Quantum model for phonon-assisted tunnel ionization of deep levels in a semiconductor

S. Makram-Ebeid

Laboratoires d'Electronique et de Physique Appliquée, 3 avenue Descartes, 94450 Limeil Brevannes, France

M. Lannoo

Institut Supérieur d'Electronique du Nord, 3 rue François Baës, 59046 Lille Cedex, France

(Received 28 September 1981)

We have developed a new quantum theory for phonon-assisted tunnel emission of electrons from deep semiconductor levels. Linear coupling of a deep level with lattice-phonon modes is assumed and a perturbation approach is used to calculate the tunnel ionization rate. For a single-phonon mode, the resulting phonon-assisted tunneling rate is first derived with the use of the Condon approximation and is found to be a function of the phonon linear coupling constant S and of the phonon energy $\hbar\omega$. A non-Condon approach is then used and results in an expression almost identical to the "Condon" one, except that the coupling constant S is replaced by a modified effective value. The limit of validity of the Condon treatment is then clearly deduced. The new quantum model readily lends itself to generalization such as coupling to multiple phonon modes. Experimental results are presented and confirm the validity of the model.

I. INTRODUCTION

The electron-emission rate from deep levels in GaAs and GaP was frequently observed to be a rapidly varying function of electric field and temperature (e.g., by Lang,[1,2] Pons and Makram-Ebeid,[3] Makram-Ebeid,[4,5] and Makram-Ebeid et al.[6]). For sufficiently strong electric fields, the emission rate of two deep levels, the chromium-related and the so-called *EL*2 levels, was observed to reach values at large fields and low temperature which were 10−20 orders of magnitudes higher than the thermal emission value extrapolated from an Arrhenius plot. With this in mind, we cannot associate the observation with a Poole-Frenckel process, and tunneling seems to be a much more plausible explanation. A particular argument in favor of tunneling is the small electron effective mass in GaAs and GaP where the observations were made. For the same ranges of electric fields, the emission of holes in GaAs was observed by Lang[1] to be insensitive to the electric field and this again suggests that the field emission is due to tunneling and is much smaller for holes due to their large effective mass compared to that of electrons. Another observation along the same lines is that made for the chromium level in GaAs by

Makram-Ebeid et al.[6] This is a mid-gap level and it is observed to emit holes and electrons; its electron emission rate is seen to increase very fast with electric field whereas its hole emission rate remains practically constant. The fact that the emission rate is sensitive to temperature as well as electric field suggests that we are dealing with a phonon-assisted tunneling mechanism.

Pons and Makram-Ebeid[3] have presented a semiclassical theory for phonon-assisted tunneling where a single-phonon mode was assumed to be linearly coupled to a deep level. In spite of the approximate semiclassical treatment used, an agreement was found between the theory and experimental data of the capacitive transients related to electron irradiation level *E*3 in GaAs under different conditions of temperature and electric field. Makram-Ebeid[4] had subsequently suggested an experimental procedure to reliably determine the electric field and temperature dependence of the deep-level electron emission rate e_n and to use a best-fit procedure to evaluate the Franck-Condon shift $S\hbar\omega$ as well as the energy $\hbar\omega$ of the phonon linearly coupled to the level (coupling constant S). The values of $S\hbar\omega$ and $\hbar\omega$ thus evaluated were found to be in remarkable agreement with values deduced from available data for photoionization, photo-

luminescence, and multiphonon electron-capture data for levels $EL2$ (main electron trap in bulk GaAs), $E3$ [irradiation level in vapor phase epitaxy (VPE) GaAs], and the ZnO center in GaP.

The purpose of the present paper is to develop a quantum-mechanical version of the phonon-assisted tunnel-emission model more rigorous than the previous semiclassical one. Apart from the gain in logical consistency, the new model will lend itself readily to generalizations such as many phonon modes and nonlinear coupling to the lattice. Also, more general barrier shapes will be considered. As with the older version, the model's predictions are very sensitive to the quantities $S\hbar\omega$ and $\hbar\omega$, the value of which can be determined by best fitting the observed electric field and temperature dependence of e_n with theoretical predictions. The values of $S\hbar\omega$ thus evaluated with the new model were found to be systematically larger than those derived with the older version (the discrepancy being $10-20\%$ for $E3$, $EL2$ in GaAs and ZnO center in GaP). In fact, the new evaluations are closer to the experimental results. It may also be mentioned that the new model does not lead to significantly different values for $\hbar\omega$ (the uncertainty in its determination being in both cases large). The new model version has already been used for the main electron trap in bulk GaAs (Ref. 5) and for the chromium-related level in GaAs.[6] It should be noted that the use of the older semiclassical version for the chromium level in GaAs would have led to a 100% discrepancy for the best-fit Franck-Condon shift $S\hbar\omega$ as compared to the value obtained with the new model and that the latter value agrees well with the $S\hbar\omega$ value deduced by optical methods (see Sec. IX).

II. CALCULATION OF THE TUNNELING IONIZATION RATE BY PERTURBATION METHODS

Oppenheimer[7] has used a perturbation approach to calculate the tunneling rate from an initial bound state $|b\rangle = \psi_b$, energy E_b, to a continuum of free states $|f\rangle = \psi_f$, energy E_f, under the influence of an electric field F. This formulation takes a form very similar to that encountered in familiar time independent perturbation theory, namely,

$$P = \frac{2\pi}{\hbar} \sum_f |\langle f | Fz | b \rangle|^2 \delta(E_f - E_b) , \qquad (1)$$

where P is the tunneling ionization rate for the electron initially in the stationary localized state

$|b\rangle$ of a deep potential well and z is the Cartesian coordinate in the direction of the electric field F with the well's centroid taken as origin.

The above result is readily applicable to the case of an electron trapped in a deep stationary level (no coupling to phonons) in a semiconductor and which is made to tunnel to the conduction band under the influence of an electric field. It is understood, in this case, that the single-electron wave functions have to be replaced by Wannier functions to take into account the effect of the semiconductor lattice.

To simplify the calculation and yet obtain results of general validity, we assume that the defect potential is composed of a Dirac-tridimensional potential well and of a long-range Coulomb-potential tail (attractive or repulsive). These assumptions will allow us to write analytical expressions for ψ_b and ψ_f and explicitly obtain the tunneling rate from Eq. (1).

For an electron in a ground state and if the wave function $\psi_b(\vec{r})$ is assumed to be spherically symmetrical (s state) and thus to depend solely on the distance $r = |\vec{r}|$ from the defect centroid, Schrödinger's equation takes the form

$$\frac{d^2}{dr^2}[r\psi_b(r)] = \left[K\left[\Delta_b - \frac{\alpha}{r}\right]\right]^2 r\psi_b(r) .$$

$$(2)$$

The definition of the barrier height Δ_b is apparent from Fig. 1. In Eq. (2), $K(\Delta)$ is the wave-function attenuation constant assumed to be a function of the barrier height. In general, the Δ-K dispersion law cannot be assumed to be parabolic
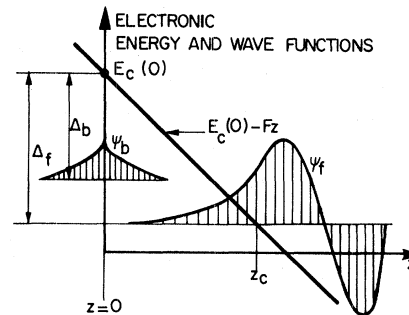

FIG. 1. Energy of the bound state (Δ_b) and of the free state (Δ_f) relative to the bottom of the conduction band at $z=0$ (trap centroid). The coordinate $z=z_c$ represents the classical turning point for the final state. The figure also shows sketches of the wave function ψ_b and ψ_f of the bound and free states, respectively.

and a two-band $K(\Delta)$ formula due to Franz[8] and Kane[9] will be used throughout this paper [Eq. (6) below]. The Coulomb-potential well tail α/r appearing in Eq. (2) will be assumed to be small; Eq. (2) can then be solved within the WKB approximation by making the Taylor's expansion:

$$K\left[\Delta_b - \frac{\alpha}{r}\right] \cong K(\Delta_b) - \frac{\alpha}{r}\left[\frac{dK(\Delta)}{d\Delta}\right]_{\Delta=\Delta_b},$$

leading to

$$\psi_b(r) = C_b r^{p_b-1} e^{-K_b r}, \tag{3}$$

where

$$p_b = \alpha[dK(\Delta)/d\Delta]_{\Delta=\Delta_b},$$

$$K_b = K(\Delta_b),$$

and the constant C_b as obtained by normalization is

$$C_b = \frac{(2K_b)^{p_b+1/2}}{[4\pi\Gamma(2p_b+1)]^{1/2}},$$

with Γ standing for Euler's gamma function.

The evaluation of the final free-electron-state wave function ψ_f will be done in a similar manner. We only have to deal with final states having negligible momentum components normal to the z axis, otherwise their probability of tunneling will be severely reduced (see, e.g., Gundlach[10]). The Coulomb tail assumed small will be treated in a one-dimensional manner whenever ψ_f is to be evaluated on the z axis. The free-electron wave function in the neutral bulk region of the semiconductor (with zero field) is assumed to be

$$\psi_f(\vec{r}) = \sqrt{2}\cos(k_{zf}z + \varphi_c), \tag{4}$$

where $z >> z_c$ and where k_{zf} is the wave vector in the z direction in the bulk neutral region and φ_c a constant phase angle. After Landau and Lifshitz,[11] this wave function corresponds, in the classically forbidden region $(z < z_c)$, to the expression:

$$[\psi_f(\vec{r})]_{r=z} = \frac{1}{2}\left[\frac{k_{zf}}{K(\Delta_f - Fz - \alpha/z)}\right]^{1/2}$$

$$\times \exp\left[\int_{z_c}^z K(\Delta_f - Fz - \alpha/z)dz\right].$$

We may again make a Taylor's expansion to take out the Coulomb potential (α/z) and simplify all the factors, except the rapidly varying exponential,

and the resulting expression is

$$[\psi_f(r)]_{r\cong z} \cong \left[\frac{k_{zf}}{2K_f}\right]^{1/2}\left[\frac{z_c}{z}\right]^{p_f}$$

$$\times \exp\left[\int_{z_c}^z K(\Delta_f - Fz)dz\right], \tag{5}$$

where $p_f = \alpha[dK(\Delta)/d\Delta]_{\Delta=\Delta_f}$ and $K_f = K(\Delta_f)$.

The expressions (3) and (5) for bound- (initial) and free- (final) state wave functions have both been obtained by making use of a Taylor series expansion in the exponentials to deal with the Coulomb tail of the potential well. It must be recalled that the calculation of the matrix element $\langle f | Fz | b \rangle$ is aimed to be used in Eq. (1) and involved the product $\psi_f\psi_b$ and the errors will tend to cancel.

In the Appendix, the matrix element $\langle f | Fz | b \rangle$ is explicitly evaluated. We may now substitute in Eq. (1) and note that the occurence of the delta function $\delta(E_f - E_b)$ therein implies that we have only to deal with elastic tunneling $(E_f = E_b$ or $\Delta_f = \Delta_b)$. The summation over the final states is transformed into a triple integral in $\vec{k}$ space and thus into the expression:

$$P = \frac{1}{\pi}\frac{m^{*2}}{\hbar^5}\left[\int_{E=0}^{\infty}\delta(E - E_b)\right.$$

$$\left.\times \int_{E_\perp=0}^E |\langle f | Fz | b \rangle|^2\frac{dE_\perp}{k_{zf}}dE\right],$$

where m^* is the electron effective mass in the conduction band and $E_\perp = \hbar^2 k_\perp^2/2m^*$, $\hbar k_\perp$ being the component of momentum perpendicular to the z direction. The integral over E is readily evaluated on account of the delta function $\delta(E - E_b)$ whereas that over $E_\perp$ is evaluated by noting that the expression of $|\langle f | Fz | b \rangle|^2$ as deduced in the Appendix is proportional to tunneling probability $e^{-A(E_\perp)}$, where

$$A(E_\perp) = \frac{2}{F}\int_0^\Delta K(\Delta, E_\perp)d\Delta,$$

in which use is made of the Franz-Kane relation[8,9] for $K(\Delta, E_\perp)$:

$$K(\Delta, E_\perp) = \left[\frac{2m^*}{\hbar^2}\right]^{1/2}\left[\frac{E_g - \Delta}{E_g}\Delta + E_\perp\right]^{1/2}, \tag{6}$$

and in particular, we define

$$K(\Delta) \equiv K(\Delta, E_\perp)_{E_\perp=0},$$

where m^* is the effective electron mass at the conduction-band minimum and the energy E_g is the band-gap width. It is seen that the factor $e^{-A(E_\perp)}$ decreases very quickly when $E_\perp$ increases

from zero to E and consequently $e^{-A(E_\perp)}$ has a very sharp maximum. Near this maximum, we can write after elementary calculations:

$$A \equiv [A(E_\perp)]_{E_\perp=0} = \frac{1}{2F} \left[\frac{2m^*}{\hbar^2} \right]^{1/2} E_g^{3/2} \left\{ \sin^{-1} \left[\left[\frac{\Delta}{E_g} \right]^{1/2} \right] - \left[1 - \frac{2\Delta}{E_g} \right] \left[\frac{\Delta}{E_g} \left[1 - \frac{\Delta}{E_g} \right] \right]^{1/2} \right\}$$

(7)

and

$$e^{-A(E_\perp)} = e^{-A} \exp(-E_\perp/\Delta E_\perp) ,$$

where

$$\Delta E_\perp = -1 \bigg/ \left[\frac{\partial A}{\partial E_\perp} \right]_{E_\perp=0} = \frac{2}{F} \left[\frac{2m^*}{\hbar^2} \right]^{1/2} \sin^{-1} \left[\left[\frac{\Delta}{E_g} \right]^{1/2} \right] ,$$

and thus

$$P = \frac{m^{*2}}{\pi \hbar^5} (| \langle f | Fz | b \rangle |^2)_{\substack{\Delta_f = \Delta_b \\ E_\perp = 0}} \frac{\Delta E_\perp}{k_{zf}} , \qquad (8)$$

Considerable simplification results from using a parabolic Δ-K (one-band) approximation (amounting to setting $E_g = \infty$ in the above relations). This approximation results in insignificant errors if it is only made for the evaluation of preexponential terms. In particular, we obtain

$$\Delta E_\perp \cong \frac{F}{2K_f} = \frac{2\Delta_b}{3A} ,$$

which together with Eqs. (A6) and (8) yields

$$P = \frac{2\Delta_b}{3\hbar} \frac{(3A/2)^{2p}}{\Gamma(2p+1)} \frac{e^{-A}}{A} \left[1 + \frac{1}{2A} - \left[\frac{\pi}{3A} \right]^{1/2} \right] .$$

(9)

A particularly interesting special case to examine is that of the absence of the Coulomb-potential tail ($p=0$) and an opaque barrier ($A \gg 1$); Eq. (9) gives

$$P = \frac{2\Delta_b}{3\hbar} \frac{e^{-A}}{A} , \qquad (10)$$

which is a result identical to that obtained by Korol[12] who used a Green's-function approach. Another interesting case is that of a pure Coulomb-attractive potential well for which it can then be shown that $p=1$, and which yields for $A \gg 1$

$$P = \frac{3}{4} \frac{\Delta_b}{\hbar} A e^{-A} , \qquad (11)$$

a result which should be compared with that of Landau and Lifshitz[11] for the electric field ionization of the hydrogen atom and which can be expressed in a form similar to the above, but with the numerical factor $\frac{3}{4}$ replaced by $\frac{16}{3}$. This difference in the numerical factors obtained is due to the very different treatments and approximations used.

III. INTRODUCING IN THE TUNNELING MODEL A LINEAR COUPLING TO A PHONON MODE

We now examine the effect of a linear coupling between the bound-state and lattice-vibration modes. To deal with this problem, we make use of a Born-Oppenheimer approximation according to which the electronic energy can be treated as a function of the coordinate of the lattice atoms whenever these atoms are much heavier than the electrons. This condition of validity is largely met in all semiconductors. We further assume that the Hamiltonian H_{el} of the bound electron has an "adiabatic" eigenvalue related linearly to a generalized lattice coordinate Q, for a single-phonon mode, by an equation of the form

$$H_{el} = -(2S)^{1/2} Q\hbar\omega + \text{const} , \qquad (12)$$

in which $\hbar\omega$ is the energy of the associated phonon, S the so-called Huang-Rhys coupling constant and the coordinate Q is normalized in the sense described by Messiah.[13] On account of the linear nature of Eq. (12), it can be shown that the system composed of the bound electron and the lattice vi-

bration behaves as a harmonic oscillator and that when the bound level is empty, it behaves like a harmonic oscillator with the same frequency but with an equilibrium point in $\vec{Q}$ space shifted by $-(2S)^{1/2}$. Figure 2 shows the potential energy of the system with a filled or empty bound state; this is the so-called configuration diagram.

The wave function describing the electron and the lattice when the bound state is filled is

$$\Psi_b(\vec{r},Q) = [\psi_b(\Delta_b,\vec{r})]_{\Delta_b = \Delta_b(Q)} X_{n_b}(Q) , \qquad (13)$$

where

$$\Delta_b(Q) = \Delta_T + S\hbar\omega + (2S)^{1/2}\hbar\omega Q ,$$

and $X_n(Q)$ is the normalized wave function of a harmonic oscillator with an "equilibrium point" at $Q=0$ and where the Q dependence of Δ_b is deduced from Fig. 2. The energy of the stationary composite state Ψ_b is $-\Delta_T + \hbar\omega(n_b + \frac{1}{2})$.

Similarly the composite wave function $\Psi_f(\vec{r},Q)$ corresponding to an electron in the free conduction-band state can be written as:

$$\Psi_f(\vec{r},Q) = \psi_f(\Delta_f,\vec{r}) X_{n_f}(Q + (2S)^{1/2}) , \qquad (14)$$

the eigenenergy of this stationary state being $-\Delta_f + \hbar\omega(n_f + \frac{1}{2})$.

A generalization of Oppenheimer's perturbation formula can be made by including the lattice coordinate Q as a further degree of freedom and thus, the new tunneling ionization rate R is given by

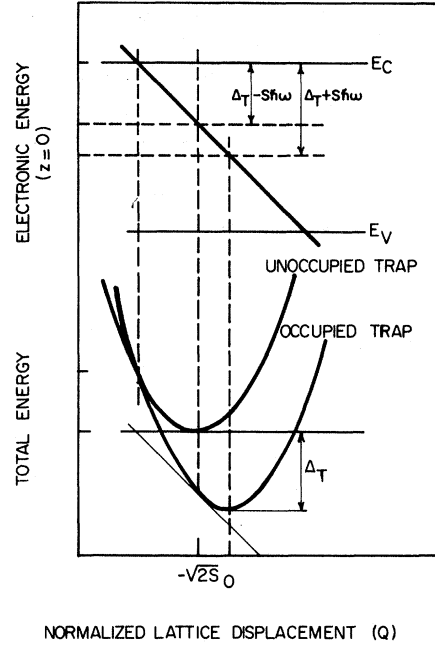NORMALIZED LATTICE DISPLACEMENT (Q)

FIG. 2. Configuration diagram showing the electronic energy (above) and the sum of elastic and electronic energy as a function of the generalized lattice coordinate Q (below).

$$R = \frac{2\pi}{\hbar} Av_{n_b} \sum_{f,n_f} | \langle \Psi_f(\vec{r},Q) | Fz | \Psi_b(\vec{r},Q) \rangle |^2$$

$$\times \delta(\Delta_T - \Delta_f + (n_f - n_b)\hbar\omega) , \qquad (15)$$

and Av_{n_b} indicates that one should take a statistical average over n_b values.

IV. CALCULATION OF THE TUNNELING IONIZATION RATE WITHIN A CONDON-TYPE APPROXIMATION

The evaluation of the tunneling ionization from Eq. (15) above requires the evaluation of the transition matrix element $\langle \Psi_f | Fz | \Psi_b \rangle$ which involves integration over both electronic and lattice coordinates. This matrix element can be written from Eqs. (13)–(15) as

$$\langle \Psi_f | Fz | \Psi_b \rangle = \int_{Q=-\infty}^{+\infty} X_{n_f}(Q + (2S)^{1/2}) X_{n_b}(Q) \left[\int \psi_f(\Delta_f,\vec{r}) Fz \psi_b(\Delta_b(Q,\vec{r}) d^3\vec{r}) \right] dQ . \qquad (16)$$

The approximation we shall use here consists in treating the triple $\vec{r}$ integral as independent of the coordinate Q. This can be justified if the triple integral value changes slightly over the range of Q values for which the product $X_{n_f}(Q + (2S)^{1/2}) X_{n_b}(Q)$ has an appreciable magnitude. Therefore we evaluate the $\vec{r}$ triple integral for a fixed value of Q which is such that

$$\Delta_b(Q) = \Delta_T + S\hbar\omega + (2S)^{1/2}\hbar\omega Q = \Delta_f .$$

This can be justified inasmuch as the value of Q thus defined corresponds to the maximum magnitude of the product $X_{n_f}(Q) X_{n_b}(Q + (2S)^{1/2})$. We leave for the next paragraph the evaluation of the error involved in

this approximation. With the above procedure, the matrix element to be calculated takes the form

$$\langle \Psi_f | Fz | \Psi_b \rangle = \langle \chi_{n_f} | \chi_{n_b} \rangle (\langle \psi_f | Fz | \psi_b \rangle)_{\Delta_b = \Delta_f} ,$$

where

$$\langle \chi_{n_f} | \chi_{n_b} \rangle \equiv \int_{-\infty}^{+\infty} \chi_{n_f}(Q + (2S)^{1/2}) \chi_{n_b}(Q) dQ .$$

The tunneling rate R of Eq. (15) now becomes

$$R = \sum_{m=-\infty}^{+\infty} \left[(\mathrm{Av}_{n_b} | \langle \chi_{n_b+m} | \chi_{n_b} \rangle |^2) \frac{2\pi}{\hbar} \sum_f (| \langle \psi_f | Fz | \psi_b \rangle |^2)_{\Delta_b = \Delta_f} \delta(\Delta_T - \Delta_f + m\hbar\omega) \right] .$$

We recognize in the inner sum the elastic tunneling ionization rate from a bound state of energy $-\Delta_b$ with $\Delta_b = \Delta_T + m\hbar\omega$. This elastic tunneling rate can be denoted by $P(\Delta_b) = P(\Delta_T + m\hbar\omega)$. The statistical average $\mathrm{Av}_{n_b} | \langle \chi_{n_b+m} | \chi_{n_b} \rangle |^2$ is a familiar expression appearing in many multiphonon calculations and has for example been expressed by Keil[14] in the form:

$$W_m^C = \mathrm{Av}_{n_b} | \langle \chi_{n_b+m} | \chi_{n_b} \rangle |^2 = \exp \left[\frac{m\hbar\omega}{2kT} - S \coth \left[\frac{\hbar\omega}{2kT} \right] \right] I_m \left[\frac{S}{\sinh(\hbar\omega/2kT)} \right] , \qquad (17)$$

T being the absolute temperature and k the Boltzmann constant. The phonon-assisted tunneling rate R within the Condon approximation can now be expressed as

$$R = \sum_{m=-\infty}^{+\infty} W_m^C P(\Delta_T + m\hbar\omega) , \qquad (18)$$

where it can be shown that

$$W_m^C > 0 \quad \text{and} \quad \sum_{m=-\infty}^{+\infty} W_m^C = 1 .$$

V. LIMITS OF VALIDITY OF THE CONDON APPROXIMATION

The result expressed in Eq. (18) above relies on the assumption that the triple $\vec{r}$ integral appearing in Eq. (16) is very slightly Q dependent. We now examine the error involved in this assumption. First, we attempt to evaluate this Q dependence. We limit ourselves for simplicity to the case where there is no Coulomb tail to the defect potential well. The results we shall obtain below can be generalized to the case where a Coulomb tail is present but no essential modification in these conclusions will be obtained in so doing. The triple $\vec{r}$ integral in question has been evaluated in the Appendix

[Eq. (A5)]; setting $p_f = p_b = 0$, we obtain

$$\langle f | Fz | b \rangle = \frac{\hbar^2}{m^*} (4\pi k_{zf})^{1/2} e^{-A/2} F(\eta) , \qquad (19)$$

where

$$\eta = \frac{z_1}{z_0} = \frac{\Delta_f - \Delta_b}{2F} \left[\left[\frac{\partial K(\Delta)}{\partial \Delta} \right]^{1/2} \right]_{\Delta = \Delta_b} ,$$

$$F(\eta) = \left[1 + \frac{1}{2A} + \sqrt{\pi} \left[\eta - \frac{1}{(3A)^{1/2}} \right] e^{\eta^2} [1 + \mathrm{erf}(\eta)] \right] ,$$

$$A = \frac{2}{F} \int_0^{\Delta_f} K(\Delta) d\Delta ,$$

$$\Delta_f = \Delta_T + m\hbar\omega ,$$

and

$$\Delta_b = \Delta_T + S\hbar\omega + (2S)^{1/2}\hbar\omega Q .$$

The dependence on Q of the matrix element $\langle f | Fz | b \rangle$ appears through the quantity η and we therefore try to put η in a simple explicit form. For simplicity, we, once more, take a parabolic Δ-K relation and obtain

$$\eta = \left[\frac{3A}{16} \right]^{1/2} \left[\frac{\Delta_f}{\Delta_b} \right]^{1/4} \frac{\Delta_f - \Delta_b}{\Delta_b} . \qquad (20)$$

The order of magnitude of the term $(3A/16)^{1/2}$

appearing above can be estimated by remembering that Eq. (18) is a first-order approximation to the tunneling rate and that the term $P(\Delta_T + m\hbar\omega)$ appearing therein is proportional to e^{-A}. The contribution due to this term would be totally negligible (less than 10^{-5} s^{-1}) if A were larger than 45 [see Eq. (10)]. Expression (20) can now be written as

$$\eta = -(Q - Q_m)\frac{(2S)^{1/2}\hbar\omega}{\Delta_0} \qquad (21)$$

where

$$Q_m = \frac{m - S}{(2S)^{1/2}}$$

and

$$\Delta_0 = \Delta_f \left[\frac{\Delta_b}{\Delta_f}\right]^{1/4}\left[\frac{16}{3A}\right]^{1/2} = \frac{2\hbar F^{1/2}}{(2m^*)^{1/4}}\Delta_b^{1/4} \gtrsim 0.35\Delta_f \ .$$

The energy Δ_0 appearing in the above expression depends only slightly on Q through the factor $\Delta_b^{1/4}$ and it will be treated in the following as a constant.

Figure 3 shows semilogarithmic plots of the function $F(\eta)$ appearing in Eq. (19) for different values of A. Also shown for comparison are the functions e^η and $e^{2\eta}$, which are straight lines in the semilogarithmic plot. We are only interested in investigating the behavior of $F(\eta)$ for the value of Q corresponding to large magnitudes of the vibronic wave-function product $X_{n_f}(Q + (2S)^{1/2})$

$\times X_{n_b}(Q)$. This range has a width of the order of $(2S)^{1/2}$ and this corresponds to an interval $\Delta\eta$ of the variable η of the order of $2S\hbar\omega/\Delta_0$. Except for very strong coupling, this interval width will be of the order or smaller than unity. Referring back
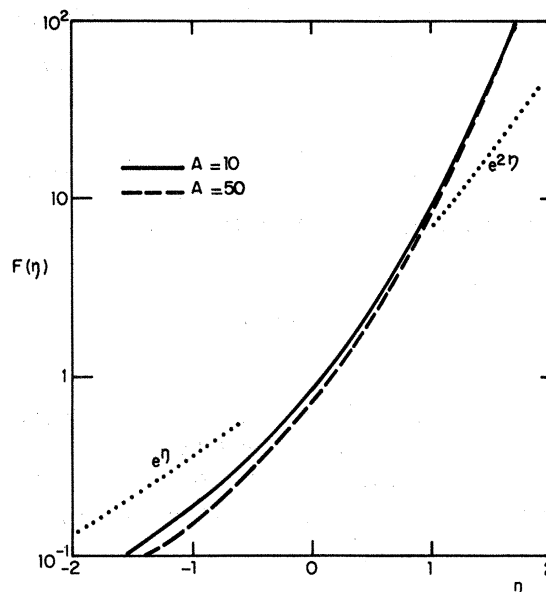

FIG. 3. The function $F(\eta)$ of the text compared to the exponentials e^η and $e^{2\eta}$.

to Fig. 3, we see that for such an interval $\Delta\eta$ containing $\eta = 0$, the function $F(\eta)$ can be approximated to an exponential function in the form

$$F(\eta) \cong F(0)e^{\zeta\eta} \cong F(0)e^{\beta(Q - Q_m)} \ ,$$

where   (22)

$$\zeta \cong 2, \quad \beta = -\zeta\frac{(2S)^{1/2}\hbar\omega}{\Delta_0} \ .$$

We are now in a position to obtain a closer approximation to the matrix element $\langle \Psi_f(\vec{r},Q) | Fz | \Psi_b(\vec{r},Q)\rangle$ than was done in the preceding section. We have

$$\langle \Psi_f(\vec{r},Q) | Fz | \Psi_b(\vec{r},Q)\rangle = \int X_{n_f}(Q + (2S)^{1/2})(\langle \psi_f | Fz | \psi_b \rangle)_{\Delta_b = \Delta_f}\frac{F(\eta)}{F(0)}X_{n_b}(Q)dQ \ .$$

$$= \left\langle X_{n_f}\left|\frac{F(\eta)}{F(0)}\right|X_{n_b}\right\rangle(\langle \psi_f | Fz | \psi_b\rangle)_{\Delta_b = \Delta_f} \ .$$

Proceeding along the lines of the preceding section, we get an equation similar to Eq. (18) but with the statistical "Condon" weights W_m^C replaced by "non-Condon" weights

$$W_m^{NC} \equiv Av_{n_b} | U_{n_b}^m |^2 \ ,$$

where

$$U_{n_b}^m = \left\langle X_n\left|\frac{F(\eta)}{F(0)}\right|X_{n_b}\right\rangle \cong \langle X_{n_b+m} | e^{\beta(Q - Q_m)} | X_{n_b}\rangle \ . \qquad (23)$$

The evaluation of the matrix elements involved in the above expression can be performed by means of operator algebra. The configuration coordinate Q can be written in operator notation:

$$Q = \sqrt{2}a - \frac{d}{dQ} \; ,$$

where a is the annihilation operator over the set of bound vibronic states χ_{n_b}. The operator $e^{\beta(Q-Q_m)}$ can now be transformed into a product with the use of Glauber theorem (see Messiah[13]), thus

$$e^{\beta(Q-Q_m)} = e^{\beta^2/2 - \beta Q_m} e^{-\beta d/dQ} e^{\sqrt{2}\beta a} \; .$$

In the above product, the factor $e^{-\beta d/dQ}$ is equivalent to a Taylor's expansion which, when acting on functions of Q is equivalent to replacing Q by $Q-\beta$. The factor $e^{\sqrt{2}\beta a}$ can be expanded in a Mac-Laurin series in $\sqrt{2}\beta a$; we then obtain after obvious manipulations

$$U_{n_b}^m = e^{\beta(\beta/2 - Q_m)} \sum_{j=1}^{n_b} \frac{(\sqrt{2}\beta)^j}{j!} \left[\frac{n_b!}{(n_b-j)!} \right]^{1/2} \langle \chi_{n_b+m}(Q + (2S)^{1/2}) | \chi_{n_b-j}(Q-\beta) \rangle \; ,$$

which involves the same type of overlap integrals seen in the previous section. Writing these overlap integrals explicitly after Keil,[14] we obtain

$$U_{n_b}^m = e^{\beta(\beta/2 - Q_m)} e^{-S_1/2} \left[\frac{n_b!}{(n_b+m)!} \right]^{1/2} S_1^{m/2} \left[\sum_{j=0}^{n_b} \frac{[(2S_1)^{1/2}\beta]^j}{j!} L_{n_b-j}^{m+j}(S_1) \right] \; ,$$

where $S_1 = \frac{1}{2}[(2S)^{1/2} + \beta]^2$ and $L_{n_b-j}^{m+j}(S_1)$ are the Laguerre polynomials as defined by Copson.[15] Making use of the relation

$$\left[\left[-\frac{d}{dX} \right]^j L_{n_b}^m(X) \right]_{X=S_1} = L_{n_b-j}^{m+j}(S_1) \; ,$$

as deduced from Copson, we see that the sum in j above is a Taylor series, so that

$$U_{n_b}^m = e^{\beta(\beta/2 - Q_m) - S_1/2} S_1^{m/2} \left[\frac{n_b!}{(n_b+m)!} \right]^{1/2} L_{n_b}^m(S_1 - \beta(2S_1)^{1/2}) \; .$$

After some manipulations, this expansion reduces to

$$U_{n_b}^m = \left[e^{-2\beta/(2S)^{1/2}} \left[\frac{1 + \beta/[2S]^{1/2}}{1 - \beta/[2S]^{1/2}} \right] \right]^{m/2} \left[\left[\frac{n_b!}{(n_b+m)!} \right]^{1/2} e^{-S_e/2} S_e^{m/2} L_{n_b}^m(S_e) \right] \; . \tag{24}$$

We recognize in the term in the second set of square brackets above the expression for the overlap integral $\langle \chi_{n_b+m} | \chi_{n_b} \rangle$ with S replaced by an equivalent value S_e where

$$S_e = S_1 - (2S_1)^{1/2}\beta = S - \tfrac{1}{2}\beta^2 = S \left[1 - \frac{\beta^2}{2S} \right] \; .$$

Substituting Eq. (24) into Eq. (23), we obtain

$$W_m^{NC} = \left[e^{-2\beta/(2S)^{1/2}} \left[\frac{1 + \beta/[2S]^{1/2}}{1 + \beta/[2S]^{1/2}} \right] \right]^m W_m^C(S_e) \; ,$$

where $W_m^C(S_e)$ is the same as W_m^C given by Eq. (17) except for the value of S being replaced by S_e. The factor in square brackets can be expanded in powers of $\beta/(2S)^{1/2}$, so we finally get

$$W_m^{NC} = \exp \left[-m \left[\frac{2}{3} \left| \frac{\beta^2}{2S} \right|^{3/2} + \frac{2}{5} \left| \frac{\beta^2}{2S} \right|^{5/2} \right] \right] W_m^C \left[S \left[1 - \left| \frac{\beta^2}{2S} \right|^{1/2} \right] \right] \; . \tag{25}$$

Thus we can see that the use of the Condon-type approximation made in the preceding section requires that the quantity $|\beta/(2S)^{1/2}|$ be small compared to unity, where from Eqs. (21) and (22):

$$\frac{\beta}{(2S)^{1/2}} = -\zeta \frac{\hbar\omega}{\Delta_0} \ ,$$ (26)

and thus we should have

$$\left| \frac{\beta}{(2S)^{1/2}} \right| \lesssim 6 \frac{\hbar\omega}{\Delta_T} << 1 \ .$$

In other words, the validity of the Condon-type approximation implies that the phonon energy $\hbar\omega$ be small compared to the free energy of ionization Δ_T. If the quantity $|\beta/(2S)^{1/2}|$ is not extremely small $[\,|\beta/(2S)^{1/2}| \sim \frac{1}{2}$, say], the exponential factor in Eq. (20) will still be close to unity and vary slowly with m so that the main departure from the Condon approximation is accounted for by replacing the Huang-Rhys constant S by an equivalent value

$$S\left[1 - [\beta/(2S)^{1/2}]\right] \cong S\left[1 - \left[\frac{6\hbar\omega}{\Delta_T}\right]^2\right] \ .$$

VI. ASYMPTOTIC EXPRESSIONS FOR THE STATISTICAL WEIGHTS W_m^C

Equation (17), giving the values of the statistical weights W_m^C, involves the modified Bessel function $I_m(X)$ with $X = S/\sinh(\hbar\omega/2kT)$. Two special cases are interesting:

(i) X is small compared to $|m|$ (low temperatures or large values of m). The Bessel function can be expanded by the first term of its MacLaurin series expansion and we obtain

$$W_m^C = \begin{cases} e^{-S(2\bar{n}+1)} \dfrac{[S(\bar{n}+1)]^m}{m!} & \text{for } m \geq 0 \\[3mm] e^{-S(2\bar{n}+1)} \dfrac{[S\bar{n}]^m}{m!} & \text{for } < 0, \end{cases}$$ (27)

and for $X = S/\sinh(\hbar\omega/2kT) << m$, where $\bar{n} = 1/[\exp(\hbar\omega/kT) - 1]$.

(ii) In the high-temperature limit (X large compared to m), we may use the following asymptotic expression given by Abramowitz and Stegun[16]:

$$I_m(X) \cong \left[\frac{X}{m + (m^2 + X^2)^{1/2}}\right]^m \frac{\exp[(m^2 + X^2)^{1/2}]}{(2\pi)^{1/2}(m^2 + X^2)^{1/4}} \cong \frac{e^X}{(2\pi X)^{1/2}} e^{-m^2/2X} \ ,$$

and thus

$$W_m^C = \exp\left\{-S\left[\tanh\left[\frac{\hbar\omega}{4kT}\right] - \frac{1}{8} \frac{(\hbar\omega/kT)^2}{\sinh(\hbar\omega/2kT)}\right]\right\} \frac{1}{(2\pi X)^{1/2}} \exp\left[-\frac{(m - m_1)^2}{2X}\right] \ ,$$ (28)

where

$$m_1 = X\frac{\hbar\omega}{2kT} = S\frac{(\hbar\omega/2kT)}{\sinh(\hbar\omega/2kT)} \quad \text{for } |m| << X \ .$$

A series expansion in $\hbar\omega/kT$ results in

$$W_m^C = \exp\left\{-\frac{S}{192}\left[\frac{\hbar\omega}{kT}\right]^3\left[1 - \left[\frac{\hbar\omega}{kT}\right]^2\right]\right\} \frac{e^{-(m - m_1)^2/2X}}{(2\pi X)^{1/2}}$$

with

$$m_1 = S \left[1 - \frac{1}{24} \left[\frac{\hbar\omega}{kT} \right]^2 \right] ,$$

and

$$X = S \left[\frac{2kT}{\hbar\omega} \right] \left[1 - \frac{1}{24} \left[\frac{\hbar\omega}{kT} \right]^2 + \cdots \right] = \frac{2kT}{\hbar\omega} m_1 .$$

Thus we see that for $kT \gtrsim \hbar\omega$, we can stop the above expansions to the zeroth-order term to obtain

$$W_m^C = \frac{e^{-(m-m_1)^2/2X}}{(2\pi X)^{1/2}} \cong \frac{e^{-(m-S)^2\hbar\omega/4kTS}}{(4\pi SkT/\hbar\omega)^{1/2}} , \tag{29}$$

which is a Gaussian-type distribution with a variance $2kTS/\hbar\omega$. This is not the only case where W_m^C follows a Gaussian law. In fact, it can be shown that, in general (see Lax[17]), W_m^C is a Gaussian distribution for $S \gg 1$ and $|m - S| \ll S$, of the form

$$W_m^C = \frac{e^{-(m-S)^2/2Y}}{(2\pi Y)^{1/2}} , \quad Y = S \coth(\hbar\omega/2kT) , \tag{30}$$

which reduces to (29) for $kT \gtrsim \hbar\omega$.

VII. AN APPROXIMATE ANALYTIC EXPRESSION FOR THE TUNNEL IONIZATION RATE

The tunnel ionization rate R has been set in the form of a sum of product terms $W_m^C P(\Delta_T + m\hbar\omega)$. These terms usually have a sharp maximum around a value of m. To evaluate this sum we can, therefore, approximate it to an integral. Even if each of one of the terms W_m^C and $P(\Delta_T + m\hbar\omega)$ varies too fast, it is the value of the product at the maximum that matters and at this maximum, these terms are, of course, not expected to vary quickly with m, and thus

$$R \cong \int_{\Delta=0}^{E_g} W_{m(\Delta)}^C P(\Delta) \frac{d\Delta}{\hbar\omega} ,$$

when $m(\Delta) = (\Delta - \Delta_T)/\hbar\omega$.

An especially interesting case to treat is that in which W_m^C is approximated by a Gaussian dependence, i.e.,

$$\frac{W_m^C}{\hbar\omega} = \frac{1}{[2\pi(\Delta_2)^2]^{1/2}} e^{(\Delta-\Delta_1)^2/2(\Delta_2)^2} \tag{31}$$

with $\Delta_1 = \Delta_T + S\hbar\omega$ and $(\Delta_2)^2 = 2S(\hbar\omega)^2 \coth(\hbar\omega/2kT)$. As far as $P(\Delta)$ is concerned, its dependence on Δ comes mainly from the WKB tunneling probability e^{-A} of Eq. (11). We again simplify by taking the case of a parabolic Δ-K relation. The product $W_m^C P(\Delta)$ will be maximum when the exponential argument

$$\theta(\Delta) = - \left[\frac{(\Delta-\Delta_1)^2}{2(\Delta_2)^2} + \frac{4}{3} \frac{2m^*}{\hbar^2} \frac{\Delta^{3/2}}{F} \right]$$

is a maximum (minimum absolute value) which amounts to

$$\theta'(\Delta_m) = - \frac{\Delta_m - \Delta_1}{(\Delta_2)^2} + 2 \left[\frac{2m^*}{\hbar^2} \right]^{1/2} \Delta_m^{1/2} = 0 \tag{32}$$

for the corresponding peak value Δ_m of Δ. Near the maximum value of θ, we have:

$$\theta(\Delta) = \theta(\Delta_m) + \frac{\theta''}{2} (\Delta - \Delta_m)^2$$

and

$$\int_0^{E_g} e^{\theta(\Delta)} d\Delta \cong e^{\theta(\Delta_m)} \int_{-\infty}^{+\infty} e^{-[|\theta''(\Delta_m)|/2](\Delta-\Delta_m)^2} d\Delta = e^{\theta(\Delta_m)} \left[\frac{2\pi}{|\theta''(\Delta_m)|} \right]^{1/2} .$$

We note that Eq. (32) is of the second degree in $\Delta_m^{1/2}$; straightforward algebra yields

$$\Delta_m - \Delta_1 = -2\Delta_1 / \{ 1 + [1 + (F/F_c)^2]^{1/2} \}^2 ,$$

with

$$F_c = \left[\frac{2m^*}{\hbar^2} \right]^{1/2} \frac{(\Delta_2)^2}{\Delta_1^{1/2}} = \left[\frac{2m^*}{\hbar^2} \right]^{1/2} \frac{2S(\hbar\omega)^2}{(\Delta_T + S\hbar\omega)^{1/2}} \coth\left[\frac{\hbar\omega}{2kT} \right] ,$$

and

$$R \cong \exp\left[-\frac{(\Delta_m - \Delta_1)^2}{2(\Delta_2)^2} \right] P(\Delta_m) \Big/ \left[1 + \frac{F_c}{F} \left\{ \frac{F_c}{F} + \left[\left[\frac{F_c}{F} \right]^2 + 1 \right]^{1/2} \right\} \right]^{1/2} \tag{33}$$

The above results depend on the use of the Gaussian approximation for the statistical weights W_m^C. As discussed above, this approximation holds true at high temperatures and also at low temperatures, provided that $|m - S| \ll S$; this inequality amounts to

$$|\Delta_m - \Delta_1| = \frac{2\Delta_1}{\{ 1 + [(F/F_c)^2 + 1]^{1/2} \}^2} \ll S\hbar\omega ,$$

and will be justified for sufficiently strong electric fields.

VIII. POSSIBLE GENERALIZATIONS OF THE MODEL

The legitimacy of the Condon-type approximation used in the preceding paragraph allows us to generalize our treatment as was done for the calculation of optical-absorption or emission spectra (for example, see Keil[14]). We can generalize the treatment to quadratic coupling by going exactly along the lines proposed by Keil.[14] A more interesting extension of the theory, however, is to include more than one phonon mode. As was shown by Keil[14] for optical spectra calculations, all we have to do is to replace the statistical weights by convolutions. In particular, for two phonon modes of phonon energy, $\hbar\omega_1$ and $\hbar\omega_2$, and coupling constants S_1 and S_2, respectively, we shall have

$$R = \sum_{m_1 = -\infty}^{+\infty} \sum_{m_2 = -\infty}^{+\infty} W_{m_1}^C(S_1, \hbar\omega_1) W_{m_2}^C(S_2, \hbar\omega_2) P(\Delta_T + m_1\hbar\omega_1 + m_2\hbar\omega_2) .$$

As discussed in the preceding section, the discrete nature of the above sums is not essential and we can replace them by integrals; thus we get after some transformations

$$R = \int_{\Delta=0}^{E_g} W^{eq}(\Delta) P(\Delta) d\Delta ,$$

with

$$W^{eq}(\Delta) = \int_{-\infty}^{+\infty} \frac{1}{\hbar\omega_1} W_{m_1}^C \frac{1}{\hbar\omega_2} W_{m_2}^C d\xi ,$$

where

$$m_1 = \frac{\xi - \Delta_T}{\hbar\omega_1} , \quad m_2 = \frac{\Delta - \xi - \Delta_T}{\hbar\omega_2} .$$

In other words, we can deal with integral-type convolutions. When the heights $W_{m_1}^C$ and $W_{m_2}^C$ can be ap-

proximated by Gaussian weights [Eq. (31)], their convolution is also Gaussian with first and second moments given by

$$\Delta_1 = \Delta_T + S_1 \hbar \omega_1 + S_2 \hbar \omega_2$$

and

$$(\Delta_2)^2 = S_1(\hbar\omega_1)^2 \coth(\hbar\omega_1/2kT) + S_2(\hbar\omega_2)^2 \coth(\hbar\omega_2/2kT) .$$

This is easily generalizable to an arbitrary number of phonon modes which are independent and linearly coupled to the level. In general, one can therefore write:

$$R = \int_{\Delta=0}^{E_g} \frac{e^{-(\Delta-\Delta_1)^2/2(\Delta_2)^2}}{[2\pi(\Delta_2)^2]^{1/2}} P(\Delta)d\Delta \tag{34a}$$

where

$$\Delta_1 = \Delta_T + \Delta_{FC} ,$$

$$\Delta_{FC} = \sum_i S_i \hbar \omega_i , \tag{34b}$$

$$(\Delta_2)^2 = \sum_i S_i(\hbar\omega_i)^2 \coth(\hbar\omega_i/2kT) , \tag{34c}$$

and at high temperatures,

$$(\Delta_2)^2 = 2kT \sum_i S_i \hbar \omega_i = 2kT\Delta_{FC} , \tag{34d}$$

with Δ_{FC} denoting the Franck-Condon shift. For the validity of Eqs. (34a)—(34d) we have assumed Gaussian approximations for each of the phonon modes. This means that we are either at high enough temperatures or that the electric field is strong enough to guarantee that $|m_i - S_i| << S_i$ for each of the terms of the expression of tunneling rate R which contributes significantly to the value R.

IX. AN EXPERIMENTAL METHOD FOR DETERMINING Δ_{FC} AND $\hbar\omega$

The tunnel ionization rate as given by Eq. (18) or Eq. (34) is very sensitive to the Franck-Condon shift and to the phonon energy of the vibration modes which are assumed to be linearly coupled to the level. As mentioned in the Introduction, this feature has been used to evaluate these quantities from the temperature and electric field dependence of the electron emission rate. The elastic tunneling rate $P(\Delta)$ appearing in Eqs. (18) and (34) has been obtained in a form containing the factor $A^{2p-1}e^{-A}$ [Eq. (9)], A being the WKB attenuation across a triangular barrier of height Δ in a field F. The ex-

ponent $2p$ has a sign and a value depending on the strength and sign of the long-range Coulomb potential of the level. In general, the Coulomb tail of a deep level will not represent a very strong potential compared to the defect localized potential, so that p will be small or, at most, near to unity and the factor A^{2p} will have a Δ dependence negligible compared to that of e^{-A}/A. Thus we take a general expression for $P(\Delta)$ similar in form to the case of a pure Dirac potential well [Eq. (10)], i.e.,

$$P(\Delta) = \gamma \frac{\Delta e^{-A}}{A} , \tag{35}$$

where γ is an adjustable preexponential factor.

The electron emission rate e_n can be measured by a differential transient capacitive technique as explained by Makram-Ebeid.[4,5] We then set

$$e_n = e_{n0} + R ,$$

where e_{n0} is the zero-field emission rate and R the tunneling rate as expressed by Eqs. (18) or (34). We then use the following procedure:

(i) We choose an arbitrary estimated value for $\hbar\omega$, we calculate R after Eq. (18), and when $kT \geq \hbar\omega$, we see that the model predicts a value of R depending solely on γ and Δ_{FC} as can be seen explicitly from the expressions (34a)—(34d) and (35). Figure 4 illustrates the method used for selecting the most suitable value of $S\hbar\omega$ for $EL2$. The error in evaluating $S\hbar\omega$ can be reduced by doing this fit at a selected set of high temperatures.

(ii) We now can change $\hbar\omega$ until a best fit can be found at low temperatures. Figure 5 shows the effect of varying $\hbar\omega$ on the temperature dependence of $e_n (\cong R)$ at relatively low temperatures (for $EL2$). It is seen that $\hbar\omega$ affects the way in which e_n saturates to its zero absolute-temperature value.

Figure 5 also illustrates the fact that, at high temperature, the model only depends on the Franck-Condon shift $\Delta_{FC} = S\hbar\omega$ and that only the low-temperature behavior is capable of yielding $\hbar\omega$. In the presence of many phonon modes, it is seen that the above procedure will give the correct value of $\Delta_{FC} = \sum_i S_i \hbar \omega_i$ since Eq. (34) shows that the high-temperature behavior of R only depends on
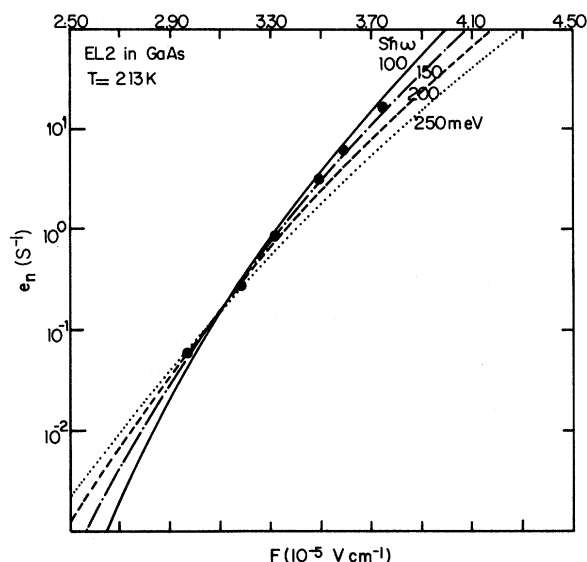
FIG. 4. Illustrating the choice of $S\hbar\omega$ for closest fitting of the experimental data in the case of $EL2$ the main electron trap in bulk and VPE GaAs.

FIG. 6. Comparison of theoretical calculations after our quantum model with the measured electric field dependence of the electron emission rate at different temperatures for level $EL2$ in GaAs after Makram-Ebeid (Ref. 5).

Δ_{FC} together with γ appearing in Eq. (35). The values $\hbar\omega$ determined from the above procedure must then be regarded as an average or effective value.

Figure 6 shows the result of the above fit for $EL2$ at different temperatures and electric field. We must note the good fit and we should remember that this fit was done at $T=213$ and 243 K to determine γ and Δ_{FC} and that the model predicted by itself in an accurate manner the behavior at $T \geq 243$ K. Similar remarks were done also for E_3 (Ref. 4) and Cr in GaAs.[6]
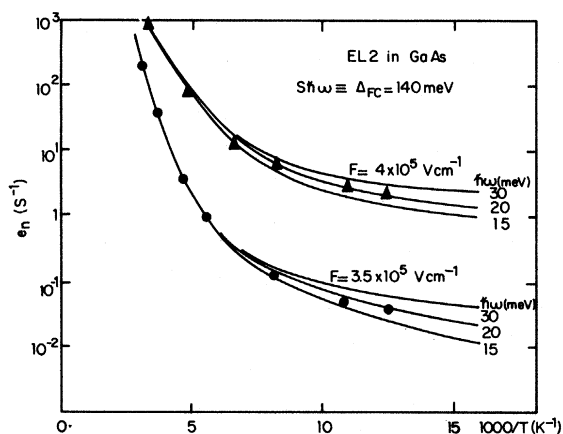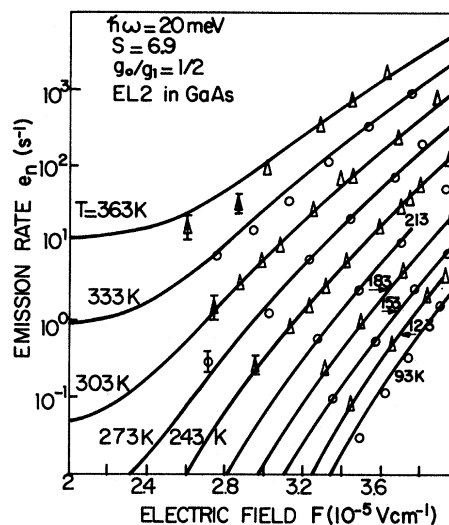
Table I gives the value of $S\hbar\omega, \hbar\omega$ and the preexponential factor γ when using the different versions of the model, which are as follows:

(i) our new quantum version as expressed in Eq. (18),

(ii) the Gaussian-type approximation as expressed by Eqs. (34a)—(34c), and

(iii) the semiclassical version of Pons and Makram-Ebeid.[3]

We see from this table that the new quantum version and the Gaussian approach yield neighboring estimation for $S\hbar\omega$ and $\hbar\omega$. The semiclassical version gives systematically lower values for $S\hbar\omega$ and especially in the case of the chromium level (100% difference).

Table II gives a comparison of the estimates for $S\hbar\omega$ and $\hbar\omega$ with the above procedure (using the new quantum version) with other types of estimates. Here again the good agreement is an experimental indication of the model's validity. In the case of $EL2$ (in GaAs), our evaluation of $S\hbar\omega$ and $\hbar\omega$ allowed the identification of a photoluminescence band frequently observed at 0.64 eV with this level.[27] However, the absolute value of the electron-capture cross section σ_n for $EL2$ at low temperature is considerably larger than would be expected from a direct multiphonon process. This discrepancy may be accounted for if we assume that the capture occurs via shallow hydrogenlike

FIG. 5. Illustrating the best-fit method for determining $\hbar\omega$ for the $EL2$ donor level in GaAs.

TABLE I. Effect of the choice of the model version for phonon-assisted tunneling on the best-fit parameter estimation ($S\hbar\omega$, $\hbar\omega$, and preexponential factor γ).

Level	$S\hbar\omega$ (meV)	$\hbar\omega$ (meV)	Preexponential $(3\hbar\gamma)/2$	Model version
E3	124 ± 10		1.2×10^{-2}	New quantum version
in GaAs	132 ± 10	10 ± 2	1.5×10^{-2}	Gaussian approximation
	100 ± 10		0.5×10^{-2}	Semiclassical
Cr^{+2}	195 ± 15		0.4×10^{-2}	New quantum version
in GaAs level	235 ± 15	35 ± 10	1×10^{-2}	Gaussian approximation
	110 ± 10		0.5×10^{-2}	Semiclassical
EL2	140 ± 10		0.075	New quantum version
in GaAs	152 ± 10	20 ± 5	0.2	Gaussian approximation
	115 ± 10		0.05	Semiclassical
ZnO	240 ± 25	Taken	0.5×10^{-2}	New quantum version
in GaP	218 ± 25	18.6	1×10^{-2}	Gaussian approximation
	195 ± 25	(photoluminescence)	0.15×10^{-2}	Semiclassical

excited states. This is particularly plausible since EL2 is known to be a donor.[28]

X. SOME REMARKS CONCERNING THE MODEL VALIDITY

In the treatment of tunneling made above, several implicit assumptions were made, among these, use of the macroscopic field F and the assumption of a long-range Δ-K relationship (or effective mass m^* for the parabolic case). This also implies the use of Wannier wave functions. Referring to the Appendix, we see that the evaluation of the electronic matrix element $\langle f | Fz | b \rangle$ depends on the product $z\psi_f(z)\psi_b(z)$ which has a sharp peak at $x=0$, $y=0$, and $z=z_0/\sqrt{2}=(1.5A/K_f^2)^{1/2}$. The order of magnitude of $z_0/\sqrt{2}$ can be estimated when A is neither too large or too small ($4 < A < 50$, say), $z_0/\sqrt{2} \sim 100$ Å. This distance is of the order of 20 interatomic distances so that we can make use of both a long-range Δ-K relation and of a macroscopic electric field (or macroscopic dielectric function).

The validity condition for the use of our "Condon-type" approximation is that $\hbar\omega << \Delta_T$, which also means that the phonon-vibrating period $(2\pi/\omega)$ is much longer than the tunneling transition time $(\hbar/\Delta_T)$. This, in fact, is another statement for the Born-Oppenheimer approximation validity. This condition is not very stringent for any level $(\Delta_T \geq 0.2$ eV) and this is because, unlike multiphonon emission (MPE) capture (see, e.g., Henry

and Lang[19]), the crossing of the electronic bound level with the conduction band is not involved in our tunneling process.

We have developed a method to evaluate the quantities S and $\hbar\omega$ characterizing the coupling of a deep level with phonon modes. One may wonder whether the unknown details of the deep-level potential can fundamentally alter this evaluation. In fact, a straightforward analysis shows that details in the nearest-neighbor potential barrier can only affect the preexponential factor (γ) in the tunneling rate expressions. The details of the long-range potential when approximated to a Coulombic (attractive or repulsive) tail introduce in the elastic tunneling rate $P(\Delta)$ of Eq. (9) a factor A^{2p-1} which varies with the energy Δ very slowly compared to the exponential factor e^{-A}. This shows that details of the potential barrier shape can, in general, be absorbed in the preexponential factor γ and have little influence on the estimation of S and $\hbar\omega$ (see the end of Sec. II).

Another important feature of the model is the use of the Franz-Kane Δ-K dispersion relation in the band gap. This relation is certainly a simplification since it does not account for example for the difference between hole and electron effective masses. To check the importance of a detailed knowledge of the Δ-K relation in the middle of the band gap, we have evaluated S and $\hbar\omega$ by our best-fit method while assigning to the gap width E_g in Eqs. (7)–(10) values from 1.4 to 1.8 eV. The corresponding alteration in the best-fit values of S and $\hbar\omega$ were found to be less than 4% for the

TABLE II. Comparison of the estimates for S and $\hbar\omega$ obtained by closest fitting the electron emission rate temperature and electric-field dependence with other independent estimations. σ_n is the electron capture cross section, σ_n^0 and σ_p^0 stand for the photoionization cross section with level full and empty, respectively, and $h\nu$ is the photon energy. VPE denotes vapor phase epitaxy; LPE denotes liquid phase epitaxy.

Level	Franck-Condon shift $S\hbar\omega$ (meV)	Phonon energy $\hbar\omega$ (meV)	Quantity measured	Theory used or Reference (for best fit)	Reference for the experimental work
Electron irradiation level (E3) in GaAs	125±10	10±2	e_n vs F and T	Present quantum model	Present and Makram-Ebeid (Ref. 4)
	Taken as above	11±2	σ_n, T=100−180 K ~2×10⁻¹⁷ cm²	Burt (Ref. 18)	Present work
	95±10	assumed small	Activation energy of σ $T>220$ K	Henry and Lang (Ref. 19)	Pons and Makram-Ebeid (Ref. 3)
	140 to 200	assumed small	$\sigma_n^0(h\nu)$	Bois and Chantre (Ref. 20)	Bois and Chantre (Ref. 19)
Cr acceptor level in (LPE) GaAs	195±15	35±10	e_n vs F and T	Present quantum model	Makram-Ebeid et al. (Ref. 6)
	Taken as above	27±3	σ_n, $T<200$ K $\simeq 2\times10^{20}$ cm²	Burt (Ref. 18)	Jesper et al. (Ref. 21)
	200	35	$\sigma_p^0(h\nu)$	Bois and Chantre (Ref. 20)	Leyral et al. (Ref. 22)
	170	28	Optical absorption	Piekara et al. (Ref. 23)	Hennel et al. (Ref. 24)
Electron trap (EL2) in bulk VPE GaAs	140±10	20±5	e_n vs F and T	Present quantum model	Makram-Ebeid (Ref. 5)
	20 to 160	20±3	σ_n vs $1/T$	Ridley (Ref. 25)	Mitonneau et al. (Ref. 26)
	120		$\sigma_n^0(h\nu)$ and $\sigma_p^0(h\nu)$	Bois and Chantre (Ref. 20)	Bois and Chantre (Ref. 20)
			σ_n at $T<80$ K too large to be accounted for by MPE theory		
ZnO center in GaP	240±25	taken 18.6	e_n vs F and T	Present quantum model	Lang (Ref. 1)
	190	18.6	Luminescence	First and second moments	Henry and Lang (Ref. 19)

trap investigated in Table II. This insensitivity to E_g can best be put in evidence by making a MacLaurin expansion of A [Eq. (7)] in terms of Δ_f:

$$A \cong \frac{4K_f \Delta_f}{3F} \left[1 - \frac{3\Delta_f}{10E_g} \right] .$$

Owing to multiphonon absorption, the most probable tunneling transitions will occur for $\Delta_f \lesssim \frac{1}{4} E_g$ and hence, E_g (or details in the mid gap Δ-K relation) will have a minor influence.

XI. SUMMARY AND CONCLUSIONS

We have built a new quantum theory for the phonon-assisted tunneling process from a localized level to the conduction band in a semiconductor. The tunneling rate is calculated by using a perturbation approach. A Condon-type approximation is first used. Another approximation goes beyond a pure Condon treatment and proves that the error in the Condon-type treatment is equivalent to replacing the value of the Huang-Rhys coupling constant S by an effective value $S_e \cong S(1 - (2\hbar\omega/\Delta_0)^2)$ where Δ_0 is an energy comparable to one third of the free Gibbs ionization energy Δ_T.

Experimental observation support the validity of the model. Only two best-fit parameters, Δ_{FC} and γ are sufficient to accurately predict the high-temperature behavior of the tunnel ionization rate. A best-fit procedure is used and the parameter values deduced are found to be in good agreement

with various other sources of estimation. This is a second experimental evidence of the model's validity.

From a practical viewpoint, the theory we have developed allows us to use the electric field ionization data for the evaluation of the Franck-Condon shift Δ_{FC} and of $\hbar\omega$ by electrical means. This provides a link between the optical spectra related to a deep level and its electrical ionization energy. An illustration for exploiting this type of link is given by the 0.64-eV luminescence band observed in semi-insulating GaAs and which was identified by Mircea-Roussel and Makram-Ebeid as the $EL2$ level in GaAs.

Another practical utility of the present theory is its ability to predict the high-field behavior of deep-level transients. In particular, the deep-level transient spectra (DLTS) are observed to be severely distorted in shape and position at high fields which renders their identification difficult and the concentration evaluation erroneous. The knowledge of the electric field and temperature dependence of the emission rate allows us to simulate the DLTS spectra and to overcome the above mentioned difficulties.

ACKNOWLEDGMENTS

APPENDIX

In this Appendix, we evaluate the electronic transition matrix element $\langle f \,|\, Fz \,|\, b \rangle$ appearing in the text. We start by rewriting the wave function of the final and initial (bound) states in the simplified forms:

$$\psi_f(\vec{r}) = \left[\frac{k_{zf}}{2K_f} \right]^{1/2} \left[\frac{z_c}{z} \right]^{p_f} \exp\left[\int_{z_c}^{z} K(\Delta_f - Fz) dz \right] ,$$

and (A1)

$$\psi_b(\vec{r}) = \frac{(2K_b)^{p_b + 1/2}}{[4\pi\Gamma(2p_b + 1)]^{1/2}} r^{p_b - 1} \exp(-K_b r) ,$$

where $K_f = K(\Delta_f)$, $K_b = K(\Delta_b)$, and p_f and p_b are defined in the text. The matrix element to be evaluated involves a triple integral which is easier to evaluate with spherical coordinates

$$x = r \sin\theta \cos\varphi, y = r \sin\theta \sin\varphi, z = r \cos\theta .$$

This change to spherical coordinates yields

$$\langle f \,|\, Fz \,|\, b \rangle = 2\pi F \int_{r=0}^{\infty} \psi_b(r) r \left[\int_{r=\text{const}} \psi_f(z) z \, dz \right] dr .$$ (A2)

In this last equation, use will be made of expressions (A1) over all space. This will give rise to minor errors because, as it will become obvious later, the major contribution to the integrals comes from the neighborhood of the defect in the classically forbidden region where expressions (A1) hold true. The above z integral can be easily evaluated by noting that

$$\frac{\partial \ln(\psi_f(z))}{\partial z} \cong K_f - \frac{p_f}{z} \cong K_f \quad \text{for } z \gg \frac{p_f}{K_f} \ .$$

Therefore, $\psi_f(z)$ can be approximated to the exponential function of z:

$$\psi_f(z) \cong (\psi_f)_{z=r} \exp[K_f(z-r)] \ ,$$

for $|z| \gg p_f/K_f$. We may note however that, due to the factor z appearing in the z integral of Eq. (A2), the contribution of the region where $|z| \leq p_f/K_f$ can be safely neglected and we obtain

$$\langle f \,|\, Fz \,|\, b \rangle = \frac{2\pi F}{K_f} \int_{r=0} \psi_b(r) r(\psi_f)_{z=r} \left[\left[r - \frac{1}{K_f} \right] + \left[r + \frac{1}{K_f} \right] e^{-2K_f r} \right] dr \ .$$

Substituting for ψ_f and ψ_b from Eqs. (A1) in the above expressions, we obtain

$$\langle f \,|\, Fz \,|\, b \rangle = \frac{2\pi F}{K_f} \int_{z=0}^{\infty} f_1(z) f_2(z) dz \ , \tag{A3}$$

where

$$f_1(z) = \left[z - \frac{1}{K_f} + \left[z + \frac{1}{K_f} \right] e^{-2K_f z} \right] \exp\left[- \int_0^z [K(\Delta_f - Fz) - K(\Delta_b)] dz \right] \ ,$$

and

$$f_2(z) = \left[\frac{K_b k_{zf}}{4 K_f \Gamma(2p_b + 1)} \right]^{1/2} (2K_b z)^{p_b} \left[\frac{z_c}{z} \right]^{p_f} \exp\left[- \int_{z=0}^{z_c} K(\Delta_f - Fz) dz \right] \ .$$

In the text, we are mainly interested to the case where $\Delta_f \cong \Delta_b$ and consequently the exponents p_f and p_b will be nearly equal and hence $f_2(z)$ will be a very slowly varying function of z and the integral of the product $f_1(z) \cdot f_2(z)$ can be evaluated as follows:

$$\int_0^{\infty} f_1(z) \cdot f_2(z) dz \cong f_2(z_m) \int_0^{\infty} f_1(z) dz \ ,$$

where z_m is the value of z for which the rapidly varying function $f_1(z)$ is maximum. Another considerable simplification results by approximating the last exponential factor in the expression for $f_1(z)$ to a Gaussian function. This can be done by expanding $K(\Delta_f - Fz)$ in a Taylor's series in z about $z=0$ and retaining the first two terms. Thus

$$\exp\left[\int_0^z [K(\Delta_f - Fz) - K(\Delta_b)] dz \right] = \exp\left[\int_0^{z_1} [K(\Delta_f - Fz) - K(\Delta_b)] dz \right] \exp\left[\int_{z_1}^z [K(\Delta_f - Fz) - K(\Delta_b)] dz \right]$$

$$= \exp\left[\left[\frac{z_1}{z_0} \right]^2 - \left[\frac{z - z_1}{z_0} \right]^2 \right] \ , \tag{A4}$$

where

$$z_1 = (\Delta_f - \Delta_b)/F, \quad z_0^2 = 2 \Big/ \left[F \left[\frac{\partial K(\Delta)}{\partial \Delta} \right]_{\Delta = \Delta_b} \right] \ .$$

The integral of $f_1(z)$ can now be easily evaluated in terms of the error function erf as defined by Abramowitz and Stegun[16] as follows:

$$\int_0^\infty f_1(z)dz \cong \int_0^\infty e^{(z_1/z_0)^2-(z-z_1)^2/z_0^2}\left[z-\frac{1}{K_f}\right]dz + \int_0^\infty \left[z+\frac{1}{K_f}\right]e^{-(K_b+K_f)z}dz$$

$$=\frac{z_0^2}{2}\left\{(1-e^{z_1^2-(z_c-z_1)^2/z_0^2})+\left[\frac{z_1}{z_0}-\frac{1}{K_f z_0}\right]\sqrt{\pi}e^{(z_1/z_0)^2}\left[\text{erf}\left[\frac{z_c-z_1}{z_0}\right]+\text{erf}\left[\frac{z_1}{z_0}\right]\right]\right\}+\frac{K_b+2K_f}{(K_b+K_f)^2 K_f} \; .$$

In the above expression, we note that $z_c \gg z_0$ except for very "transparent" tunneling barrier giving rise to very fast tunneling rates, we can therefore set $z_c = \infty$ in the above result. We may also note that the maximum value of $f_1(z)$ corresponds approximately to that of the function

$$ze^{-(z-z_1)^2/z_0^2} \; ,$$

and hence to

$$z \equiv z_m = \frac{z_1+\sqrt{2}z_0}{2} \cong (\tfrac{1}{2})^{1/2}z_0 \; .$$

Thus,

$$\langle f\,|\,Fz\,|\,b\rangle = \frac{\pi F z_0^2}{K_f}\left[\frac{K_b k_{zf}}{4K_f\Gamma(2p_b+1)}\right]^{1/2}(2K_b)^{p_b}\left[\frac{z_0}{\sqrt{2}}\right]^{p_b-p_f}z_c^{p_f}\exp\left[-\int_{z=0}^{z_c}K(\Delta_f-Fz)dz\right]$$

$$\times\left\{1+\sqrt{\pi}\left[\frac{z_1}{z_0}-\frac{1}{K_f z_0}\right]e^{(z_1/z_0)^2}\left[1+\text{erf}\left[\frac{z_1}{z_0}\right]\right]+\frac{2(K_b+2K_f)}{(K_b+K_f)^2 K_f z_0^2}\right\} \; .$$

The nonexponential terms in the above expressions are unduly complex, they can considerably be simplified by making the assumption that the Δ-K relationship is parabolic. The use of the more accurate Franz-Kane Δ-K relationship will introduce correction factors of the order of unity in these terms. We therefore conserve the essential features of an accurate calculation by approximating the nonexponential terms in a simplified manner and yet more accurately calculate the exponential factor as well as (z_1/z_0) in the term

$$e^{(z_1/z_0)^2}[1+\text{erf}(z_1/z_0)]$$

with the help of Franz-Kane Δ-K relationship. The use of parabolic relationship yields:

$$z_0^2 \cong \frac{4\Delta_f}{FK_f} = \frac{3A}{K_f^2} \; , \quad z_c \cong \frac{3A}{4K_f}$$

and thus,

$$(z_c/z_0) = \frac{(3A)^{1/2}}{4} \; ,$$

where

$$A = 2\int_0^{z_c}K(\Delta_f-Fz)dz$$

is the WKB attenuation of $|\psi_f|^2$ across a triangular potential barrier of height Δ_f. Further, by recalling that we are mainly interested in transition for which $\Delta_f \cong \Delta_b$, we may set $K_b \cong K_f$; hence, we obtain

$$\langle f\,|\,Fz\,|\,b\rangle = \frac{2\pi\hbar^2}{m^*}\left[\frac{k_{zf}}{4\pi\Gamma(2p_b+1)}\right]^{1/2}[2(6A)^{1/2}]^{p_b}\left[\frac{(6A)^{1/2}}{4}\right]^{p_f}$$

$$\times\exp\left[-\frac{A}{2}\right]\left[\left[1+\frac{1}{2A}\right]+\sqrt{\pi}\left[\frac{z_1}{z_0}-\frac{1}{(3A)^{1/2}}\right]e^{(z_1/z_0)^2}[1+\text{erf}(z_1/z_0)]\right] \; . \tag{A5}$$

A special case of this expression which is of particular interest is that for which $\Delta_f = \Delta_b$ exactly and the above expression becomes, in this case,

$$\langle f \mid Fz \mid b \rangle = \frac{2\pi \hbar^2}{m^*} \left[\frac{k_{zf}}{4\pi \Gamma(2p+1)} \right]^{1/2} e^{-A/2} \left[\frac{3A}{2} \right]^p \left[1 + \frac{1}{2A} - \left[\frac{\pi}{3A} \right]^{1/2} \right], \tag{A6}$$

where $p = p_f = p_b$.

A remarkable feature of the above result is the fact that the square of the matrix element $\mid \langle f \mid Fz \mid b \rangle \mid^2$ is proportional to the e^{-A} which is the WKB probability of tunneling through a triangular barrier of height Δ_b, the remaining factors appearing in Eq. (A6) vary relatively slowly with Δ_b as compared to the variation in e^{-A}.

---

[1]D. V. Lang, J. App. Phys. 45, 3014 (1974).

[2]D. V. Lang, J. Appl. Phys. 47, 3587 (1976).

[3]D. Pons and S. Makram-Ebeid, J. Phys. (Paris) Appl. F 40, 1161 (1979).

[4]S. Makram-Ebeid, Appl. Phys. Lett. 37, 464 (1980).

[5]S. Makram-Ebeid, Defects in Semiconductors, MRS Meeting Proceedings, Vol. 2, edited by J. Narayan and T. Y. Tan (North-Holland, New York, 1981), p. 495.

[6]S. Makram-Ebeid, G. M. Martin, and D. W. Woodard, J. Phys. Soc. Jpn. 49, Suppl. A, 287 (1980).

[7]J. R. Oppenheimer, Phys. Rev. 31, 66 (1928).

[8]W. Franz, in Handbuch der Physik, edited by S. Flügge (Springer, Berlin, 1956), p. 155.

[9]E. O. Kane, J. Phys. Chem. Solids 12, 181 (1959).

[10]K. H. Gundlach, J. Appl. Phys. 44, 5005 (1973).

[11]L. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon, Oxford, 1958), pp. 158 and 275.

[12]E. N. Korol, Fiz. Tverd. Tela (Leningrad) 19, 22 (1977) [Sov. Phys.—Solid State 19, 1327 (1977)].

[13]A. Messiah, Mécanique Quantique (Dunod, Paris, 1959), Vol. I, p. 367.

[14]T. Keil, Phys. Rev. 140, A601 (1966).

[15]E. T. Copson, An Introduction to the Theory of a Function of a Complex Variable (Oxford Univeristy Press, London, 1935), p. 270.

[16]M. Abramowitz, and L. A. Stegun, Handbook of Mathematical Functions (Dover, New York, 1965), p. 378.

[17]M. Lax, J. Chem. Phys. 20, 1752 (1952).

[18]M. G. Burt, J. Phys. C 12, 4827 (1979).

[19]C. H. Henry and D. V. Lang, Phys. Rev. B 15, 989 (1977).

[20]D. Bois and A. Chantre, Rev. Phys. Appl. F 15, 631 (1980).

[21]T. Jesper, B. Hamilton, and A. R. Peaker, in Semi-insulating III-V Materials, edited by G. J. Rees (Shiva, Orpington, 1980), p. 233.

[22]P. Leyral, F. Litty, S. Loualiche, A. Nouailhat, and G. Guillot, Solid State Commun. (in press).

[23]V. Piekara, J. M. Langer, and E. B. Krulowska-Fuld, Solid State Commun. 23, 583 (1980).

[24]A. M. Hennel, W. Szuskiewicz, G. Martinez, and B. Clerjaud, Rev. Phys. Appl. F 15, 697 (1980).

[25]B. K. Ridley, J. Phys. C 11, 2323 (1980).

[26]A. Mitonneau, A. Mircea, G. M. Martin, and D. Pons, Rev. Phys. Appl. F 14, 853 (1979).

[27]A. Mircea-Roussel and S. Makram-Ebeid, Appl. Phys. Lett. 38, 1007 (1981).

[28]A. Mircea, A. Mitonneau, L. Hollan, and A. Brière, Appl. Phys. (Berlin) 11, 153 (1976).