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Theory of Raman Scattering in Solids

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The Raman effect due to phonons, Landau levels, and Stark ladder levels is analyzed theoretically. For the phonons, three mechanisms are identified, and their orders of magnitude are estimated for both $\Delta n = 1$ and 2. The ratio of the intensities can be of order unity, especially when the crystal has only one narrow band gap. The resonance Raman effect is particularly strong in the band. For the electronic Raman effect from Landau levels, three similar mechanisms can be distinguished. The $\Delta n = 1$ transition can occur only in crystals without a center of symmetry, and has a strength comparable to the $\Delta n = 2$ process. It can also occur in case of broken symmetry, as in *n*-type Si. The Raman effect from a Stark ladder should in principle give the Fourier components of the *E*-*k* curve. Finally, it is shown that effective-mass theory for donor levels is reliable only for materials with $\epsilon > 5$, irrespective of m^*.

I. INTRODUCTION

The Raman effect in solids has been the subject of much experimental and theoretical research in recent years.[1] The theoretical approach has been generally rather phenomenological, and it is felt that as a result several characteristic features of Raman scattering in solids have not received an adequate explanation. For example, the ratio of the intensities of the $\Delta n = 2$ and $\Delta n = 1$ lines is often surprisingly large, even off-resonance. Furthermore, existing theories have difficulty explaining the large Raman cross section when the laser energy enters the continuum of excited states. Raman scattering from conduction electrons in a magnetic field (Landau levels) has been detected for $\Delta n = 1$, 2, but published theories only account for the $\Delta n = 2$ process. The role of inversion symmetry has not been elucidated.

We shall consider these points below and be more specific about the effective-interaction Hamiltonian, which is shown to arise from three mechanisms. A complete theory would become very involved, and therefore only the leading matrix elements will be shown; complete calculations can easily be made for each individual case. In addition to the inelastic light scattering from Landau levels, the possibility of a Raman effect from conduction electrons in a strong static electric field is also analyzed. In order for the band index to be a good quantum number, in both cases the fields cannot be too strong. Such a limit also exists for the validity of effective-mass theory for donor levels and is shown to imply that the dielectric constant ϵ must be substantially larger than 5, independent of the magnitude of the effective mass.

II. PHONON SCATTERING

The interaction Hamiltonian of em radiation with matter will be taken of the form

$$H_r = H_L + H_R = (e/mc)\,(\vec{A}_L \cdot \vec{p} + \vec{A}_R \cdot \vec{p}) \;, \qquad (1)$$

where $\vec{p}$ is the momentum of the electron under consideration and $\vec{A}_L$ and $\vec{A}_R$ are the vector potentials of the incident (laser) and Raman light beams, respectively. These vector potentials can be expressed in terms of creation and annihilation operators of photons according to

$$A_L = c\,(h/\omega\epsilon\, V)^{1/2}\,(a_L^\dagger + a_L)$$

in the dipole approximation. In first approximation, the wave function is a product of electronic, phonon, and photon wave functions. The p operator in (1) gives matrix elements between the total electronic ground state $|g\rangle$ and the excited states $|e\rangle$, but it does not change the phonon quantum number. The phonons enter into the problem in three ways. Process (a)—the equilibrium positions of the ions in $|e\rangle$ are shifted with respect to those in $|g\rangle$. Process (b)—the elastic properties of the lattice are different in $|e\rangle$ and $|g\rangle$, resulting in a change in frequency of the phonons. Process (c)—the electron-phonon interaction causes the total wave function no longer to be a single product of an electronic and a phonon wave function, giving polarization of the electrons by the phonons.

The basis for all three effects is the electron-phonon interaction; in the quasistatic approximation for the phonons, the one-electron operator can be expanded in the amplitudes of the phonons $\vec{R}_{\vec{q}}$,

$$H_{\text{el-ph}} = \sum_{\vec{q}} \vec{R}_{\vec{q}} \cdot \vec{F}_{\vec{q}}(\vec{r}) + \tfrac{1}{2} \sum_{\vec{q}} \sum_{\vec{q}\,'} \vec{R}_{\vec{q}}\, G_{\vec{q}\vec{q}\,'}(\vec{r})\, \vec{R}_{\vec{q}\,'} + \cdots \ . \tag{2}$$

The summation over $\vec{q}$, $\vec{q}\,'$ includes all phonon bands. Since

$$R_{\vec{q}} = Q_{\vec{q}}\,(a^{\dagger}_{\vec{q}} + a_{-\vec{q}}) \ , \tag{3}$$

where $Q_{\vec{q}}$ is the zero-point amplitude and $a^{\dagger}_{\vec{q}}$ the creation operator of a phonon, (2) changes the number of phonons. The electron operators F and G are such that, apart from a reciprocal lattice vector, (2) leaves the total wave vector unchanged. Usually the wave vectors of the em radiation are relatively small and can be neglected for the determination of the electronic matrix elements. This introduces the diagonal-matrix elements A and B over the total electronic wave functions of F and G, respectively, which give a change in the phonon Hamiltonian for each excited electronic state $|e\rangle$:

$$\delta H^{\text{ph}}_{e} = A_e R_0 + \tfrac{1}{2} \sum_{\vec{q}} B_{e\vec{q}} R_{\vec{q}} R_{-\vec{q}} \ . \tag{4}$$

This implies that in the excited electronic state the ions show a static displacement

$$\delta R_e = A_e / c \ , \tag{5}$$

where c is the appropriate elastic constant. For instance in the diamond lattice the shift $a(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ of the two interpenetrating fcc sublattices will change by $\delta\vec{R}$. We take $\delta R = 0$ in the ground state $|g\rangle$, so that $A_g = 0$. The A_{ee} of (4) for an excited state $|e\rangle$ in which an electron of a valence-band state $|v\rangle$ is promoted to a conduction-band state $|c\rangle$ is given by $A_e = F_{cc} - F_{vv}$.

The B term in (4) gives for each electronic excitation $|e\rangle$ a change in stiffness for the phonons

$$\delta c_{e\vec{q}} = B_{e\vec{q}} \tag{6}$$

which causes a change in frequency. Including the off-diagonal elements C_{ij} of F, which can be both intraband and interband, the total effective-interaction Hamiltonian is in second-quantized form

$$\begin{aligned} H_{\text{pert}} = H_r &+ N^{-1/2} \sum_{j\neq g} \sum_{\vec{k}} A_{jj}\, c^{\dagger}_{j\vec{k}}\, c_{j\vec{k}}\, (a^{\dagger}_0 + a_0) \\ &+ N^{-1} \sum_{j\neq g} \sum_{\vec{k}} \sum_{\vec{q}} B_{jj}\, c^{\dagger}_{j\vec{k}}\, c_{j\vec{k}}\, (a^{\dagger}_{\vec{q}}\, a^{\dagger}_{-\vec{q}} + a_{\vec{q}}\, a_{-\vec{q}}) \\ &+ N^{-1/2} \sum_{i} \sum_{j} \sum_{\vec{k}} \sum_{\vec{q}} C_{ij}\, c^{\dagger}_{j(\vec{k}+\vec{q})}\, c_{i\vec{k}}\, (a^{\dagger}_{-\vec{q}} + a_{\vec{q}}) \ , \end{aligned} \tag{7}$$

which operates on single-product wave functions with phonons which are independent of the electronic states. The c's stand for fermion operators. The band indices i, j also include the k, q dependence. The electronic energy matrix elements A, B, C are independent of the number of atoms N. The term with A stands for the displacement effect, that with B for the change in elastic properties, whereas C represents the polarization of the electrons. If not more than two phonons are considered, the off-diagonal part of B can be omitted. The reason that we expose the A term explicitly, rather than incorporating it in C, is that A is usually much smaller than C. It is to be expected that $F(\vec{r})$ is largest inside an ionic core, where it is approximately $-\operatorname{grad} V(\vec{r})$, with $V(\vec{r})$ the ionic (pseudo) potential. This $\operatorname{grad} V$ is a predominantly odd function of $\vec{r}$, and will therefore give a very small contribution to the diagonal-matrix element, and thus to A. On the other hand, if the atomic electronic wave functions in i and j have different parity, $\operatorname{grad} V$ will give a large contribution to C_{ij}. The magnitude of the latter will be at least $(Q/d)\Delta$, where d is the interatomic distance and Δ a band gap. Moreover the optical-phonon admixture in the electronic wave function is $(C/\Delta)^2$; since in most covalent semiconductors this is a few percent, we estimate that C has the order of magnitude of 0.3 eV. Then A is caused by the part of $F(\vec{r})$ more midway between the ions; its magnitude can be estimated by noting that the shift δR is similar to that in a Jahn-Teller system, which is usually smaller than 10% of d, making it comparable to Q of (3). This implies that A in (7) is about $\hbar\omega_p$.

$$A \approx 0.03 \text{ eV} \ ,$$

$$\text{Then, for } \hbar\omega_p = 0.03 \text{ eV}, \quad C \approx 0.3 \text{ eV} \ . \tag{8}$$

A. One-Phonon Processes ($\Delta n = 1$)

We consider first the effective second-order perturbation matrix elements of (7) for the $\Delta n = 1$ process off-resonance, to which both process (a) and process (c) may contribute. For each (a) process one intermediate electronic excited state must be considered. If this has an energy Δ_1 above the ground state, the leading effective matrix element between the initial and final state is

$$M^{a}_{fi} \propto N^{-1/2} \sum_{k} A / (\Delta_1 - \hbar\omega)^2 \ , \tag{9}$$

where matrix elements of $\vec{A}\cdot\vec{p}$ are left out and ω_p is neglected in comparison with ω_L. After summation over the continuum of excited states k, $M^{a}_{fi} \propto N^{1/2}$, so that the transition probability is proportional to N.

For the (c) process, which changes the electronic state, two electronic excited states must be considered, both having the same $\vec{k}$. For each pair there are 2.3! = 12 contributions to M_{fi} of which the

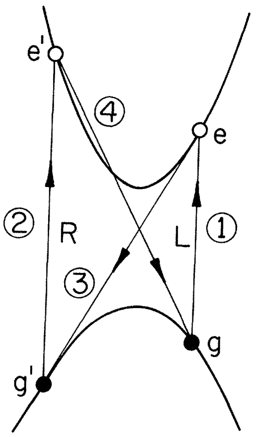

FIG. 1. Diagram of the virtual transitions for $\Delta n = 2$ according to the (c) process. The sequence of 1 and 2 can be interchanged, and also that of 3 and 4.

largest one will be

$$M^c_{fi} \propto N^{-1/2} \textstyle\sum_k C/(\Delta_1 - \hbar\omega)(\Delta_2 - \hbar\omega). \tag{10}$$

For many semiconductors there exists only one set of bands with a small Δ_1, in which case $\Delta_2 \gg \Delta_1$. Otherwise (10) will be larger than (9).

B. Two-Phonon Processes (Δn=2)

The (a) process gives $\Delta n = 2$ in second order of perturbation theory:

$$M^a_{fi} \propto N^{-1} \textstyle\sum_k A^2/(\Delta_1 - \hbar\omega)^3 . \tag{11}$$

Because only $q = 0$ phonons are involved, there is only a summation over k, as for (9). The result is therefore of order N^0 and is infinitesimally small for uniform lattices. For localized states, however, experimental results[2] up to $\Delta n = 10$ in resonance Raman scattering have been described with this mechanism.[3]

For the (b) process, one obtains for each q,

$$M^b_{fi} \propto N^{-1} \textstyle\sum_k B/(\Delta_1 - \hbar\omega)^2. \tag{12}$$

In this case there is an extra summation over q of the square of (12), so that the integrated intensity is proportional to N.

For the $\Delta n = 2$ (c) process, three excited electronic states are involved. Two of the transitions are induced by H_c, thereby creating one phonon with wave vector $\vec{q}$ and one with $-\vec{q}$. For each q the leading term of the part depending on H_c of the effective second-order matrix element is

$$M^c_{fi} \propto N^{-1} \textstyle\sum_k C^2/(\Delta_1 - \hbar\omega)(\Delta_2 - \hbar\omega)(\Delta_3 - \hbar\omega) , \tag{13}$$

where we can take the same state for 1 and 3. It is even possible to avoid the high-energy gap Δ_2 and to have only interactions between states in the conduction band and in the valence band at Δ_1. After passing to $(\vec{k}, \Delta)$, an electron must be able to return to $(\vec{k} + \vec{q})$ in the valence band. This state must therefore be vacated by a previous transition. Thus we consider two electrons simultaneously. Denoting the electronic state by g_k, $e_{k'}$, etc., or for brevity g, e' (see Fig. 1), we find for the effective matrix element

$$M^c_{fi} = \frac{\langle g'g | H_R | g'e' \rangle \langle g'e' | H_c | ee' \rangle \langle ee' | H_c | eg' \rangle \langle eg' | H_L | gg' \rangle}{(E_{e'} - E_g - \hbar\omega_q)(E_e - E_g + E_{e'} - E_{g'} - 2\hbar\omega_q)(E_e - E_g - \hbar\omega_L)} + \cdots . \tag{14}$$

Many more terms exist corresponding to permutations of the four matrix elements. For instance, in Fig. 1 processes 3 and 4 can be interchanged, and also 1 and 2. In a complete calculation all terms must be included. The H_c part of (14) is then approximately proportional to

$$M^c_{fi} \propto N^{-1} \textstyle\sum_k C^2/(\Delta_1^2 - \hbar^2\omega^2)\Delta_1 , \tag{15}$$

where Δ and C still depend on k and q.

C. Summation Over States

In all cases M_{fi} is to be summed over all excited states k. Special features occur when the laser frequency enters a continuum of excited states. This problem has been treated before for a parabolic band.[4] We shall consider the $\Delta n = 1$ transition for both the (a) and the (c) processes.

The density of states is assumed to be proportional to $x^{1/2}$, where $x = E - E_{g'}$, up to $x = \infty$. Then near or in the band, the leading terms are

$$M_{fi} \propto A \int_0^\infty \frac{x^{1/2}\,dx}{(x - L)(x - L + \hbar\omega_p)} + C \int_0^\infty \frac{x^{1/2}\,dx}{(x - L)(x - L + \Delta)} , \tag{16}$$

where $L = \hbar\omega_L - E_g$ and $\Delta = \Delta_2 - \Delta_1 + \hbar\omega_p$; this Δ is assumed to be constant; the result will not depend critically on this assumption. The integrals will be performed using

$$\int \frac{f(x)}{x - a}\,dx = P \int \frac{f(x)}{x - a}\,dx + i\pi f(a) , \tag{17}$$

where P denotes the principle value. In Ref. 4 the imaginary part was not taken into account. For all values of L the result can be written as

$$M_{fi} \propto (A/\hbar\omega_p)[(-L)^{1/2} - (\hbar\omega_p - L)^{1/2}] + (C/\Delta)[(-L)^{1/2} - (\Delta - L)^{1/2}] . \tag{18}$$

For $\hbar\omega_L < E_g$, i.e., $L < 0$, all terms are real and the square roots tend to cancel. For $0 < L < \hbar\omega_p$ or Δ, respectively, one of the square roots is real and the other imaginary; the absolute magnitude of each of the terms is then constant in that region. For $L > \hbar\omega_p$ the A term will decrease in a symmetrical way, but the C term will stay constant up to Δ in the band; in most practical cases this limit will not be reached by the laser frequency.

Depending on the signs of A and C the two contributions can either add or subtract. Recently the interesting case of a zero in the Raman-scattering intensity at a frequency below resonance has been reported.[5] It was suggested that cancellation of the resonance term and a nonresonant term took place. It seems more likely that two resonance terms, such as A and C, are involved. In Fig. 2 an example is given in which the squares of the (a) and (c) terms have been added. It is seen that the Raman intensity is higher inside the band than outside. Existing theories[4] predict the opposite. The high intensity in the band has been observed in CdS.[6]

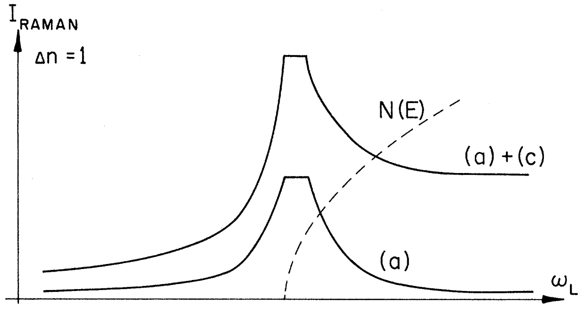

FIG. 2. Raman intensity as a function of the laser frequency ω_L. The density of the excited states in $N(E)$. Curve (a) is for the displacement effect (a), whereas curve (a) + (c) includes the (c) process, where the interference has been neglected.

D. Ratio of the Δn=1, 2 Intensities

We now estimate the ratio of the intensities I_2/I_1 of the $\Delta n = 2$ and $\Delta n = 1$ Raman lines off-resonance. For the $\Delta n = 2$ processes we integrate (12) and (15) over the parabolic band, as in (18), and find

$$I_2 \propto \left| \frac{B}{(\Delta_1 - \hbar\omega)^{1/2}} + C^2 \frac{(\Delta_1 + \hbar\omega)^{1/2} + (\Delta_1 - \hbar\omega)^{1/2} - 2(\Delta_1)^{1/2}}{(\hbar\omega)^2} \right|^2 , \tag{19}$$

where Δ_1 is now essentially the band gap. It is clear that for off-resonance in (18) the C term dominates if $\Delta_2 \approx \Delta_1$; then $M_{fi} \approx C/(\Delta_1)^{1/2}$, and its square is much larger than I_2 of (19), i.e., $I_1 \gg I_2$. If however, $\Delta_2 \gg (\Delta_1 - \hbar\omega)$, then, due to the C term alone,

$$I_2/I_1 \approx (C/\Delta_1)^2 (\Delta_2/\Delta_1) ,$$

which can be of order unity. Of course the $\Delta n = 2$ Raman spectrum is smeared out over the phonon band, so that its integrated intensity must be compared with that of the sharper $\Delta n = 1$ Raman line.

III. SCATTERING FROM LANDAU LEVELS

In semiconductors subjected to a static magnetic field $\vec{B}$, Raman lines of comparable intensity have been observed[7] with frequency shifts of ω_c and $2\omega_c$ ($\Delta n = 1$ and 2, respectively), where ω_c is the cyclotron frequency. The existing theories only predict the $\Delta n = 2$ transition.[8] We shall show that in crystals without center of symmetry the $\Delta n = 1$ transition can occur. As in the preceding theories, we shall only identify the type of matrix elements responsible for the effect, and not go into details of special crystals. In particular we shall not take into account spin-orbit interaction, since this mechanism does not in itself lead to a Raman effect.

Also it will appear that in this case three separate mechanisms can be distinguished, which bear a strong resemblance to those of Sec. II. Because only electrons are involved, the parameters are calculable for a known band structure. This may then help to visualize the phonon Raman effect.

We shall assume that $\mu_B B \ll E_g^2/E_b$, where μ_B is the Bohr magneton, E_g the band gap, and E_b the bandwidth. Under this condition the electron can be described by a linear superposition of Bloch wave functions of one band only with energy $E_i(\vec{k})$. Jones and Zener[9] have shown that for large k a wave packet can be formed, the central $\vec{k}$ of which satisfies

$$R_0^2 \dot{k}_x = \frac{\partial E_i}{\partial(\hbar k_y)} , \quad \hbar \dot{k}_y = \frac{-\partial E_i}{\partial(R_0^2 k_x)} , \tag{20}$$

with $R_0^2 = \hbar c/eB$ for $B = 50\,000$ G, $R_0 \cong 100$ Å. The equations (20) have the form of classical Hamilton equations of motion with $R_0^2 k_x$ and $\hbar k_y$ (or similar combinations) as conjugate coordinate and momentum, respectively. According to Dirac,[10] systems satisfying such equations should be quantized by assigning to their conjugate variables a nonzero commutator, which for this case is

$$[k_x, k_y] = i/R_0^2 . \tag{21}$$

By substituting $-iR_0^{-2}\partial/\partial k_x$ for k_y in $E_i(\vec{k})$, a new Schrödinger equation for each band i is obtained:

$$E_i\left(k_x, -iR_0^{-2}\frac{\partial}{\partial k_x}\right)\psi_i(k_x) = W_i\psi_i(k_x) . \tag{22}$$

Here k_z is a constant of the motion and occurs as a parameter in (22). A similar equation could have been written down for k_y. As in regular q-p space, we accept all solutions of (22), even if they have appreciable values for small k, for which (20) is not justified. We shall only consider solutions near an extremum in E_i, and assume that E is analytic in k, so that it can be expanded up to quadratic terms in k. This excludes degenerate bands as occur, for example, in the diamond structure. Then,

$$E(\vec{k}) = \tfrac{1}{2}\hbar^2 [(k_x^2/m_1) + (k_y^2/m_2)]$$
$$= \tfrac{1}{2}\hbar\omega_c [(m_2/m_1)^{1/2} (k_x R_0)^2 + (m_1/m_2)^{1/2} (k_y R_0)^2] \ . \tag{23}$$

For this $E(\vec{k})$, Schrödinger's equation has harmonic-oscillator solutions $\psi_n(k_x b_i)$, with $b_i = (m_2/m_1)_i^{1/4} R_0$. For the calculation of the matrix elements of (1) we need the $\vec{r}$-dependent wave function

$$\Phi_{ni}(\vec{r}) = \int \psi_n(k_x b_i) \varphi_{i\vec{k}}(\vec{r})\, dk_x \ . \tag{24}$$

Here $\varphi_{i\vec{k}}$ is the Bloch function of band i, which also depends on k_y, for which (21) holds. For a classical cyclotron orbit, k_y would be a function of k_x. Because $\vec{p}$ conserves $\vec{k}$,

$$\langle j, m | H_r | i, n \rangle = (e/mc)\vec{A} \cdot \int \psi_m^*(k_x b_j)$$
$$\times \left(\int \varphi_{j\vec{k}}^* \vec{p}\, \varphi_{i\vec{k}}\, d\vec{r} \right) \psi_n(k_x b_i)\, dk_x \ , \tag{25}$$

where we have assumed that both bands i and j have an extremum for the same value of $\vec{k}(=0)$. For $i=j$, the $\vec{r}$ integral gives $(m/m^*)\hbar\vec{k}$, and the k_x integral gives a nonzero result only if $m-n=\pm 1$. This describes the ordinary cyclotron absorption.

For the Raman effect we take $i \neq j$. If the $\vec{k}$ dependence of the $\vec{r}$ integral is neglected, the k_x integral can still be nonzero if $b_i \neq b_j$ and $(m-n)$ is even. We shall consider this case first.

A. Anisotropic Mass Effect

The nonorthogonality of $\psi_m(k_x b_j)$ and $\psi_n(k_x b_i)$ in (25) is completely analogous to effect (b) in Sec. II and can be treated in the same way. That is, we shall construct an effective Hamiltonian which gives the same result as the nonorthogonal wave functions. We use the Landau levels of the excited state $|e\rangle$ as the basis set. Their energy operator is, according to (23),

$$H_e = \tfrac{1}{2}\hbar\omega_{ce} [b_e^2 k_x^2 + (R_0^4/b_e^2) k_y^2] = \tfrac{1}{2}\hbar\omega_{ce} (\xi^2 + \eta^2) \ , \tag{26}$$

with $\xi = b_e k_x$ and $\eta = (R_0^2/b_e) k_y$, so that $[\xi, \eta] = i$. For the ground state $|g\rangle$, we find

$$H_g = \tfrac{1}{2}\hbar\omega_{cg} [(b_g/b_e)^2 \xi^2 + (b_e/b_g)^2 \eta^2] \ . \tag{27}$$

With $\xi = a_c^\dagger + a_c$ and $\eta = i(a_c^\dagger - a_c)$, the off-diagonal part of (27) is the effective Hamiltonian operating on Landau levels in the excited band $|e\rangle$:

$$H_b = \tfrac{1}{2}\hbar\omega_c [(m_{2g} m_{1e}/m_{1g} m_{2e})^{1/2}$$
$$- (m_{1g} m_{2e}/m_{2g} m_{1e})^{1/2}] (a_c^\dagger a_c^\dagger + a_c a_c)_e \ , \tag{28}$$

similar to the B term in (7). In this case there is no summation over k or q, and therefore the N^{-1} is missing. In contrast to (7), it is possible to know the coefficient in (28) exactly. As in (8), it is of the order of the harmonic-oscillator quantum $\hbar\omega_c$.

B. $\vec{k}\cdot\vec{p}$ Effect

Next, we will consider the effect of the k dependence of the p-matrix element for the Bloch functions in (25). In p_{ij} only u of

$$\varphi = u_{\vec{k}}(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$$

enters. In lowest approximation one takes the $k=0$ value. For small k one can approximate $u_{\vec{k}}$ as

$$u_{i\vec{k}} \cong u_{i0} + (\hbar/m) \textstyle\sum_j [\vec{k} \cdot \vec{p}_{ij}/(E_i - E_j)] u_{j0} \ , \tag{29}$$

where the matrix elements p_{ij} are to be taken for $k=0$. The result (29) is identical to that of an extra term $(\hbar/m)\vec{k}\cdot\vec{p}$ in the Hamiltonian; k_x and k_y then act as operators on the Landau-level states. For an isotropic effective mass one then obtains in addition to (1)

$$H_c = (\hbar/mR_0) [(p_x - ip_y) a_c^\dagger + (p_x + ip_y) a_c] \ . \tag{30}$$

One might object that the $\vec{k}\cdot\vec{p}$ operator has already been used for obtaining $E(\vec{k})$, necessary for the definition of the Landau levels; in this case we use it only in conjunction with the radiation interaction operator $\vec{A}\cdot\vec{p}$. The present procedure bears a strong resemblence to the (c) effect of Sec. II, and the analysis is henceforth the same.

We shall show for the Landau levels that (10) will not exist if the crystal has a center of symmetry (diamond). By including both the interaction with the radiation and (30), M_{fi} in (10) contains the product of three matrix elements of p. When the center of symmetry coincides with the origin of the coordinate system $V(\vec{r})$ is even, and the Bloch functions can be chosen to obey $\varphi_{i,\vec{k}}(-\vec{r}) = \pm \varphi_{i,-\vec{k}}(\vec{r})$. Thus, instead of changing the sign of $\vec{k}$ one may reverse $\vec{r}$ in the wave functions. If the sign of $\vec{p}$ was also reversed, the matrix elements with $\vec{k}$ would be equal to those with $-\vec{k}$. However, p occurs in (10) an odd number of times, so that $M_{fi}(\vec{k}) + M_{fi}(-\vec{k}) = 0$.

The coefficient of a_c in (30), corresponding to the C term in (7), is of the order of magnitude $2\pi\hbar^2/mdR_0$. For $B = 50\,000$ G it is about 0.1 eV, whereas $\hbar\omega_c$ in (28) will usually not exceed 0.01 eV.

C. Displacement Effect

Sometimes the energy of the conduction band of a semiconductor has extra minima; for Si they occur along the cubic k axes at about $0.85(2\pi/a)$. In both the valence bands and the higher conduction bands extrema occur at the zone edges, which are thus shifted from that of the state under consideration by $\delta k = 0.15(2\pi/a)$. This shift can give a Raman effect for Landau levels in the same way as does the displacement effect (a) of Sec. II for phonons.

For this large δk, the excited Bloch states with k values within $\pm R_0^{-1}$ from the central k of the conduction electron state comprise many Landau levels. Their quantization is therefore unimportant, and we shall consider only matrix elements of $\vec{A}\cdot\vec{p}$ between Landau-level states and pure Bloch functions of the excited states:

$$\vec{A}\cdot\int\psi_n(k_x' b_g)\,dk_x'\int\varphi^*_{\vec{k}e}(\vec{r})\,\vec{p}\,\varphi_{\vec{k}'g}(\vec{r})\,d\vec{r} = \vec{A}\cdot\vec{p}_{eg}(\vec{k})\,\psi_n(k_x b_g)\;.$$

The electronic part of the second-order matrix element between Landau states n and m is

$$M^{\mathrm{el}}_{mn} = \sum_e \int \psi^*_m\,(k_x b_g)\,\frac{p_{ge}(\vec{k})\,p_{eg}(\vec{k})}{E_e(\vec{k}) - E_g - \hbar\omega}\,\psi_n(k_x b_g)\,dk_x\;. \tag{31}$$

The $\vec{k}$ dependence of the central part of the integrand in (32) will cause cyclotron-quantum jumps. As in Sec. II, we can introduce the $\vec{k}\cdot\vec{p}$ operator for the variation with $\vec{k}$ of the matrix elements of $\vec{p}$. In addition there is the $\vec{k}$ dependence of $E_e(\vec{k})$ which is described by the diagonal matrix element of $\vec{k}\cdot\vec{p}$,

$$E_e(\vec{k}) = E_e(0) + \vec{k}\cdot\frac{dE_e}{d\vec{k}} = E_e(0) + \frac{\hbar}{m}\,\vec{k}\cdot\vec{p}^{\,e}_{kk}\;. \tag{32}$$

The off-diagonal part can be represented by H_c of (30), and for $\Delta n = 1$ the result is similar to (10). Because of the asymmetry introduced by $\delta\vec{k}$, this process is now allowed. The ellipsoids in $\vec{k}$ space contribute independently. Each true wave function, consisting of a linear combination of these six wave functions, would be symmetrical, but their overlap is so small ($\approx e^{-(\delta k R_0)^2}$), that there is no transition from the one cyclotron orbit to the other in finite times. Thus the possibility of a $\Delta n = 1$ cyclotron Raman effect in n-type Si is due to broken symmetry.

In this case it is not necessary to go to two different excited states, as in (10). Because of the nonzero p^e_{kk}, one excited state can give the total contribution, as for the A term in (7). The p^e_{kk} can be used for either the $\vec{k}\cdot\vec{p}$ or $\vec{A}\cdot\vec{p}$ operators, corresponding to the variation with k or the $E(\vec{k})$ and p_{eg} parts in (31), respectively. In this way there are six contributions to $H_{n,n+1}$, which, in case all p's are in the same direction, sum up to

$$M^{\mathrm{el}}_{01} = 2p^2_{eg}R_0^{-1}\,\frac{dE_e}{dk}\,\frac{3\Delta^2 - (\hbar\omega)^2}{[\Delta^2 - (\hbar\omega)^2]^2}\;. \tag{33}$$

For $B = 50\,000$ G the term $R_0^{-1}(dE_e/dk)$ is expected to be of order 0.01 eV.

D. Ratio of Δn=1, 2 Intensities

For the $\Delta n = 2$ processes we shall consider only mechanisms (b) (anisotropic mass) and (c) $(\vec{k}\cdot\vec{p})$. The (b) effect (28) is identical to (12), where $B \approx \hbar\omega_c \cong 0.01$ eV. For the $\vec{k}\cdot\vec{p}$ effect we need to consider again only one band on the other side of the gap, although now three electrons must be taken into account; the result is similar to (15):

$$M^c_{f1} \propto 4C_L^2/\Delta[\Delta^2 - (\hbar\omega)^2] \qquad (\Delta n = 2)\;. \tag{34}$$

It was estimated from (30) that $C_L \cong 0.1$ eV.

As in (19), we shall estimate the ratio I_2/I_1 for the (b) and (c) processes. Not too far from resonance for a crystal without inversion symmetry, using (10), (12), and (34), we have

$$\frac{I_2}{I_1} \cong \left(\frac{\Delta_2 - \hbar\omega}{\Delta_1}\right)^2 \left|\frac{C_L}{\Delta_1} + \frac{B_L}{C_L}\,\frac{\Delta_1}{\Delta_1 - \hbar\omega}\right|^2, \tag{35}$$

which for $\Delta_2 \gg \Delta_1$ can easily exceed unity.

IV. RAMAN EFFECT FROM STARK LADDER LEVELS

Next, we consider the light scattering in the presence of a strong static electrical field $E_x = F/e$, directed along one of the principal axes of the crystal. It has been shown by Wannier[11] that under such circumstances quantization of electron states occurs with an energy spacing $\hbar\omega_s = Fa$. The probability of tunneling across a band gap E_g is

$$(\tfrac{1}{2}\pi)^2 \exp[-(\tfrac{1}{8}\pi^2)E_g^2/E_b Fa]\;,$$

where

$$E_b = (\hbar^2/2m)(\pi/a)^2\;.$$

The preexponential factor given by Houston[12] is about $(2\pi)^2$. If

$$Fa \ll E_g^2/E_b\;, \tag{36}$$

the electron can be described by a Bloch function of one band with a wave vector $\vec{k}$ obeying $\hbar\dot{k}_x = F$. Introducing $H(\vec{k}, X) = E(\vec{k}) - FX$,

$$\hbar\dot{k}_x = -\frac{\partial H}{\partial X}\;, \quad \hbar\dot{X} = \frac{\partial H}{\partial k_x}\;, \tag{37}$$

where X stands for the average value of x for a wave packet. Equations (37) form a set of Hamilton equations of motion. These should be quantized according to

$$[X, k_x] = i\;, \tag{38}$$

so that $X = i d/dk_x$ and

$$H = E(\vec{k}) - \frac{iF\partial}{\partial k_x}\,, \tag{39}$$

of which the time-independent eigenfunctions are

$$\psi_i(k_x) = \left(\frac{a}{2\pi}\right)^{1/2} \exp\left(\frac{i}{F}\int^{k_x}[W - E_i(k_x')]\,dk_x'\right)\,, \tag{40}$$

where W is the energy. Because of translational symmetry, $W-naF$ must also be an allowed energy, with n an integer. In a box of length $L=Na$ the potential varies by NaF, with the same spread in W. Since there can be only N different states for each band, the allowed energy levels are separated by aF, and form the Stark ladder. Then,

$$\psi_{ni}(k_x)=(a/2\pi)^{1/2} \times\exp\left[-ink_x a-(i/F)\int^{k_x} E_i(k_x')\,dk_x'\right]. \tag{41}$$

The $\vec{r}$-dependent wave function is

$$\Phi_{ni}(\vec{r})=\int_{-\pi/a}^{\pi/a} \psi_{ni}(k_x)\varphi_{ki}(\vec{r})\,dk_x\,. \tag{42}$$

For the Raman effect we must again calculate the $\vec{A}\cdot\vec{p}$ matrix elements between states in different bands. Usually aF is relatively small, so that many states of the excited band overlap with the ground state (42). We therefore ignore the quantization in the excited band, as we did in (31). The total second-order matrix element then is

$$M_{n0}^{\text{el}}=\frac{a}{2\pi}\sum_e\int_{-\pi/a}^{\pi/a} e^{-ink_x a} \times\frac{p_{ge}(\vec{k})p_{eg}(\vec{k})}{E_e(\vec{k})-E_g(\vec{k})-\hbar\omega}\,dk_x\,, \tag{43}$$

which is very similar to (31). When $\hbar\omega$ is much smaller than the band gap, the central part of the integrand in (31) or (43) contains

$$-\tfrac{1}{2}\frac{m^2}{m^*}=-\tfrac{1}{2}\left(\frac{m}{\hbar}\right)^2\frac{\partial^2 E_g}{\partial k_x^2}\,.$$

The Raman effect for conduction electrons can thus be visualized as being caused by the modulation of the effective mass during the acceleration produced by either a magnetic or an electrical field. For bound electrons, as treated in Sec. II, it is the stiffness which is modulated, in that case by lattice vibrations.

In the limit $\omega\to 0$, (43) becomes

$$M_{n0}^{\text{el}}\simeq n^2\frac{a}{4\pi}\left(\frac{ma}{\hbar}\right)^2\int_{-\pi/a}^{\pi/a} E_g(\vec{k})\cos nk_x a\,dk_x\,, \tag{44}$$

so that in principle the Fourier components of the E-k curve can be obtained from a set of Raman lines produced by the Stark ladder. In case ω cannot be ignored, the more general (43) must be used, and should be complemented with a similar expression with opposite ω.

It is interesting to compare the strength of (44) with that for the light scattering in a magnetic field. For $E_b=10$ eV and $a=3$ Å, (43) is about $4m$. The effective second-order electronic matrix element due to (30) is $p_{eg}^2 C_L/(\Delta_1-\hbar\omega)^2$, which is about $2m/(\Delta_1-\hbar\omega)^2$, where the energies are expressed in electron volts. Therefore the Raman-scattering cross sections per electron in an electrical and in a magnetic field may be of the same order of magnitude. In the magnetic case it depends on the strength of the magnetic field, but for the Stark ladder, M is independent of the electrical field. For small fields, however, the effect is completely obscured by scattering.

V. EFFECTIVE-MASS APPROXIMATION FOR IMPURITY LEVELS

An electron in a lattice with a wide shallow perturbing potential $U(\vec{r})$ can be treated in a way which is very similar to that discussed in the preceding sections. If U is many atom distances wide, a wave packet of wave functions of one band can be formed of which the position $\vec{R}$ and the (large) wave vector $\vec{K}$ are well defined. The force in the x direction on the electron is $-\partial U/\partial X$, so that with $H(\vec{K},\vec{R})=E(\vec{K})+U(\vec{R})$,

$$\hbar\dot{K}_x=-\frac{\partial H}{\partial X}\,,\quad \hbar\dot{X}=\frac{\partial H}{\partial K_x}\,, \tag{45}$$

similar to (37). The quantization condition then is

$$[X,K_x]=i\quad\text{or}\quad K_x=\frac{-i\partial}{\partial X}\,, \tag{46}$$

which gives the usual effective-mass formalism. The solution is $\psi(\vec{R})$, which can be Fourier analyzed:

$$\chi(\vec{k})=\int\psi(\vec{R})e^{-i\vec{k}\cdot\vec{R}}\,d\vec{R}\,,$$

from which we find the eigenfunction as a function of $\vec{r}$:

$$\Phi(\vec{r})=\int\chi(\vec{k})\varphi_{\vec{k}}(\vec{r})\,d\vec{k} =\int\psi(\vec{R})\,d\vec{R}\int e^{i\vec{k}\cdot(\vec{r}-\vec{R})}u_{\vec{k}}(\vec{r})\,d\vec{k}\,. \tag{47}$$

If $\vec{R}$ is a lattice point $\vec{R}_n$, the last integral is just the Wannier function $w(\vec{r}-\vec{R}_n)$. For a slowly varying function $\psi(\vec{R})$, as for a donor state, the integral over $\vec{R}$ can be replaced by a sum over lattice points:

$$\Phi(\vec{r})=N^{-1/2}\textstyle\sum_n\psi(\vec{R}_n)w(\vec{r}-\vec{R}_n)\,. \tag{48}$$

Equation (47) is, however, also valid for a rapidly varying wave function $\psi(\vec{R})$, as for metals, where (48) does not apply. The unperturbed wave functions are then $e^{i\vec{k}\cdot\vec{R}}$. This means that the scattering by a shallow extended perturbation potential in a metal can be calculated as for free electrons with the true dE/dk.

So far we have assumed that the electron stays in the same band, as in Sec. IV. Instead of (36) we now have the condition

$$a\,|\vec{\nabla}U|_{\max}\ll E_g^2/E_b\,. \tag{49}$$

This condition is, of course, not satisfied for the potential $-e^2/\epsilon R$ of a charged impurity. We shall show that in spite of this the effective-mass theory may still be approximately valid. For that purpose we shall truncate the Coulomb potential, so that (49) is satisfied. For instance

$$\begin{aligned} U &= -e^2/\epsilon R \quad (R > R_c) \\ &= -e^2/\epsilon R_c \quad (R < R_c) \ . \end{aligned} \tag{50}$$

The first-order perturbation in the energy ΔE is given by

$$\Delta E/|E| = 2(R_c/R_B)^2 \quad \text{with } R_B = \epsilon \hbar^2/m^* e^2 \ . \tag{51}$$

We want (51) to be small with (49) obeyed:

$$a e^2/\epsilon R_c^2 \ll E_g^2/E_b \ . \tag{52}$$

For a two-band model,

$$E_g/m^* \cong 2\pi^2(\hbar/ma)^2 \ .$$

For $a = 3$ Å, (52) is equivalent to

$$\epsilon > 2(\Delta E/|E|)^{-1/3} \ . \tag{53}$$

Taking arbitrarily $|\Delta E/E| = 0.05$, (53) gives

$$\epsilon > 5 \tag{54}$$

as the condition for the effective-mass approximation to be valid for a donor level. Note that this condition is independent of m^*. For $R_B = 50$ Å, from (51) $R_c \cong 8$ Å, so that the use of ϵ is still justified. A value $\epsilon \geqslant 10$ is probably already safe, so that the effective-mass approximation predicts the correct energies of the donor states for the majority of semiconductors.

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