave function. This has the effect of reducing the

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[23] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Inc., New York, 1960), p. 87.

spin-orbit coupling (for example, from 6 to 2 meV) without destroying the s character of the total wave function of the ground state.[20] (ii) The first excited state at 0.3045 eV with a relatively large width (~6 meV) remains unresolved, in view of a spin-orbit splitting of about 3 meV for the levels $\Gamma_6(4)$ and $\Gamma_8(4)$ as estimated by EMA. The $\Gamma_6(4)$ level is placed above $\Gamma_8(4)$ [and the $\Gamma_8(5)$ above $\Gamma_7(5)$]. The large width can be explained by Kane's theory. [24,19] (iii) The transition $\Gamma_7(g) \rightarrow \Gamma_7(5)$ is the only one forbidden according to the selection rules for electric dipole transitions. However, such a transition appears as a weak shoulder at 0.3405 eV and is attributed to distortions of the ideal T_d impurity-site symmetry. An additional level $\Gamma_7(2)$ is postulated to explain the band of 0.3464 (not shown in Fig. 1).

4. STARK EFFECT OF SHALLOW ACCEPTOR LEVELS

The perturbation Hamiltonian introduced by an electric field applied at the impurity center along the z axis is given by

$$H^E = eEz = erE\cos\theta. \qquad (5)$$

As mentioned earlier, the wave functions of the hole state, are given by (2) in the EMA, with a twofold or fourfold degeneracy. Since the effective-mass Hamiltonian has even parity with respect to inversion in the impurity center, the envelope functions $F_j(\mathbf{r})$ have a definite parity.[10,11] On the other hand, H^E has an odd parity. As shown by Kohn,[7] on applying first-order perturbation theory, the matrix elements of H^E between any two states $\Psi^{(a)}(\mathbf{r})$ and $\Psi^{(b)}(\mathbf{r})$ correspond to

$$(\Psi^{(a)}, H^E\Psi^{(b)}) = \sum_j (F_j^{(a)}, H^E F_j^{(b)}), \qquad (6)$$

remembering that $F_j(\mathbf{r})$ varies slowly over the unit-cell volume, and that $|\varphi_j(\mathbf{r})|^2 = 1$ in that cell. But a matrix element $(F_j^{(a)}, H^E F_j^{(b)})$ with H^E of odd parity is zero if $F_j^{(a)}$ and $F_j^{(b)}$ are of the same parity. Therefore, in view of the definite parity of $F_j(\mathbf{r})$ no first-order Stark effect is expected in the EMA. This conclusion is based on the assumption that there are no accidental degeneracies such as the $2s,2p$ degeneracy in hydrogen, and that the EMA Hamiltonian has even parity. However, if the impurities are introduced as substitutional ones, the net symmetry of the bound state is tetrahedral, and the center of inversion is absent. Therefore, the true eigenfunctions have no definite parity, and one should expect a first-order Stark effect, which might be appreciable particularly for the ground state. Bir *et al.*[25] estimated a first- and second-order splitting for the ground state of Si:B to be 10^{-4} and 10^{-3} meV, respectively, for $E = 10^3$ V/cm. In view of the usual experimental limits in resolution (~10^{-1} meV), splittings of this order should be undetectable.

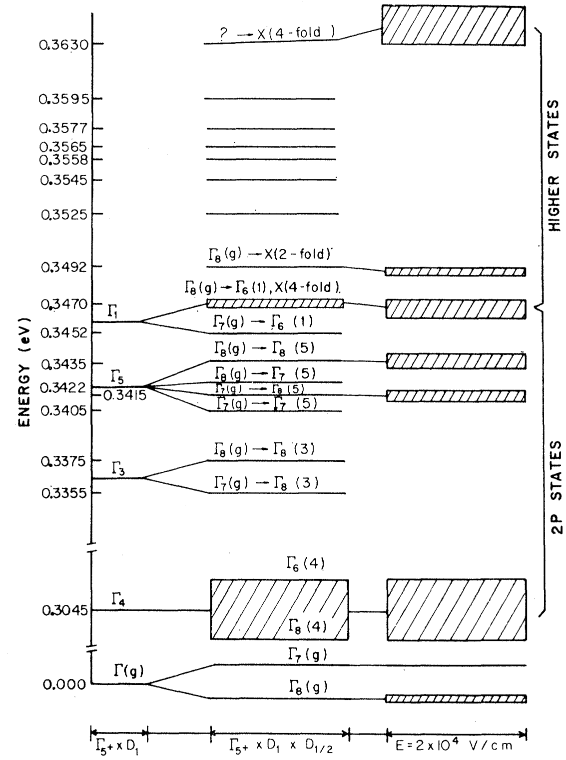

FIG. 1. Energy-level diagram of the shallow acceptor states in semiconducting diamond. The effects of the spin-orbit coupling and of an applied electric field are shown in the second and third column, respectively.

If second-order perturbation theory is applied, any level belonging to the Γ_7 or Γ_6 twofold representations is expected to shift, but not to split, since an electric field does not remove the twofold time-reversal degeneracy. Therefore, if the electric field appears to have no effect on the shape or linewidth of a particular absorption band, except shifting, the corresponding level is twofold degenerate. (We assume that the field has negligible effect on the ground state, in both first and second order.) On the other hand, the field will shift and split any fourfold degenerate level into two twofold levels. Thus, a fourfold state can be identified from a splitting or at least a broadening of the absorption band (due to an unresolved splitting).

If we start with two degenerate functions $\Psi^{(k)}$ and $\Psi^{(m)}$, the energy corrections $\delta E_m^{(2)}$ in second order are given by the solutions of the secular equation[26]

$$\begin{vmatrix} \sum\limits_{l\neq m} \dfrac{H_{ml}^E H_{lm}^E}{E_m - E_l} - \delta E_m^{(2)} & \sum\limits_{l\neq m} \dfrac{H_{ml}^E H_{lk}^E}{E_m - E_l} \\ \sum\limits_{l\neq m} \dfrac{H_{kl}^E H_{lm}^E}{E_m - E_l} & \sum\limits_{l\neq m} \dfrac{H_{kl}^E H_{lk}^E}{E_m - E_l} - \delta E_m^{(2)} \end{vmatrix} = 0, \qquad (7)$$

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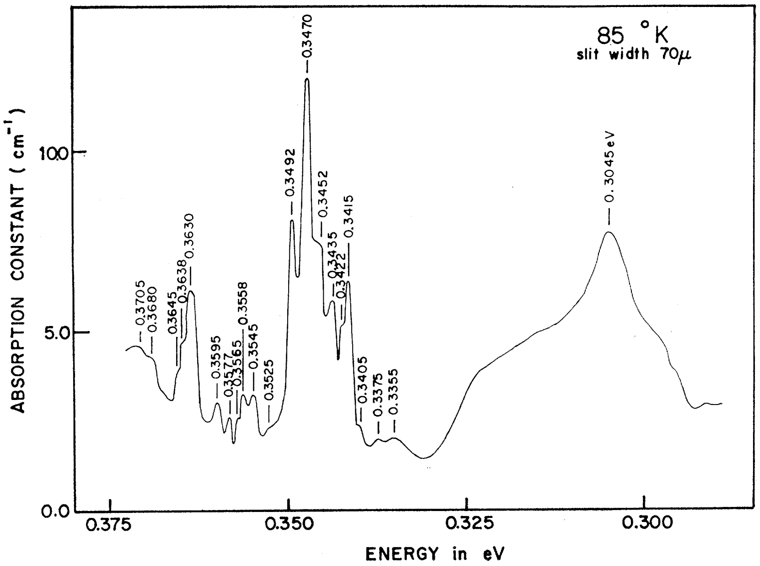

FIG. 2. Absorption spectrum of the excited states of the shallow acceptor levels, in semiconducting diamond. The sample was cooled at 85°K and the slit width was 70 μ.

or

$$\delta E_m^{(2)}=\Delta\pm(\Delta^2-\beta)^{1/2},\quad \Delta^2>\beta\,, \tag{8}$$

where Δ and $2(\Delta^2-\beta)^{1/2}$ are the shift and splitting, respectively, of the (k,m) degenerate state. Δ and β are given by

$$\Delta=\tfrac{1}{2}\sum_{l\neq m}\frac{H_{ml}{}^EH_{lm}{}^E+H_{kl}{}^EH_{lk}{}^E}{E_m-E_l}\,, \tag{9}$$

$$\beta=\sum_{\substack{l\neq m\\ j\neq m,l}}\frac{H_{ml}{}^EH_{lm}{}^E\times H_{kj}{}^EH_{jk}{}^E-H_{kl}{}^EH_{lm}{}^E\times H_{mj}{}^EH_{jk}{}^E}{(E_m-E_l)(E_m-E_j)}\,. \tag{10}$$

If $E_m>E_l$, i.e., if the perturbing state is a higher excited state,[27] then $\Delta>0$ and the perturbed state shifts toward the ground state. For $E_m<E_l$, the argument is reversed. From Eq. (9) it becomes clear that for a given set of perturbing levels E_l, the shift Δ is larger for higher perturbed levels E_m, i.e., higher excited states show larger Stark shift. Finally, if the major influence of a degenerate level comes from a single nearby state, $\beta=0$, $\delta E=0$, 2Δ; in this special case, the unresolved splitting 2Δ is twice as large as the apparent shift (Δ) of the degenerate state. All these remarks have been made in connection with, and for application to, the experimental data of Si:B.[16]

5. APPARATUS

The experimental setup basically included a 4-mm Nernst Glower IR source, a Perkin Elmer 12C-type monochromator with a Bausch and Lomb grating (150 lines/mm), and a home-made Ge:Au detector operating at 77°K. The beam was chopped by a PAR BZ-1 type chopper at 600 cps, and the signal was taken from the detector to the type-A preamplifier of a PAR HR8-type lock-in amplifier. The sample cell was made of glass with KBr windows. The polished diamond plate ($8.1\times5\times1$ mm^3) was gently held between two copper blocks which were highly polished to assure good contacts. The spectrometer was calibrated against gas lines, between 0.30–0.37 eV. Two band-pass interference filters 2–4 μ were used. The first was placed before the sample to keep the photocurrent at a low level, and the second at the entrance slit of the monochromator to filter the transmitted radiation further. The sample was placed between the source and the monochromator. More details about the experimental setup and the field techniques are given elsewhere.[28]

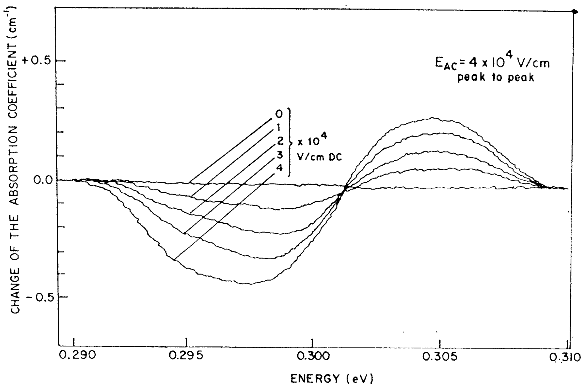

FIG. 3. Recorded signal of the 0.3045-eV band using differential technique with a bias. E_{ac} was kept constant and E_{dc} was varied. Slit width 160 μ.

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[27] Energies are measured from the top of the valence band.

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6. RESULTS AND DISCUSSION

The transmission spectrum between 0.290 and 0.370 eV was taken at 300 and 85°K. The temperature behavior of the absorption bands was found to be in agreement with previous results,[19–21] although our energy values for the 85°K spectrum, shown in Fig. 2, agree more with those of CDS, within 0.1~0.3 meV.

The instrument resolution was estimated to about 0.15 meV. We were unable to observe the fine structure of the 0.3470-eV band as reported by CDS for one of their samples, but we did see the shoulderlike forbidden transition at 0.3405 eV. All the following data were taken at 85°K and with natural (unpolarized) light.

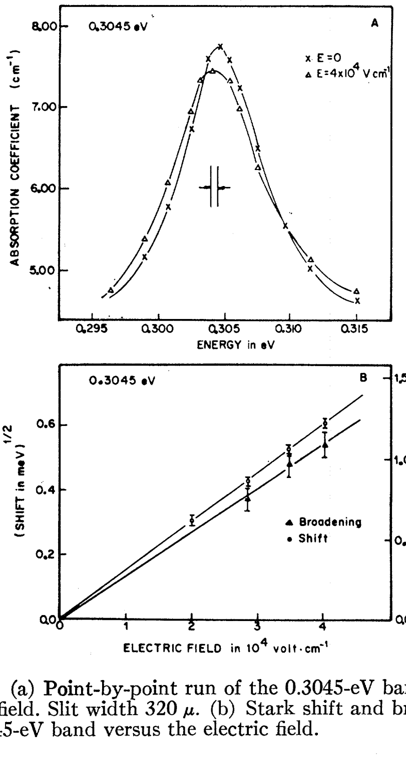

FIG. 4. (a) Point-by-point run of the 0.3045-eV band with and without field. Slit width 320 μ. (b) Stark shift and broadening of the 0.3045-eV band versus the electric field.

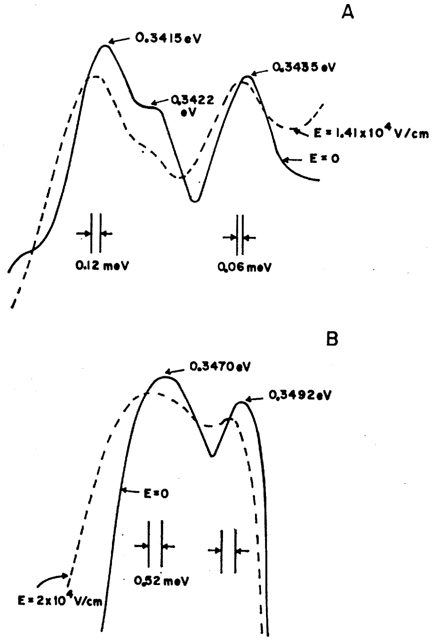

FIG. 5. Recorded signal for two pairs of bands, with and without field. Slit width, 80 and 160 μ.

When a static electric field of 4×10^4 V/cm was applied, all the fine structure of the spectrum of Fig. 2 disappeared, and the whole spectrum was similar to that at 300°K. Careful temperature measurements on the sample, in the presence of the field, showed that this was not due to heating of the sample. We therefore concluded that for these fields there was considerable interference of the closely lying levels due to their shift, and of broadening due to unresolved splitting. We then removed the chopper and modulated the field, instead. A dc bias field E_{dc} was applied on one face of the diamond plate (up to 4×10^4 V/cm) and a sinusoidal field $E_{\mathrm{ac}}\cos2\pi ft$ was applied on the other (at 600 cps, up to 4×10^4 V/cm pick to pick). Under these conditions it can be shown[28] that any effect, quadratic with the applied field, will produce two time-varying signals, proportional to $E_{\mathrm{dc}}E_{\mathrm{ac}}\cos2\pi ft$ and $E_{\mathrm{ac}}^2\cos4\pi ft$, which can be detected separately if the lock-in amplifier is appropriately tuned at the frequencies f and $2f$, respectively. This differential technique did not give any further information for most of the bands because of the complexity of the spectrum. It did, however, work well for the isolated band at 0.3045 eV, as shown in Fig. 3. The two halves of the recorded trace indicate the shift of the band with the field. The observed asymmetry is due to the broadening and intensity lowering of the band in the presence of the field. This can be easily understood by looking at the same band, recorded with and without an applied dc field. This is shown in Fig. 4(a). The asymmetry in the differences about the crossing point of the two bands, corresponds to the asymmetry of the two halves of Fig. 3. If these halves were symmetric, one could immediately and accurately measure the shift (and its direction) as twice the difference between the 0.0 cm^{-1} crossing point, and the zero-field band position (i.e., 0.3045 eV). The quadratic character of the effect is clearly exhibited by the recordings of Fig. 3, with linearly different dc fields, and the E_{ac} kept constant (any effect, quadratic in the field, varies as $E_{\mathrm{dc}}E_{\mathrm{ac}}$ when detected at the fundamental of the modulation, as discussed before). Detailed quantitative measurements for the same band are given in Fig. 4(b) for the shift and broadening, based on Fig. 4(a). Since this band is a superposition of the two levels $\Gamma_8(4)$ and $\Gamma_6(4)$ which lie close to each other, we can assume that the observed shift towards the ground state is a parallel shift for both of them. On the other hand, only the $\Gamma_8(4)$ is fourfold degenerate, and we can therefore attribute the observed broadening

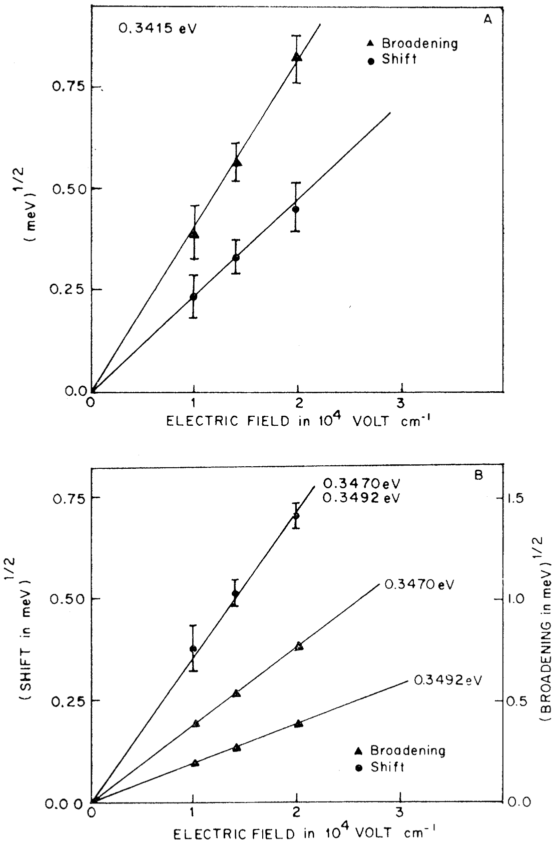

FIG. 6. Stark shift and broadening versus E_{dc} for the bands of Figs. 5(a) and 5(b).

(or asymmetry of Fig. 3) to an unresolved splitting of the fourfold degeneracy of the level $\Gamma_8(4)$.

Of the remaining bands, we were able to study only the strongest ones, because of the tendency of the weaker to disappear even at small fields.

The effect of the field on the pair of $\Gamma_8(5)$ levels is shown in Fig. 5(a) (recording) and Fig. 6(a), for the 0.3415-eV band. At least similar broadening and almost half of the same shift towards the ground state was observed for the 0.3435-eV band, for the same field. (The study of the quadratic character for this was not possible.) The former indicates a fourfold multiplicity for the $\Gamma_8(5)$ levels (as expected), and the latter is probably due to the repelling action of the $\Gamma_7(5)$ level, lying between the two, [see discussion following Eq. (10)].

The results for the pair of bands at 0.3470 and 0.3492 eV are shown in Figs. 5(b) and 6(b). The situation here is not clear. Equal shifts were observed for both bands, but the broadening was smaller for the 0.3492 eV. No symmetry assignment for these levels is available from stress data, although the Zeeman splittings imply a twofold and fourfold degeneracy for the 0.3492- and 0.3470-eV levels, respectively.[20] This is consistent with our results, assuming that their separation of 2.2 meV is accidental rather than due to the ground-state splitting, that the band at 0.3492 eV represents a transition from the $\Gamma_8(g)$ state to a twofold higher (non-p-like) excited state, and that its small broadening is due to a Stark broadening of $\Gamma_8(g)$. Similar contribution to the broadening of the other levels originating from $\Gamma_8(g)$ is very likely, and corrections could be made accordingly. The final level studied, at 0.3630 eV, showed a considerable broadening indicating a fourfold degenerate final excited state, and a shift away from the ground state. Both conclusions agree with those of Ref. 20. The results are shown in Fig. 7.

As discussed earlier, an electric field can shift and split (broaden) a fourfold level (Γ_8), and shift (but not split) a twofold level (Γ_6,Γ_7). The new levels and selection rules can be derived with the help of group theory, by reducing the zero-field level representations of Fig. 1 into those of the new symmetry group, which describes the crystal in the presence of an electric field. The choice of the latter group depends, of course, on the direction of the field relative to the crystallographic axes. In view of the new irreducible representations, one generally expects interesting anisotropic effects in the absorption processes (change in the electric dipole transition-selection rules), in contrast with the isotropic behavior of the transitions in the absence of the field (all the light polarizations are equally absorbed). Since the orientation of our sample did not allow application

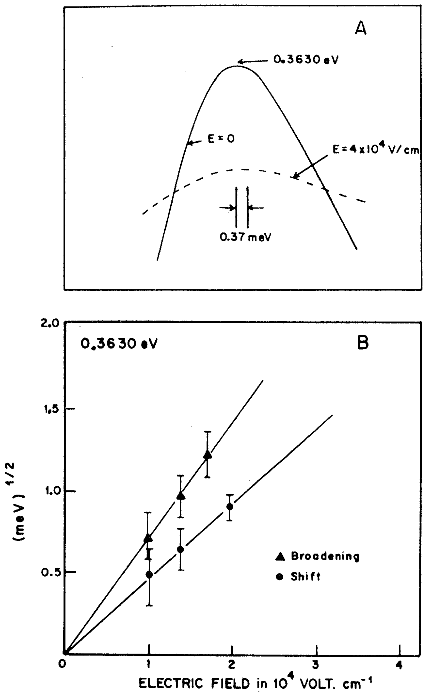

FIG. 7. (a) Recorded signal of the 0.3630-eV band with and without field. Slit width 320 μ. (b) Stark shift and broadening versus E_{dc} for the same band.

of the field along any of the high-symmetry axes, an explicit presentation of the above discussion was not considered worthwhile.

The rate of shift and splitting (or broadening), or empirical Stark coefficients t_s and t_b, respectively, are defined by

$$\text{shift} = t_s E^2,$$
$$\text{broadening} = t_b E^2.$$

The measured values for t_s and t_b are presented in Table I. No instrumental broadening corrections have been made, although the slit-width used was relatively small (80 and 160 μ). It is interesting to notice that these coefficients for diamond are 20–100 times smaller than those for acceptors in Si.[16] This is not surprising, in view of the fact that $(a_{\text{Si}}^*/a_{\text{C-C}}^*)^2 \approx 25$, (where a^* is defined as an average Bohr radius for the bound hole), and that the Stark shift is quadratic with the Bohr radius.[7] Also, the general increase of the shift (absolute value) as we pass from the lower to the higher excited states, seems to follow this argument, at least qualitatively. On the other hand, the shift of the high excited state at 0.3630 eV away from the ground state is understood in connection with the fact that most of the perturbing states lie between the ground state and the state at 0.3630 eV.

If we assume a splitting comparable to the observed broadening, and caused by the influence of only one level, i.e., equal to 0 and 2Δ as discussed earlier, it turns out[16] that the theoretical value for the ratio $|t_b/t_s|$ is 2. The observed ratio (Table I) is close to this value for some of the states.

Internal Coulomb fields, due to the presence of ionized impurities, although considerable in value ($\sim$500 V/cm), have been neglected, since such fields are independent of the external field.

No attempts were made to study the phonon-assisted absorption bands on the higher energy continuum (or the band at the single optical-phonon energy of 0.165 eV). Since such transitions are replicas of the fundamental spectrum[19] (0.30–0.37 eV), one should expect the phonon-assisted levels to shift and split accordingly in the presence of an electric field, assuming that there is no other field effect of different origin at these energies. It is clear from existing experimental work that a stress or a magnetic field as perturbations provide a more sensitive technique for this kind of experiments, rather than an electric field. We feel that a study of these features in the presence of a stress could possibly give more information about the nature of the mechanism involved and a check of the existing theoretical interpretation.[29]

TABLE 1. Numerical values of the empirical Stark coefficients and their ratios, based on the present measurements.

eV	$\Gamma_8(g)$	0.3045	0.3415	0.3435	0.3470	0.3492	0.3630
t_s[a]		−0.23	−0.60	−0.30?	−1.30	−1.30	+2.30
t_b[a]	0.40?	0.75	1.50	$\gtrsim$1.50	1.60	0.40	5.20
$\lvert t_b/t_s \rvert$		3.20	2.50		1.20		2.30

[a] In 10^{-9}-meV cm^2/V^2 units. (Values within 10%).

Note added in manuscript. While this work was in preparation, the article of Ref. 30 appeared in print, entitled *Photothermal Ionization and Photon-Induced Tunneling in the Acceptor Photoconductivity Spectrum of Semiconducting Diamond.* In trying to justify the partial or complete broadening of the bands in the presence of a dc field, Collins and Lightowlers assumed that the field disturbs the radius of the states when it exceeds the field at the hole position, because of the impurity center. While this may be true to some extent for the higher excited states, they ignore completely the possibility of Stark broadening, which, as mentioned earlier, is even more appreciable for the higher excited states. For the lower excited states, in view of the strong binding between the hole and the impurity center in diamond, we feel that the field has a negligible effect on the levels, other than the Stark effect. The quadratic character of our results confirms this. We do, however, believe that the large broadening of the 0.3630-eV band is partially due to hole-tunneling in the presence of the field via the Franz-Keldysch effect.[31]

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