some mathematical description of μ_z. Following Rorschach, it is assumed that μ_z is a randomly fluctuating stationary function of time, which can be described by the autocorrelation function given in Eq. (3).

The spectral density given in Eq. (4) gives the amplitude of that part of the random motion of μ_z occurring at frequency ω. Substituting Eq. (4) into Eq. (17) and averaging over the solid angle yields, for the average direct interaction transition probability of these nuclei at a radius r from the impurity,

$$\langle W(r)\rangle = (C/2)r^{-6} = \tfrac{3}{5}\gamma_I^2(\langle\mu_z^2\rangle - \langle\mu_z\rangle^2)(\tau_c/(1+\omega_0^2\tau_c^2))r^{-6}. \quad (18)$$

The substitution of the average Larmor frequency ω_0 for ω is valid for all nuclei except for those within a distance b' of the impurity, whose resonant frequency is shifted out of the resonance line shape. This radius b', the critical radius, may or may not correspond to the spin-diffusion barrier radius b, as pointed out by Blumberg,[5] but the two are of comparable magnitude and usually small compared with the distance between impurities. Now by integrating Eq. (18) from b' to R, where R is the radius of the sphere associated with each impurity, one has for the spin-lattice relaxation time

$$T_1 = 3(b')^3/4\pi C\rho_J, \quad (19)$$

where ρ_J is the impurity concentration $(4/3\pi R^3)^{-1}$. This agrees with Blumberg's expression for the rapid-diffusion T_1.

Rorschach[4] has recently derived a general expression for T_1 which has two asymptotic forms, according to the magnitude of a dimensionless parameter. This parameter δ is equal to $\frac{1}{2}(\beta/b)^2$, where β is the pseudopotential radius as defined by DeGennes[6] and b is the barrier radius for spin diffusion. For $\delta \ll 1$, the asymptotic form is the same as that above, while for $\delta \gg 1$, the form is that of the original diuffsion limited expression of DeGennes.

It should be pointed out that, if one knows the energy-level configuration of the impurity and the impurity concentration, then the only unknown in the expression for T_1 is the autocorrelation time τ_c of the impurity. By measuring T_1 as a function of magnetic field, temperature, and sample orientation one should be able to determine τ_c as a function of these experimental parameters as in the case for ξ.

CONCLUSION

Preliminary measurements of the second moment and T_1 have been made on $CaF_2:Eu^{2+}$ for two concentrations as a function of temperature and magnetic field intensity. The results tend to confirm the essential features of the theory. Currently a number of other rare-earth and iron-group ions doped in CaF_2 are being studied and the results will be published shortly.

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Phonon-Assisted Electroabsorption*

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Recently several experiments have been reported on electroabsorption spectra in indirect-bandgap materials. These observations refer essentially to the change in absorption produced by an applied electric field $\mathcal{E}$ in the material under study. The particular photon-energy region explored has been that where phonon-assisted interband absorption obtains. Usually, considerable structure appears in the experimental curves. The absorption change $\Delta\alpha$ varies quite radically with photon energy both in amplitude and in sign. All theories extant on the phenomenon of electroabsorption are concerned with direct-bandgap transitions. In the light of recent experimental results, however, in the neighborhood of indirect transitions, it is appropriate to calculate the electroabsorption spectrum for phonon-assisted processes in order to have a more applicable theoretical model with which to compare experimental results. The present paper reports just such a calculation. A formula for $\Delta\alpha$ is presented in the case of phonon-assisted interband absorption.

INTRODUCTION

RECENTLY, several experiments have been reported on electroabsorption spectra in indirect-bandgap materials.[1–3] These observations refer essentially to the change $\Delta\alpha$ in absorption produced by an applied electric field $\mathcal{E}$ in the material under study. The particular photon energy region explored has been

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that where phonon-assisted interband absorption obtains. Usually considerable structure appears in the experimental curves. The absorption change $\Delta\alpha$ varies quite radically with photon energy both in amplitude and in sign. Such structure is not obtained characteristically with direct-bandgap experiments.[4–12]

The theory for the electroabsorption was worked out originally by Franz[13] and Keldysh[14] and more recently in greater detail by Callaway.[15,16] The latter has predicted considerable structure in the spectrum. In Callaway's theory, the structure is due to several different effects. Perhaps the most interesting of these is that due to the Wannier-Stark ladder.

These theories are applicable to direct-bandgap transitions. But the experimentally observed structure is seen in phonon-assisted transitions and not in direct ones. Hence, it is appropriate to calculate the absorption spectrum for indirect processes in the presence of an electric field in order to have an applicable theoretical model with which to compare experimental results. It is the purpose of this paper to report on just such a calculation.

THEORETICAL PREMISES

The essential premise of the calculation is that an electron, whose valence-band state is modified by the presence of an electric field, is lifted into the electric-field-modified conduction band by the absorption of an incoming photon of frequency ω plus the emission (or absorption) of a lattice phonon of angular frequency ω. The problem is then to calculate the transition rate for this process from which the absorption coefficient is immediately obtainable. This rate R is

$$R=\sum_{\substack{\text{final}\\\text{states}}}\sum_{\substack{\text{initial}\\\text{states}}}(\text{Probability of initial state})\times w_{fi}, \quad (1)$$

where w_{fi} is the transition probability per unit time for state i (initial) to state f (final).

The initial state consists of n photons, N phonons, and one valence electron in the presence of an electric field. Symbolically

$$|i\rangle=|v,N,n\rangle=|\text{initial state}\rangle. \quad (2)$$

The final state, in the case of phonon emission, is

$$|f\rangle=|c,N+1,n-1\rangle=|\text{final state}\rangle. \quad (3)$$

The c indicates that the electron ends up in the conduction band. The phonon-absorption case will involve a final state with $N-1$ instead of $N+1$. The result for this case is easily obtained by some obvious modifications of the phonon-emission result so that the detailed analysis need not be pursued independently.

The perturbation is

$$\Delta H=\Delta H_{e\gamma}+\Delta H_{e\phi}, \quad (4)$$

where the photon-electron interaction is

$$\Delta H_{e\gamma}=(e/m)\mathbf{A}\cdot\mathbf{p} \quad (5)$$

or in the dipole approximation

$$\Delta H_{e\gamma}=[e/m(\epsilon V)^{1/2}]\boldsymbol{\varepsilon}\cdot\mathbf{p}Q_\gamma, \quad (6)$$

where $\mathbf{A}$ is the vector potential and Q_γ is the annihilation operator corresponding to $\mathbf{A}$. The volume is V, and the scalar ϵ is the dielectric constant whereas the vector $\boldsymbol{\varepsilon}$ is the polarization of the light. The vector $\mathbf{p}$ refers to the momentum of the electron. The phonon-electron interaction reduces to

$$\Delta H_{e\varphi}=(1/\sqrt{V})P(\mathbf{r},\mathbf{q})Q_\varphi^*\exp(-i\mathbf{q}\cdot\mathbf{r}), \quad (7)$$

where P is a function with the periodicity of the lattice and Q_φ^* is the creation operator for a phonon of wave vector $\mathbf{q}$. The function P is connected, of course, with the polarization of the phonon under consideration and with spatial derivatives of the lattice-electron interaction potential.

Following Callaway[15] and his use of the effective Hamiltonian idea,[17,18] we accept for the wave functions of a band-b electron in the presence of an electric field $\mathcal{E}$, the following:

$$\Psi_b(\nu,\mathbf{k}_x,\mathbf{r})=\textstyle\sum_{k_x}c_b(\nu,\mathbf{k})\psi_b(\mathbf{k},\mathbf{r}), \quad (8)$$

where

$$c_b(\nu,\mathbf{k})=\frac{1}{\sqrt{N_x}}\exp\left\{\frac{i}{e\mathcal{E}}\int_0^{k_x}[E-E_b(k_x'\mathbf{k}_\perp)]dk_x'\right\} \quad (9)$$

and

$$E=\frac{2\pi e\mathcal{E}}{\kappa}\nu+\frac{1}{\kappa}\int_{-\kappa/2}^{\kappa/2}E_b(k_x',\mathbf{k}_\perp)dk_x', \quad (10)$$

where κ is the width of the Brillouin zone in the x direction of the crystal and $\psi_b(\mathbf{k},\mathbf{r})$ and $E_b(k_x,\mathbf{k}_\perp)$ refer to the usual Bloch wave functions and energies of electrons in a crystal in zero field. The quantum number ν takes on N_x integral values, where N_x is the

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number of states in the Brillouin interval κ in the x direction. The different ν designate the steps of the Wannier-Stark ladder. The bands b assume values v for the valence band or c for the conduction band in the present problem.

Within this framework, it is immediately clear that the process is a second-order one exactly as in the case of zero-field phonon-assisted transitions. The first-order matrix elements of ΔH vanish. Hence, the transition probability w_{fi} is given by

$$w_{fi}=\frac{2\pi}{\hbar}\delta(E_f-E_i)\left|\sum_j \frac{\langle f|\Delta H|j\rangle\langle j|\Delta H|i\rangle}{E_j-E_i}\right|^2. \quad (11)$$

Here E_i, E_j, and E_f refer, respectively, to the initial, intermediate, and final energies of the entire system—N phonons, n photons plus an electron.

CALCULATION OF w_{fi}

With regard to the intermediate states $|j\rangle$ these are of two types. The first consists of one less photon in the system and the electron in some band b. The phonon population is undisturbed. The second type of intermediate state is one in which the photon population remains undisturbed, but the number of phonons is increased by one and the electron is again in some band b. Further calculation indicates that, of all of these possible intermediate states, one dominates the rest for band structures like that of silicon and germanium. This happens because only one intermediate state yields an energy denominator of a few tenths of an electron volt, while all the others yield denominators not less than about one electron volt. Assuming that the matrix elements are about the same order of magnitude for the intermediate states of possible interest, we ignore, in first approximation, all of them but the one with the smallest energy denominator. For this one, the intermediate state is represented symbolically by $|c, N, n-1\rangle$. The dominating process, therefore, is one in which a photon is absorbed into the system first, raising an electron from the valence band into a virtual state in the conduction band. Afterward, a phonon is created and the electron goes to a real state in the conduction band. This is just the process that dominates in the zero-field case. As the calculation proceeds, it will become clear that this process also dominates in the presence of a field $\mathcal{E}$.

We must now fix our attention on the matrix elements

$$\langle j|\Delta H|i\rangle=\langle c, N, n-1|\Delta H_{\gamma e}|v, N, n\rangle \quad (12)$$

and

$$\langle f|\Delta H|j\rangle=\langle c, N+1, n-1|\Delta H_{e\varphi}|c, N, n-1\rangle, \quad (13)$$

which are to be divided by the energy denominator

$$E_j-E_i=\frac{2\pi e\mathcal{E}}{\kappa}(\nu'-\nu)+\frac{1}{\kappa}\int_{-\kappa/2}^{\kappa/2}[E_c(k_x,\mathbf{k}_\perp)-E_v(k_x,\mathbf{k}_\perp)]dk_x-\hbar\omega. \quad (14)$$

It is found because of the vanishingly small momentum of a photon, that the intermediate state $\mathbf{k}_\perp'$ is equal to the initial state $\mathbf{k}_\perp$. However, there is not a selection rule on the Wannier-Stark ladder step ν' $(\neq\nu)$ so that all intermediate steps ν' must be summed. Hence the sum over j, designating the intermediate states, reduces to a sum over ν'. The final-state ladder step is ν'', and the final electron momentum is $\mathbf{k}_\perp''\neq\mathbf{k}_\perp'$. These disappear in the sum over final states when obtaining the transition rate R of Eq. (1).

A careful evaluation of the matrix element (12), on the assumption that the usual interband optical matrix element of the electron momentum $\mathbf{P}_{cv}$ is independent of $\mathbf{k}$, yields

$$\langle c, N, n-1|\Delta H_{e\gamma}|v, N, n\rangle=-\delta_{\mathbf{k}_\perp',\mathbf{k}_\perp}\frac{e}{m}\left(\frac{n\hbar}{2\omega\epsilon V}\right)^{1/2}|\boldsymbol{\varepsilon}\cdot\mathbf{P}_{cv}|\frac{1}{\kappa}\mathcal{g}, \quad (15)$$

where

$$\mathcal{g}=\int_{-\kappa/2}^{\kappa/2}dg\,\exp G(g,\nu'-\nu,\mathbf{k}_\perp). \quad (16)$$

And employing the following notation for convenience

$$\mathbf{E}_b(g,\mathbf{k}_\perp)\equiv\frac{1}{\kappa}\int_0^g E_b(k_x,\mathbf{k}_\perp)dk_x, \quad (17)$$

the exponent G may be written

$$G(g,\nu'-\nu,\mathbf{k}_\perp)=-(2\pi i/\kappa)g(\nu'-\nu)-(i/e\mathcal{E})g[\mathbf{E}_c(\kappa,\mathbf{k}_\perp)-\mathbf{E}_v(\kappa,\mathbf{k}_\perp)]+(i/e\mathcal{E})\kappa[\mathbf{E}_c(g,\mathbf{k}_\perp)-\mathbf{E}_v(g,\mathbf{k}_\perp)]. \quad (18)$$

Somewhat analogously, the matrix element (13) may be evaluated to yield the result

$$\langle c, N+1, n-1|\Delta H_{e\varphi}|c, N, n-1\rangle=-i\delta_{\mathbf{k}_\perp'',\mathbf{k}_\perp-\mathbf{q}_\perp}[(N+1)\hbar/2\omega V]^{1/2}|\Phi_c|(1/\kappa)\mathfrak{L}, \quad (19)$$

where

$$\mathfrak{L}=\int_{-\kappa/2}^{\kappa/2}df\,\exp F(\nu'',\nu',\mathbf{q},f,\mathbf{k}_\perp), \quad (20)$$

and Φ_c represents the usual zero-field phonon-electron matrix element for a conduction-band transition. It is completely analogous to the quantity $e\boldsymbol{\varepsilon}\cdot\mathbf{p}_{cv}(m\epsilon^2)^{-1}$ in the photon case. And, perhaps somewhat unjustifiably, this matrix element is assumed to be independent of $\mathbf{k}$ as was its analog. In fact, this is only a first-order approximation. It is not too difficult to take Φ_c under the integral sign where it properly belongs. The integral may be evaluated if Φ_c does not vary too rapidly with $\mathbf{k}$. Since we will use steepest descent methods, any slowly varying function multiplying the exponential merely contributes the value of the function at the point of steepest descent as obtained from the exponential $F(\nu'',\nu',\mathbf{q},f,\mathbf{k}_\perp)$. Therefore, since one does not expect the phonon-electron matrix element to be a violently oscillating one, it seems appropriate to extract

it from the integral and assume it to be approximately constant. The function $F(\nu'',\nu',\mathbf{q},f,\mathbf{k}_\perp)$ is found to be

$$F(\nu'',\nu',\mathbf{q},f,\mathbf{k}_\perp)=-(2\pi i/\kappa)f(\nu''-\nu') -(if/e\mathcal{E})[\mathbf{E}_c(\kappa,\mathbf{k}_\perp-\mathbf{q}_\perp)-\mathbf{E}_c(\kappa,\mathbf{k}_\perp)] +(i\kappa/e\mathcal{E})[\mathbf{E}_c(f-q_x,\mathbf{k}_\perp-\mathbf{q}_\perp)-\mathbf{E}_c(f,\mathbf{k}_\perp)] +iq_x[(2\pi/\kappa)+(1/e\mathcal{E})\mathbf{E}_c(\kappa,k_\perp-\mathbf{q}_\perp)]. \quad (21)$$

Combining the results of the foregoing discussion and Eqs. (14), (15), and (19), the sum of Eq. (11) is found to take the form

$$\sum_j \frac{\langle f|\Delta H|j\rangle\langle j|\Delta H|i\rangle}{E_j-E_i}=i\delta_{\mathbf{k}_\perp'',\mathbf{k}_\perp-\mathbf{q}_\perp}\frac{e}{m}|\boldsymbol{\varepsilon}\cdot\mathbf{P}_{cv}||\Phi_c| \times\left[\frac{n(N+1)\hbar^2}{4\omega\omega\epsilon V^2}\right]^{1/2}\frac{1}{\kappa^2}\sum_{\nu'}\frac{\int\int df dg\exp(F+G)}{E_j-E_i}. \quad (22)$$

Now since the terms in the summation over ν' depend upon the number ν' in a particularly simple way, the summation can, in fact, be easily performed. If we interchange the order of integration—over f and g—with summation over ν', the problem can be solved by employing the following approximate result

$$\sum_{\nu'=1}^{N_x}\frac{\exp(2\pi i/\kappa)(f+g)\nu'}{\nu'-\boldsymbol{\nu}} =\pi i\exp(2\pi i/\kappa)(f-g)\boldsymbol{\nu}+\cdots \quad \text{if} \quad f>g =-\pi i\exp(2\pi i/\kappa)(f-g)\boldsymbol{\nu}+\cdots \quad \text{if} \quad f<g. \quad (23)$$

This result is an approximate one, good for relatively small electric fields where the Wannier-Stark ladder levels are spaced close enough together to be approximated by a continuum. The corrections to the foregoing are, in fact, easily added on.

Inserting the result (23) back into (22), we arrive at the expression

$$\sum_j \frac{\langle f|\Delta H|j\rangle\langle j|\Delta H|i\rangle}{E_j-E_i} =-\delta_{\mathbf{k}_\perp'',\mathbf{k}_\perp-\mathbf{q}_\perp}\frac{e}{m}|\boldsymbol{\varepsilon}\cdot\mathbf{P}_{cv}||\Phi_c|\left[\frac{n(N+1)\hbar^2}{4\omega\omega\epsilon V^2}\right]^{1/2}\frac{1}{\kappa\epsilon\mathcal{E}} \times\int_{-\kappa/2}^{\kappa/2}df\exp A(f)\int_{-\kappa/2}^{f}dg\exp B(g)+\cdots, \quad (24)$$

where $A(f)$ and $B(g)$ differ from the functions F and G, respectively, only in that the quantity ν' in the latter is replaced by the $\boldsymbol{\nu}$ of (23). This number is given by the identity

$$\boldsymbol{\nu}\equiv\nu-(\kappa/2\pi e\mathcal{E})[\mathbf{E}_c(\kappa,\mathbf{k}_\perp)-\mathbf{E}_v(\kappa,\mathbf{k}_\perp)-\hbar\omega]. \quad (25)$$

The A and B functions are, therefore, given, respectively, by

$$A(f)=-(2\pi i/\kappa)f(\nu''-\nu) -(if/e\mathcal{E})[\mathbf{E}_c(\kappa,\mathbf{k}_\perp-\mathbf{q}_\perp)-\mathbf{E}_v(\kappa,\mathbf{k}_\perp)-\hbar\omega] +(i\kappa/e\mathcal{E})[\mathbf{E}_c(f-q_x,\mathbf{k}_\perp-\mathbf{q}_\perp)-\mathbf{E}_c(f,k_\perp)] +iq_x[(2\pi/\kappa)+(1/e\mathcal{E})\mathbf{E}_c(\kappa,\mathbf{k}_\perp-\mathbf{q}_\perp)] \quad (26)$$

and

$$B(g)=(i/e\mathcal{E})\{\kappa\mathbf{E}_c(g,\mathbf{k}_\perp)-\kappa\mathbf{E}_v(g,\mathbf{k}_\perp)-g\hbar\omega\}. \quad (27)$$

And the other terms, represented by the dots in (24), are discarded on the grounds that they cannot contribute to the process under investigation. Basically, this happens because only the term exhibited couples the photon and phonon process. All other terms do not do so. They refer to pure photon or pure phonon processes not under consideration here.

The problem now reduces to that of evaluating the pair of coupled integrals in (24). Employing the result derived in Appendix A, and keeping in mind the presence of the δ function in (11), and the fact that the photon energy $\hbar\omega$ of interest is just about that which causes interband phonon-assisted transitions in the absence of a field ($\mathcal{E}=0$), only one term need be kept. This is because, upon applying energy conservation at the energy $\hbar\omega$ of interest, this is the only one which would yield a nonzero contribution.

$$\int_{-\kappa/2}^{\kappa/2}df\exp A(f)\int_{-\kappa/2}^{f}dg\exp B(g) =\int_{-\kappa/2}^{\kappa/2}\frac{d\xi}{dB/d\xi}\exp[A(\xi)+B(\xi)]. \quad (28)$$

In the above, we have introduced a new variable ξ (cf. Appendix A) which replaces both f and g. That is, the functions $A(\xi)$ and $B(\xi)$ are just the functions exhibited in Eqs. (26) and (27) where f and g are both replaced by ξ.

We note here, as an aside, that the energy denominator which was temporarily obscured during the step represented by Eq. (24) is now before us again in step (28) through the term $dB/d\xi$. This term does not involve the Wannier-Stark ladder steps and is, in fact, just the denominator one obtains in the field-free case.

$$dB/d\xi=(i/e\mathcal{E})[E_c(\xi,\mathbf{k}_\perp)-E_v(\xi,\mathbf{k}_\perp)-\hbar\omega]. \quad (29)$$

Calculation of other possibly interfering processes, in each case, returns a denominator proportional to the field-free one just as in the present case. And since, of all of these competing processes, the present one yields a significantly smaller energy denominator than all others, we are justified in concentrating only on this process.

CALCULATION OF R

We return now to the original quantity R of Eq. (1) and note, first, that when applied to the present

problem, R may be written:

$$R=\sum_{\substack{\text{phonon}\\ \text{states}}}\sum_{\mathbf{k}_\perp''}\sum_{\nu''=1}^{N_x}\sum_{\nu=1}^{N_x}(1/N_x)w_{fi}, \tag{30}$$

where now our expression for w_{fi} is obtained by inserting the results of (28) and (24) back into (11). A careful examination of the resulting function w_{fi} shows that its dependence on ν'' and ν arises only in the form $\nu''-\nu$. We may therefore write

$$w_{fi}=w_{fi}(\nu''-\nu,\mathbf{k}_\perp,\mathbf{q}). \tag{31}$$

In this connection, it must be noted that this fact obtains because terms such as the last bracketed one of (26) do not contribute to w_{fi} since the latter is the square of the absolute value of (24) and the term mentioned is a phase factor which disappears on taking absolute values.

We now wish to perform the finite double sum of (30). Since the function to be summed is of the form (31), the result is given by

$$R=\sum_{\substack{\text{phonon}\\ \text{states}}}\sum_{\mathbf{k}_\perp''}\sum_{l=-N_x}^{N_x}(1-|l|/N_x)w_{fi}(l,\mathbf{k}_\perp,\mathbf{q}). \tag{32}$$

In this equation, one merely replaces the difference $\nu''-\nu$ of Eq. (31), wherever it appears, by the variable l. The foregoing discussion enables us to write (32) in terms of an integral $\mathcal{J}(\mathbf{k}_\perp,\mathbf{q})$ related to that of (28) as follows

$$R=\sum_{\substack{\text{phonon}\\ \text{states}}}\sum_{\mathbf{k}_\perp''}\delta_{\mathbf{k}_\perp'',\mathbf{k}_\perp-\mathbf{q}_\perp}\frac{e^2n(N+1)h}{4\pi m^2\omega\omega\epsilon V^{5/3}}\times|\boldsymbol{\varepsilon}\cdot\mathbf{P}_{cv}|^2|\Phi_c|^2\frac{1}{(e\mathcal{E})^3}|\mathcal{J}(\mathbf{k}_\perp,\mathbf{q})|^2. \tag{33}$$

The boldface $\mathbf{l}$ is obtained from the δ-function condition on the conservation of energy between initial and final states;

$$\mathbf{l}\equiv-(\kappa/2\pi e\mathcal{E})[\mathbf{E}_c(\kappa,\mathbf{k}_\perp'')-\mathbf{E}_v(\kappa,\mathbf{k}_\perp)-\hbar\boldsymbol{\omega}+\hbar\boldsymbol{\omega}]. \tag{34}$$

The term $|\mathbf{l}|/N_x$ has been dropped because it is quite small compared to unity. (The photon frequency is the boldface $\boldsymbol{\omega}$ and the phonon frequency is ω.) The integral $\mathcal{J}(\mathbf{k}_\perp,\mathbf{q})$ is exactly that exhibited in Eq. (28), where $A(\xi)$ is now slightly modified from that given in (26)—the phase factor is discarded because it contributes nothing after the square of the absolute value of the integral is taken. As previously mentioned,

$$A(\xi)=-(2\pi i/\kappa)\mathbf{l}\xi-(i/e\mathcal{E})\xi\{\mathbf{E}_c(\kappa,\mathbf{k}_\perp-\mathbf{q}_\perp)-\mathbf{E}_v(\kappa,\mathbf{k}_\perp)-\hbar\boldsymbol{\omega}\}+(i\kappa/e\mathcal{E})[\mathbf{E}_c(\xi-q_x,\mathbf{k}_\perp-\mathbf{q}_\perp)-\mathbf{E}_c(\xi,\mathbf{k}_\perp)], \tag{35}$$

and the function B is just that exhibited in (27) with g replaced by ξ.

We must now examine the integral $\mathcal{J}(\mathbf{k}_\perp,\mathbf{q})$ more carefully. Keeping in mind its definition Eq. (28) and the relations (27) and (35) to be inserted in this definition, and employing the relation (34) to eliminate the $\mathbf{l}$ dependence, the integral becomes

$$\mathcal{J}(\mathbf{k}_\perp,\mathbf{q})=\int_{-\kappa/2}^{\kappa/2}\frac{d\xi}{dB/d\xi}\exp C(\xi), \tag{36}$$

where the exponent $C(\xi)$ is

$$C(\xi)=-(i/e\mathcal{E})\xi(\hbar\boldsymbol{\omega}-\hbar\omega)+(i\kappa/e\mathcal{E})[\mathbf{E}_c(\xi-q_x,\mathbf{k}_\perp'')-\mathbf{E}_v(\xi,k_\perp)]. \tag{37}$$

This integral may be evaluated by the method of steepest descents. This method indicates immediately, upon picking the proper path in the complex ξ plane, that the major contributions to the integral always come from points in the neighborhood of $\xi=\xi_1$, where, if $dB/d\xi$ is slowly varying,

$$(dC/d\xi)|_{\xi_1}=0=(i/e\mathcal{E})\{E_c(\xi_1-q_x,\mathbf{k}_\perp'')-E_v(\xi_1,\mathbf{k}_\perp)-\hbar\boldsymbol{\omega}+\hbar\omega\}. \tag{38}$$

Since we are interested in the absorption for photons of energy $\hbar\boldsymbol{\omega}$ near the zero-field phonon-assisted transition onset, there is only a limited range of $\mathbf{k}_\perp$ and $\mathbf{q}$ for which real values of ξ_1 can be found which satisfy (38). Imaginary values of ξ_1 result if $\hbar\boldsymbol{\omega}$ is too small or if $\mathbf{k}_\perp$ or $\mathbf{q}$ are chosen inappropriately. This regime corresponds to an exponential early absorption onset. For sufficiently high values of $\hbar\boldsymbol{\omega}$ and proper choice of $\mathbf{k}_\perp$ and $\mathbf{q}$, real values of ξ_1 result. These lead to the field-induced modification of the ordinary phonon-assisted absorption process. Hence, the only region of interest is near zero-field phonon-assisted transitions. Therefore, the energy difference in (38) may be expanded around the minimum for this difference—or around the indirect gap in energy. If we, further, take both the conduction-band minima and the valence-band maximum to be isotropic in the neighborhood of these extrema, we arrive at the following result:

$$E_c(\xi-q_x,\mathbf{k}_\perp'')-E_v(\xi,\mathbf{k}_\perp)=E_g+\hbar^2\mathbf{q}'^2/2(m_c+m_v)+(\hbar^2/2\mu)\left(\mathbf{k}_\perp-\frac{\mu}{m_c}\mathbf{q}'_\perp\right)^2+(\hbar^2/2\mu)\left(\xi-\frac{\mu}{m_c}q'_x\right)^2. \tag{39}$$

In the foregoing, the quantity E_g refers to the usual indirect energy gap and the $\mathbf{q}'$ is a shorthand notation for the quantity $\mathbf{k}_{\min}+\mathbf{q}$, where $\mathbf{k}_{\min}$ is the value of the $\mathbf{k}$ vector at one of the minima of the conduction band. The masses m_v and m_c refer to the valence- and conduction-band masses, respectively, and $\mu=(1/m_v+1/m_c)^{-1}$ is the reduced mass. Inserting the approximation (39) into (37) and (29), we find that our integral $\mathcal{J}$ of (36) has exactly the same form as that exhibited by Callaway[15] for the direct case if we employ as a variable $\xi-(\mu/m_c)q'_x$ instead of ξ, and if we realize that certain exponential phase factors which are independent of the integration variable may be ignored because they

will eventually contribute nothing to the quantity of ultimate interest $|\mathcal{J}|^2$. In the light of the foregoing, we arrive at the result that the integral $\mathcal{J}$ may be represented simply as

$$\mathcal{J}=-2\pi i\frac{(e\mathcal{E})^{4/3}}{(E_g{}^D-\hbar\omega)}\left(\frac{2\mu}{\hbar^2}\right)^{1/3}Ai(z), \tag{40}$$

where $E_g{}^D$ represents the direct energy gap at $\mathbf{k}=0$ (as distinguished from the indirect one E_g) and μ is the reduced mass of an indirect conduction-band minimum plus the valence-band maximum. The Airy[15,19] integral $Ai(z)$ has the argument z, where

$$z=\left[\frac{2\mu}{(e\mathcal{E}\hbar)^2}\right]^{1/3}\left[E_g-\hbar\omega+\hbar\omega+\frac{\hbar^2\mathbf{q}'^2}{2(m_c+m_v)}+\frac{\hbar^2}{2\mu}\left(\mathbf{k}_\perp-\frac{\mu}{m_c}\mathbf{q}'_\perp\right)^2\right]. \tag{41}$$

We may now exhibit the full solution to the problem in terms of a single integral over a radius ρ in five-dimensional space. We define the magnitude of this radius as follows:

$$\rho^2\equiv(\mu/(m_c+m_v))\mathbf{q}'^2+(\mathbf{k}_\perp-(\mu/m_c)\mathbf{q}'_\perp)^2. \tag{42}$$

This radius is in the space with axes

$$\mu q'_x/(m_c+m_v),\quad \mu q'_y/(m_c+m_v),$$
$$\mu q'_z/(m_c+m_v),\quad k_y-\mu q'_y/m_c,$$

and

$$k_z-\mu q'_z/m_c.$$

We are interested in the number of states (electron and phonon) near the region $\rho\simeq 0$. This is because we are concerned primarily with photon energies $\hbar\omega$ which are near $E_g+\hbar\bar{\omega}$ ($\hbar\bar{\omega}$ is just the critical phonon energy at which the onset of the zero-field phonon-emission-assisted transition can occur). By steepest descent arguments, only the region near $z\simeq 0$ is of interest mathematically. To satisfy both of these conditions plus the fact that the small correction to $\hbar\omega\simeq\hbar\bar{\omega}=$ constant is negligible for the pertinent values of $\mathbf{q}'$ and $\mathbf{k}_\perp$, we are justified in taking

$$z=[2\mu/(he\mathcal{E})^2]^{1/3}\{E_g-\hbar\omega+\hbar\bar{\omega}+(\hbar^2/2\mu)\rho^2\}, \tag{43}$$

and in noting that

$$\sum_{\substack{\text{phonon}\\ \text{states}}}\sum_{\mathbf{k}_\perp''}\delta_{\mathbf{k}_\perp'',\mathbf{k}_\perp-\mathbf{q}_\perp}=\frac{6V^{5/3}}{(2\pi)^5}\left(\frac{m_c+m_v}{\mu}\right)^{3/2}\int d^5\rho$$
$$=\frac{6V^{5/3}}{(2\pi)^5}\left(\frac{m_c+m_v}{\mu}\right)^{3/2}\frac{16\pi^2}{3!}\times\int_0^\infty\rho^4 d\rho. \tag{44}$$

With the foregoing in combination with (40) and (33), we may now write a formula for the transition rate—which, of course, is directly proportional to the absorption coefficient—in closed form as follows

$$R=\left(\frac{e}{m}\right)^2\frac{4n(N+1)(m_cm_v)^{3/2}\mu^{-7/3}}{(2\pi)^2(2\hbar e\mathcal{E})^{1/3}w\omega\epsilon(E_g{}^D-\hbar\omega)^2}\times\int_0^\infty\rho^4|Ai[z(\rho)]|^2d\rho. \tag{45}$$

In order to obtain a compact and viable result with which experimental data may be easily compared, we change the variable in the integral of (45) to z, the argument of the Airy function. For this we must introduce a parameter ζ which comes quite naturally into the problem,

$$\zeta=[2\mu/(he\mathcal{E})^2]^{1/3}(\hbar\omega-E_g-\hbar\bar{\omega}). \tag{46}$$

Next we take note of the fact that experimentally one measures not R (or α—the absorption coefficient corresponding to R), but rather ΔR [or better $\Delta\alpha=\alpha(\mathcal{E})-\alpha$]. Here α refers to the absorption coefficient which would obtain through the phonon-emission-assisted process in the absence of the field $\mathcal{E}$. And $\alpha(\mathcal{E})$ is the absorption coefficient with the field $\mathcal{E}$. The absorption $\alpha(\mathcal{E})$ corresponds to the rate R of (45).

One may either calculate α from (45) by letting $\mathcal{E}\to 0$ or else consult the well-known results[20] for α. In either case, one finds that α may be expressed in terms of the ζ of (46) as follows:

$$\alpha=(\text{factors})(\hbar\omega-E_g-\hbar\bar{\omega})^2$$
$$=\tfrac{3}{32}K[(he\mathcal{E})^2/2\mu]^{2/3}\zeta^2H(\zeta), \tag{47}$$

where H is the Heaviside unit function. It is unity for positive argument and zero otherwise. In the above, recourse to standard work[20] on phonon-assisted absorption will easily unearth the "factors"$=3K/32$ so that (47) defines K. Note that K is field-independent.

Employing the foregoing ideas, we may now exhibit the complete solution to the problem as follows:

$$\Delta\alpha=K\left[\frac{(he\mathcal{E})^2}{2\mu}\right]^{2/3}\left\{\int_{-\zeta}^\infty(z+\zeta)^{3/2}|Ai(z)|^2dz-\frac{3}{32}\zeta^2H(\zeta)\right\}, \tag{48}$$

where, as mentioned, ζ is defined in (46).

Note added in proof. Dr. C. Penchina has pointed out, quite correctly, that the factor $\frac{3}{32}$ which appears in Eqs. (47) and (48) should, in fact, be $\frac{3}{16}$.

DISCUSSION OF RESULTS

The expression in (48) is applicable in all regimes—below, above, and at the absorption edge due to a

[19] H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, New York, 1950), p. 508.

[20] T. P. McLean, *Progress in Semiconductors*, edited by A. F. Gibson (Heywood & Company, Ltd., London, 1960) Vol. 5, p. 55.

phonon-assisted interband transition involving a phonon emission. The analogous phonon-absorption process is easily obtained by modifying the meaning of ζ to correspond to an earlier onset and modifying K to contain N phonons instead of $N+1$. Furthermore, (48) is applicable at zero field as well as at moderately large fields.

Experimentally, one takes data on essentially two features of the observed $\Delta\alpha$ versus $\hbar\omega$. One measures the *positions* of the zeros and of the positive and negative peaks as a function of field $\mathcal{E}$ and the *intensities* of the peaks as a function of field strength $\mathcal{E}$. Equation (48) indicates immediately that, for the process considered, all the positions, except that of the first positive peak, must vary with the $\frac{2}{3}$ power of $\mathcal{E}$ and all the peaks must increase with the $\frac{4}{3}$ power of $\mathcal{E}$. The position of the first positive peak remains independent of $\mathcal{E}$, but its amplitude should increase with the $\frac{4}{3}$ power of $\mathcal{E}$ as do the other amplitudes.

In the matter of obtaining numerical values for the positions, in photon energy, of the zeros and the positive and negative peaks of $\Delta\alpha$, it is merely a matter of finding those numbers ζ_n at which the zeros or zero derivatives of the bracketed function in (48) occur.

APPENDIX A

We wish to understand how to evaluate the integral

$$\mathcal{J}=\int_{-\kappa/2}^{\kappa/2} df \exp A(f) \int_{-\kappa/2}^{f} dg \exp B(g). \qquad \text{(A1)}$$

We may write this, of course, as

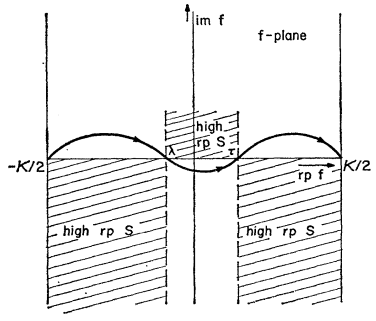
$$\mathcal{J}=\int_{-\kappa/2}^{\kappa/2} df \exp S(f), \qquad \text{(A2)}$$

where it is clear that the meaning of $S(f)$ is the following:

$$\exp S(f)\equiv \exp A(f) \int_{-\kappa/2}^{f} dg \exp B(g). \qquad \text{(A3)}$$

Now suppose that we have some intuitive reason to expect that we know the saddle points of the f integral (A2). We imagine that we know where the real part of $S(f)$ is large, small, or zero. We outline this in the f plane as in Fig. 1. (It will turn out, in fact, that for the problem at hand the figure is approximately correct. It corresponds to the case of absorption above the bandgap.) We would then, of course, integrate along the path shown so as to pick up the large contributions from the saddle points λ and τ to perform the integration. One must, of course, investigate the end points because they may yield contributions to the integral besides those from the two saddle points. However, it is clear that we would end up with a result like

$$\mathcal{J}=\left(-2\pi \Big/ \frac{d^2S}{df^2}\Big|_{\lambda}\right)^{1/2} \exp S(\lambda) + \left(-2\pi \Big/ \frac{d^2S}{df^2}\Big|_{\tau}\right)^{1/2} \exp S(\tau) + \text{contributions from the end points if they exist.} \qquad \text{(A4)}$$



PATH OF INTEGRATION FOR $\mathcal{J}$ IN f PLANE.

FIG. 1. Path in integration for $\mathcal{J}$ in the f plane.

Therefore, in fact, one need estimate $S(f)$ or $\exp S(f)$ only near the critical points λ and τ (and possibly at $\frac{1}{2}\kappa$ and $-\frac{1}{2}\kappa$). It is not necessary to know $S(f)$ in detail over the whole f plane. We will estimate S at λ (and then later near τ) and then use analytical continuation to understand S on the approach to λ.

To make this evaluation, we must first find out the value near λ of the integral

$$\int_{-\kappa/2}^{f} dg \exp B(g)=\exp[S(f)-A(f)]. \qquad \text{(A5)}$$

We know the saddle points of $B(g)$ because both B and A are given functions; S is not. Let the points at which $dB/dg=0$ be called a and b. These are the saddle points of B. We hypothesize that these points are relatively far from the points λ and τ. And, in fact, for the problem at hand they are located about as shown in Fig. 2. This figure represents the g plane and the regions of high and low real part of $B(g)$.

Since we wish to evaluate the integral (A5) for a point f near λ, we choose the path shown in Fig. 2. We may choose this path because of the special properties of $B(g)$ characteristic of our problem. Keeping in mind that we are only concentrating on values of $\hbar\omega$ which span the indirect gap, not the direct one, it is clear that for all real values of g, the derivative of B (29) is essentially constant at a rather large imaginary value $\sim i\times 10^4$ Å. Inspection of the equation for B (27) indicates concommitantly that B is essentially linear in g. And not until g approaches very small magnitudes, indeed—of the order of 10^{-4} Å^{-1}—does the phase of B approach unity. Furthermore, if we travel off the real axis into the upper half plane as shown in Fig. 2, it is

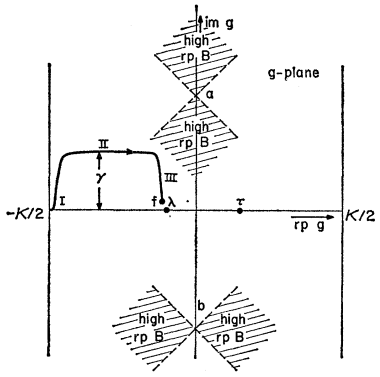


FIG. 2. Path of integration in the g plane to estimate $S(f)$ near $f=\lambda$.

clear that $\exp B(g)$ becomes exponentially small quite quickly. It follows, therefore, that any integral along path II will have a vanishingly small amplitude if the distance γ is chosen to be sufficiently greater than about 10^{-4} Å^{-1}. We are left with the result, therefore, that

$$\int_{-\kappa/2}^{\kappa/2} dg\, \exp B(g) = \int_{\mathrm{III}} dg\, \exp B(g) + \text{end-point contributions}. \quad \text{(A6)}$$

The integral over part III of the path is, of course, quite straightforward. For this, we merely use

$$B(g) = B(f) + (g-f)(dB/dg)|_f. \quad \text{(A7)}$$

This is an appropriate form for B in this region since B has no saddle point here. Hence $(dB/dg)|_f$ does not vanish. We employ the variable y, where

$$g-f=iy, \quad \text{(A8)}$$

and y will run between γ and 0—or more appropriately between ∞ and 0— since this will clearly amount to a vanishingly small error as γ is taken larger and larger. Upon integration, we obtain

$$\int_{\mathrm{III}} = \left(\frac{dB}{dg}\bigg|_f\right)^{-1} \exp B(f). \quad \text{(A9)}$$

For this integral to converge to the value exhibited, the real part of $iy(dB/dg)|_f$ must be negative over the domain of y of interest. This condition is, of course, met since the region of the path was chosen by virtue of the nature of B in that region.

Similar, but somewhat modified, arguments hold for the vicinity of the point τ. And in general, the following result may be written down

$$\exp S(f) = (dB/dg|_f)^{-1} \exp[A(f)+B(f)]$$
$$+\text{possible end-point contributions}$$
$$+\text{possible saddle-point terms of}$$
$$\text{the form } \left(-2\pi \Big/ \frac{d^2B}{dg^2}\bigg|_a\right)^{-1}$$
$$\exp[B(a)+A(f)]. \quad \text{(A10)}$$

Of all the terms in (A10), one expects only the first one to be significant. On physical grounds it is unlikely that terms which uncouple f and g contribute to a process in which they are inherently coupled. (The symbols f and g arose originally from the x component of the $\mathbf{k}$ vector for the two processes: phonon transition and photon transition, respectively.) This is illustrated quantitatively, for example, in the term involving $B(a)$. A rough calculation, using the B of (27) in the main text, indicates that $B(a)\simeq -10^4$, so that $\exp B(a)$ is indeed small. The reason for this is simply that the photon energy employed is quite far from bridging the direct gap—to which $B(g)$ refers. Since the calculation is predicated on the idea that $\hbar\omega$ is about the order necessary to bridge the indirect gap, only terms which couple photon and phonon can be expected to contribute because only for these terms does the energy match properly. In the light of this discussion, we only use the first term of (A10) and combining this with (A2) we obtain the result

$$\mathcal{J} = \int_{-\kappa/2}^{\kappa/2} \frac{d\xi}{(dB/d\xi)} \exp[A(\xi)+B(\xi)]. \quad \text{(A11)}$$