Effect of surface and nonuniform fields in electroreflectance: Application to Ge

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The effect of crystal termination and nonuniform modulation fields is investigated theoretically in the one-electron approximation. Beginning with the nonlocal dielectric susceptibility expression previously obtained by Del Sole, it is shown that under suitable conditions the surface and field inhomogeneity contributions can be separated. Odd and even line shape components are obtained. The odd component, which at low fields varies linearly with the modulation field, arises from crystal termination. It depends on the mass difference between the electron and the hole and vanishes if the electron and hole masses are equal. The even component includes both crystal termination and field inhomogeneity effects and does not reduce completely to the Franz-Keldysh theory even in the uniform-field limit. Experimental results are presented for the odd electron reflectance component for the E_0 transition of Ge. The results are in good agreement with theory.

I. INTRODUCTION

The Franz-Keldysh[1-4] effect is an important tool to obtain information about the band structure of solids. However, the results of electroreflectance (ER) and electroabsorption experiments[5-9] in semiconductors do not agree with the simple one-electron uniform-field theory, even if a phenomenological broadening parameter is included.[10] It is now understood that the Coulomb interaction between electrons and holes, nonuniform field effects, and crystal termination effects must be taken into account to explain data. The first effect has been studied by many workers[11-16] and numerical line shapes have been constructed. It has been shown that Coulomb effects on the line shape can be neglected only if excitons are thermally ionized in absence of the electric field.[14] However, the theory including Coulomb effects alone is not sufficient to explain ER results as function of the electric field.[7]

The second effect arises because the electric field can be strongly nonuniform near a semiconductor surface[6] due to free-carrier screening. Evangelisti and Frova[6] assumed the position-dependent dielectric function to be given by the uniform-field formula[10] using the local value of the electric field, that is,

$$\epsilon(\omega, z) = \epsilon_{\mathrm{UF}}(\omega, F(z)), \tag{1}$$

where z is the distance from the surface, and $\epsilon_{\mathrm{UF}}(\omega, F)$ is the dielectric function in a uniform electric field F. This seems to be a reasonable assumption for slowly varying fields, but no attempt has been made so far to test its validity. Aspnes and Frova[17] solved the equation for light propagation in inhomogeneously perturbed media and found expressions for the changes in reflection and transmission coefficients by using the same assumption. These expressions gave a qualitative account of ER line shapes at the direct gap of Ge,[18] but they explained absolute values measured by the electrolyte technique only if excitonic effects were included.[9]

Yang and Buckman[19] performed quantum-mechanical calculations of absorption and reflection coefficients of a crystal in a position-dependent electric field in the small-wave-number approximation. Their theory is valid for rapidly varying fields, and is complementary to that of Aspnes and Frova.[17]

It has been shown[20,21] that the presence of the crystal termination itself greatly modifies wavelength-modulated and ER spectra. In particular, the surface breaks down the field reversal ER invariance of Franz-Keldysh[1,10,22] and excitonic[13-16] theories, so that the field reversal asymmetry that is observed in ER measurements[9] could be explained in terms of surface effects.[23] Tyagai and others[24] found that the differential ER signal is not vanishing at the flat-band position in some cases, by contrast to bulk-theory predictions. (We neglect here the trivial case of unequal inhomogeneity effects caused by doping.) This effect can also be explained in terms of surface-induced field reversal asymmetry. We call these effects crystal-termination effects or surface effects; however, it must be emphasized that the microscopic structure of the surface is not involved. The surface provides only the boundary condition that electron wave functions vanish at it. Of course, this is rigorously appropriate only to experimental arrange-

ments where electrons cannot escape from the crystal, but it represents a better approximation to actual physical systems than does the usual periodic boundary condition approach.

A contribution to linear ER could also come from some noncentrosymmetric surface layer that could be produced by surface atom rearrangements. We neglect it here, in the spirit of not taking into account the microscopic features of the surface.

Since it is very difficult to take into account excitonic, nonuniform field, and crystal-termination effects together, we think that it is worthwhile to neglect Coulomb effects and to provide a one-electron theory as exact as possible for comparison to experiment for conditions for which the Coulomb interaction is expected to be less important. Furthermore, only by comparing an exact one-electron theory to experiment can one see how significant excitonic effects are. One of the objectives of the present paper is to provide a one-electron theory as rigorous as possible, with a known range of validity.

To investigate the validity of the surface-termination aspects of the theory, we have also measured the odd (nonvanishing) component of an ER spectrum of Ge in an aqueous electrolyte, a system which has been thoroughly investigated, can be accurately controlled, and is not subject to interpretational uncertainties due to the presence of additional dielectric overlayers on the surface of the semiconductor. The strong weakly broadened E_0 structure of the fundamental absorption edge at 0.796 eV at 300 K was used for these measurements. Experimental details are given in Sec. II. In Sec. III, the theory of surface effects is extended to that case of a nonuniform electric field that is most frequent in practice. In Sec. IV we discuss the comparison of the theory to experiment.

II. EXPERIMENTAL

The general approach and experimental configuration has been described in the literature.[9,18] Because a trivial linear ER effect would be observed in electromodulation of an extrinsic sample, the sample used in these measurements was cut from a Ge single crystal with a measured net donor concentration of less than 6% of the intrinsic electron concentration at 300 K. The sample itself was also checked to be intrinsic to this accuracy by a combination of capacitance and photovoltage measurements as previously described.[9,18]

The active sample area consisted of a {110} face of the order of 2×3 mm^2, which was polished flat with 1-μm diamond paste and electrochemically etched *in situ* for at least 0.5 h before measurements were taken. The aqueous electrolyte,[25] a 0.10M K_2SO_4 solution buffered with 0.025M Na_2HPO_4 and 0.025M KH_2PO_4, was purified before use by gettering with Ge crushed *in situ*. The continued purity of the electrolyte and the absence of surface states on the Ge electrode were verified by capacitance and photovoltage measurements performed between measurements of ER spectra.

Both fundamental and first harmonic components of the ER signal were obtained simultaneously by modulating the interface potential by means of a repetitive 52-Hz three-level waveform of equal duration, separately adjustable voltage levels V_1, V_2, V_3, and V_2. The odd and even ER components in the reflected intensity were obtained using phase-sensitive detectors set at 52 and 104 Hz, respectively. Phases were calibrated by direct measurement of the modulation waveform adjusted so that V_3 equalled V_2. For the odd response, the spectra correspond to the definition

$$(\Delta R/R)_{\text{odd}} = \tfrac{1}{2}[R(+F_s) - R(-F_s)]/R_0 = \pi V_{\text{ac}}^{(1)}/\sqrt{2}\, V_{\text{dc}} , \quad (2)$$

where F_s is the surface field, $V_{\text{ac}}^{(1)}$ is the amplitude of the 52 Hz component as read by the phase-sensitive detector (responding to rectified average, displaying equivalent rms), and V_{dc} is the dc level of the detector output. The sign convention is such that $(\Delta R/R)_{\text{odd}}$ is positive if $R(F)$ is greater for electron accumulation than for hole accumulation. For the 104 Hz even response, we have

$$(\Delta R/R)_{\text{even}} = \tfrac{1}{2}[R(+F_s) + R(-F_s) - 2R(0)]/R(0) = (\pi/2) V_{\text{ac}}^{(2)}/V_{\text{dc}} , \quad (3)$$

where $V_{\text{ac}}^{(2)}$ is the amplitude of the 104 Hz component as read by the phase-sensitive detector. Here, $(\Delta R/R)_{\text{even}}$ is positive if $R(|F_s|) > R(0)$.

The flat-band or zero-field reference condition is of minor importance in the even spectrum. But since the odd response is a small-amplitude subharmonic of the main signal, the zero-field condition is of critical importance in the odd term. A slight offset of V_2 from the flat-band position, or an inequality of the surface field magnitudes in the V_1 and V_3 segments of the operating cycle, will result in the admixture of the even spectrum into the odd spectrum. As in previous work,[9] we found that the "electrical flat-band" position did not correspond exactly to the "ER flat-band" position, which occurred at about $F_s = 260$ V cm^{-1}. The "ER flat-band" position was obtained by establishing equal surface-field differences between the V_1 and V_2 and V_2 and V_3 levels of the operating cycle, and then performing small adjustments of V_2 to minimize the peak-to-peak amplitude of the odd signal. The resulting odd spectra were observed to scale lin-

early with field *difference* from the *difference-independent* "ER flat-band" surface field of approximately 260 $V\,cm^{-1}$ which was measured electrically at the V_2 portion of the cycle. This linearity, as well as the line-shape uniformity observed for different field differences, agrees with theoretical predictions to be discussed in Secs. III and IV and shows that these odd spectra indeed contain a negligible admixture of even spectra.

III. THEORY

A. Wave functions

We solve the Schrödinger equation for electrons and holes in a nonuniform electric field in the limit of slow spatial field variation. Let $V(z)$ be the potential energy of electrons in the electrostatic field. We assume it to be everywhere negative and increasing in magnitude with increasing z. The effective-mass-approximation (EMA) wave functions for electrons in a conduction band with isotropic effective mass, m_e^* are

$$F(\vec{r}) = A^{-1/2} e^{i(k_x x + k_y y)} \psi(z), \tag{4}$$

where $\psi(z)$ obeys the wave equation

$$-\frac{\hbar^2}{2m_e^*}\frac{d^2}{dz^2}\psi(z) + V(z)\psi(z) = E\psi(z), \tag{5}$$

where E is measured from E_g, the conduction-band edge.

The appropriate boundary conditions of the problem are[20,21]

$$\psi(0) = \psi(L) = 0. \tag{6}$$

We assume that there is a negligible charge transport through the surface, which is true in some ER experimental arrangements,[9,18] and that electrons are specularly reflected from the surface. The potential and boundary conditions produce discrete energy levels in the conduction band for $E < 0$ in addition to continuous states for $E > 0$. The discrete levels are responsible for light absorption at energies smaller than E_g. Only continuum states are present in the valence band.

Equation (5) can be solved by the WKB method. However, this is not valid in a range centered on z_c, the classical turning point, defined by

$$V(z_c) = E \quad \text{(for electrons)}.$$

We assume in this range that the electric field is constant in order to solve Eq. (5) with Airy functions.[26] The wave functions are matched with an analytic form that simplifies to an Airy function for small $|z - z_c|$, and to a WKB wave function otherwise.

We consider first the discrete-level wave functions

$$F_{nk_xk_y} = A^{-1/2}\exp[i(k_x x + k_y y)]\,\psi_n(z); \tag{7}$$

$$E_{nk_xk_y} = E_g + (\hbar^2/2m_e^*)(k_x^2 + k_y^2) + E_n; \tag{8}$$

$$\psi_n(z) = N_n^{-1}|k_n(z)|^{-1/2} \times |\phi_n(z)|^{1/4}\,\mathrm{Ai}(\phi_n(z)), \tag{9}$$

where

$$k_n(z) = \{(2m_e^*/\hbar^2)[E_n - V(z)]\}^{1/2}, \tag{10}$$

$$P_n(z) = \int_{z_n} z\,dz\,|k_n(z)|, \tag{11}$$

$$V(z_n) = E_n, \tag{12}$$

$$\phi_n(z) = [(z - z_n)/|z - z_n|][\tfrac{3}{2}P_n(z)]^{2/3}, \tag{13}$$

where N_n is the normalization factor. These are the correct wave functions if

$$\frac{1}{F(z_n)}\left|\frac{dF(z_n)}{dz_n}\right| \ll \frac{F(z_n)}{\Theta_e(z_n)}, \tag{14}$$

where $F(z) = dV/dz$ is the force acting on the electrons, and

$$\Theta_e(z) = \hbar^{2/3}F^{2/3}(z)/(2m_e^*)^{1/3}. \tag{15}$$

Boundary conditions give the quantization rule

$$[\tfrac{3}{2}P_n(0)]^{2/3} = \alpha_n, \tag{16}$$

where $\xi = -\alpha_n$ are the zeroes of $\mathrm{Ai}(\xi)$.

For large $|z_n - z|$, $N_n\psi_n$ approaches the WKB wave function

$$\psi_{WKB} = [\pi k_n(z)]^{-1/2}\sin(P_n + \tfrac{1}{4}\pi)\Theta(z_n - z), \tag{17}$$

as can be seen using the following asymptotic expansion of Ai,[26]

$$\mathrm{Ai}(-\xi) \cong (\pi^2\xi)^{-1/4}\sin(\tfrac{2}{3}\xi^{3/2} + \tfrac{1}{4}\pi) \quad \xi \to -\infty \tag{18}$$

where $\Theta(z)$ is the step function.

For small $|z - z_n|$, we use the linear approximation

$$V(z) = E_n + F(z_n)(z - z_n), \tag{19}$$

and find that $N_n\psi_n$ approaches the function ψ_s, where

$$\psi_s(z) = [\Theta_e(z_n)/F(z_n)]^{1/2} \times \mathrm{Ai}((z - z_n)F(z_n)/\Theta_e(z_n)). \tag{20}$$

Since ψ_{WKB} can be simplified in the same way for z near z_n, we obtain a new function

$$\psi_{WKB}^s = [\pi k_n(z)]^{-1/2} \times \sin[P_n^s(z) + \tfrac{1}{4}\pi]\Theta(z_n - z), \tag{17a}$$

where k_n^s and P_n^s are calculated from Eq. (19). These auxiliary functions are useful in evaluating the normalization factor,

$$N_n^2 = \int_0^\infty dz\, N_n^2 \psi_n^2(z)$$

$$= \int_0^\infty dz\, \psi_{\mathrm{WKB}}^2(z) + \int_0^\infty dz\, (N_n^2\psi_n^2 - \psi_{\mathrm{WKB}}^2)\,. \quad (21)$$

Since the last integrand is different from zero only for z close to z_n, ψ and ψ_{WKB} can be replaced there by ψ^s and ψ^s_{WKB}. By rearranging terms one obtains

$$N_n^2 = \frac{1}{\pi}\int_0^{z_n} dz \left(\frac{\sin^2(P_n+\frac{1}{4}\pi)}{k_n(z)} - \frac{\sin^2(P_n^s+\frac{1}{4}\pi)}{k_n^s(z)}\right) + \frac{\Theta_e(z_n)}{F(z_n)}\int_0^\infty dz\, \mathrm{Ai}^2\left(\frac{F(z_n)}{\Theta_e(z_n)}(z-z_n)\right). \quad (22)$$

The first integrand vanishes when z approaches z_n. Otherwise the WKB approximation is valid, and the two sines are strongly oscillating functions of z. No significant error is made if they are replaced by their mean values $\frac{1}{2}$, as is usually done in WKB normalization.[27] Finally we get

$$N_n^2 = \frac{1}{2\pi}\int_0^{z_n} dz\, \frac{1}{k_n(z)} - \frac{1}{\pi}\frac{\Theta_e^{3/2}(z_n)}{F^{3/2}(z_n)}\, z_n^{1/2} + \frac{\Theta_{en}^2}{F_n^2}\left[\mathrm{Ai}^2\left(-\frac{F_n z_n}{\Theta_{en}}\right) + \frac{F_n z_n}{\Theta_{en}}\,\mathrm{Ai}^2\left(-\frac{F_n z_n}{\Theta_{en}}\right)\right], \quad (23)$$

where $\Theta_{en}=\Theta_e(z_n)$ and $F_n=F(z_n)$, and where we have used[28]

$$\int^t d\xi\, \mathrm{Ai}^2(\xi) = t\,\mathrm{Ai}^2(t) - \mathrm{Ai}'^2(t)\,.$$

For large n, N_n^2 is simplified to the usual WKB normalization factor

$$N_n^2 = \frac{1}{2\pi}\int_0^{z_n}\frac{dz}{k_n(z)}\,. \quad (24)$$

Actually, Eq. (24) is valid for $n \geq 3$.

Positive energy conduction states have no turning points, so the WKB approximation can be directly applied and we get

$$F_{k_x k_y E_e} = A^{-1/2}\exp[i(k_x x + k_y y)]\,\psi_{E_e}(z)\,, \quad (25)$$

$$\psi_{E_e}(z) = \left(\frac{2}{k_e(z)}\right)^{1/2}\left(\frac{\pi\hbar^2}{m_e^*}\,\frac{dn}{dE_e}\right)^{-1/2}\sin P_e(z)\,, \quad (26)$$

$$k_e(z) = \{(2m_e^*/\hbar^2)[E_e - V(z)]\}^{1/2}, \quad (27)$$

$$P_e(z) = \int_0^z dx\, k_e(x)\,, \quad (28)$$

where

$$\frac{dn}{dE_e} = \frac{m_e^*}{\pi\hbar^2}\int_0^L \frac{dz}{k_e(z)} \quad (29)$$

is the density of states found by deriving with respect to E_e the boundary condition $P_e(L)=n\pi (n>0)$. The energy is given by

$$E_{k_x k_y E_e} = E_g + E_e + (\hbar^2/2m_e^*)(k_x^2+k_y^2)\,. \quad (30)$$

The hole wave functions satisfy the Schrödinger equation

$$-\frac{\hbar^2}{2m_h^*}\,\frac{d^2}{dz^2}\,\psi(z) - V(z)\psi(z) = E_h\psi(z) \quad (31)$$

with m_h^* and $E_h>0$. The solution is

$$F_{k_x k_y E_h} = A^{-1/2}\exp[i(k_x x + k_y y)]\,\psi_{E_h}(z)\,; \quad (32)$$

$$\psi_{E_h}(z) = \left(\frac{2m_h^*}{\hbar^2}\right)^{1/2}\left(\frac{dn}{dE_h}\right)^{-1/2}\left|\frac{\psi_h(z)}{k_h^2(z)}\right|^{1/4} \times [A\,\mathrm{Ai}(\psi_h) - B\,\mathrm{Bi}(\psi_h)]\,; \quad (33)$$

$$k_h(z) = \{(2m_h^*/\hbar^2)[E_h + V(z)]\}^{1/2}; \quad (34)$$

$$V(z_h) = -E_h\,; \quad (35)$$

$$P_h(z) = \int_{z_h}^z dx\, |k_h(x)|\,; \quad (36)$$

$$\delta = (z_h/|z_h|)[\tfrac{3}{2}P_h(0)]^{2/3}; \quad (37)$$

$$\Psi_h(z) = [(z_h - z)/|z_h - z|][\tfrac{3}{2}P_h(z)]^{2/3}; \quad (38)$$

$$A = \frac{\mathrm{Bi}(\delta)}{[\mathrm{Ai}^2(\delta)+\mathrm{Bi}^2(\delta)]^{1/2}}\,; \quad B = \frac{\mathrm{Ai}(\delta)}{[\mathrm{Ai}^2(\delta)+\mathrm{Bi}^2(\delta)]^{1/2}}\,. \quad (39)$$

From scattering theory,[29] the normalization factor is proportional to the density of states. z_h is allowed to be negative in order to describe states with $E_h > -V(0)$. For large and positive δ, that is for $|E_h + V(0)| \gg \Theta_h(0)/F(0)$, where $\Theta_h(z) = [\hbar^2F^2(z)/2m_h]^{1/3}$, B vanishes and A becomes equal to 1. If $E_h + V(0) \gg \Theta_h(0)/F(0)$, then the WKB functions can be used for any z. Equation (33) is a good approximation to the exact wave function if

$$\frac{1}{F(z)}\left|\frac{dF}{dz}\right| \ll \frac{F(z)}{\Theta_h(z)}\,. \quad (14a)$$

From now on, we assume that

$$\frac{1}{F(z)}\left|\frac{dF}{dz}\right| \ll \frac{F(z)}{\Theta(z)}\,, \quad (14b)$$

where $\Theta(z) = \hbar^2F^2(z)/2\mu$ and $\mu^{-1} = m_e^{*-1} + m_h^{*-1}$, satisfying in this way both Eqs. (14a) and (14b).

In the two following cases Eq. (33) assumes simpler forms

$$\psi_s = \left(\frac{2m_h^*\Theta_h(z_h)}{\hbar^2F(z_h)\,dn/dE_h}\right)^{1/2} \times \left[A\,\mathrm{Ai}\left(\frac{z_h - z}{F_h}\,\Theta_h\right) - B\,\mathrm{Bi}\left(\frac{z_h - z}{F_h}\,\Theta_h\right)\right] \quad (40)$$

for z near z_h, and

$$\psi_{\mathrm{WKB}} = \left(\frac{2m_h^*}{\pi\hbar^2 k_h(z)\, dn/dE_h}\right)^{1/2} \sin\left(P_h + \frac{\pi}{4} - \alpha\right), \tag{41}$$

where $\alpha = \tan^{-1}[\mathrm{Ai}(\delta)/\mathrm{Bi}(\delta)]$, for $z \gg z_h$.

B. Surface and bulk contributions to the reflectance

The imaginary part, $\epsilon''(z,z',\omega)$, of the nonlocal dielectric susceptibility[20,28] can be computed near an M_0 edge in the EMA using

$$\epsilon''(z,z',\omega) = (h\pi^2 e^2/m^2\omega^2)|P_{vc}|^2 \times \sum_{E_e E_h} \psi_{E_e}(z)\psi^*_{E_h}(z)\psi^*_{E_e}(z') \times \psi_{E_h}(z')\Theta(\hbar\omega - E_e - E_h), \tag{42}$$

where E_e and E_h label electron and hole states, P_{vc} is the momentum matrix element between valence and conduction states, and Θ is the unit-step function. The real part $\epsilon'(z,z',\omega)$ can be computed using Kramers-Kronig relations.

In this section, we show that the dielectric susceptibility tends to the uniform-field local-field bulk value as both z and z' become larger than Θ_s/F_s. Thus, surface effects are generated within a distance Θ_s/F_s of the surface, where the electric field is nearly equal to the surface field F_s if Eq. (14b) is fulfilled. Henceforth, the surface effects are determined uniquely by the surface field and can be computed in the constant field scheme.

Equation (42) can be written as

$$\epsilon''(z,z',\omega) = \sum_{E_e} \psi_{E_e}(z)\psi_{E_e}(z') I(z,z',\hbar\omega - E_e), \tag{43}$$

where

$$I(z,z',\hbar\omega - E_e) = \int_0^{\hbar\omega - E_e} dE_h \, \frac{dn}{dE_h}\, \psi_{E_h}(z)\psi_{E_h}(z'). \tag{44}$$

Let us consider the case that $z, z' \gg \Theta_s/F_s$ and $|z - z'| \lesssim \Theta(\tilde{z})$, where $\tilde{z} = (z+z')/2$. The product of wave functions in Eq. (44) can be written

$$\psi_{E_h}(z)\psi_{E_h}(z') = \psi^{\mathrm{WKB}}_{E_h}(z)\psi^{\mathrm{WKB}}_{E_h}(z') + [\psi_{E_h}(z)\psi_{E_h}(z') - \psi^{\mathrm{WKB}}_{E_h}(z)\psi^{\mathrm{WKB}}_{E_h}(z')]. \tag{45}$$

The square-bracketed term is different from zero only for z near z_h. In this case, it can be computed using a constant value of the electric field $F(z_h) = F(\tilde{z})$. Then, we obtain

$$\psi_{E_h}(z)\psi_{E_h}(z') = \psi^s_{E_h}(z)\psi^s_{E_h}(z') + \psi^{\mathrm{WKB}}_{E_h}(z)\psi^{\mathrm{WKB}}_{E_h}(z') - \psi^{\mathrm{WKB},S}_{E_h}(z)\psi^{\mathrm{WKB},S}_{E_h}(z'). \tag{46}$$

The last two terms cancel for $\tilde{z} \sim z_h$ and otherwise produce rapid oscillations around zero. Consequently, they can be neglected. Thus, we get for I, using Eq. (40) and the properties of the Airy functions,

$$I(z,z',\hbar\omega - E_e) = \frac{1}{z - z'}\left[\mathrm{Ai}'\left(-\frac{\hbar\omega - E_e + V(z)}{\tilde{\Theta}_h}\right)\mathrm{Ai}\left(-\frac{\hbar\omega - E_e + V(z')}{\tilde{\Theta}_h}\right) - \mathrm{Ai}\left(-\frac{\hbar\omega - E_e + V(z)}{\tilde{\Theta}_h}\right)\mathrm{Ai}'\left(-\frac{\hbar\omega - E_e + V(z')}{\tilde{\Theta}_h}\right)\right]. \tag{47}$$

This equation shows that only electron states with $E_e \lesssim \hbar\omega + V(\tilde{z})$ contribute to the sum Eq. (43), in order not to have vanishing Airy functions in Eq. (45). Equations with $\sim$ are understood to be satisfied within certain ranges of Θ or Θ/F. On the other hand, electron states have nonvanishing wave functions near $\tilde{z}$ only if $E_e \gtrsim V(\tilde{z})$. Thus, the only electron states contributing to Eq. (43) are in the range

$$V(\tilde{z}) \lesssim E_e \lesssim V(\tilde{z}) + \hbar\omega. \tag{48}$$

If $\tilde{z}$ is deep enough inside the crystal, only higher levels are singled out by Eq. (48) and the sum over discrete electron levels can be replaced by an integral over E_e. The same type of argument as for the sum over E_h holds for such integrals, so that the result is, for $z, z' \gtrsim \Theta_s/F_s$,

$$\epsilon''(z,z',\omega) = \frac{2m_e^*}{\hbar^2}\,\frac{\tilde{\Theta}_e}{\tilde{F}}\,\frac{1}{z - z'}\int_{-\infty}^{+\infty} dE\ \mathrm{Ai}\left(\frac{E}{\tilde{\Theta}_e}\right)\mathrm{Ai}\left(\frac{E + \tilde{F}(z' - z)}{\tilde{\Theta}_e}\right) \times \left[\mathrm{Ai}'\left(-\frac{\hbar\omega + E}{\tilde{\Theta}_h}\right)\mathrm{Ai}\left(-\frac{\hbar\omega + E + \tilde{F}(z' - z)}{\tilde{\Theta}_h}\right) - \mathrm{Ai}\left(-\frac{\hbar\omega + E}{\tilde{\Theta}_h}\right)\mathrm{Ai}'\left(-\frac{\hbar\omega + E + \tilde{F}(z' - z)}{\tilde{\Theta}_h}\right)\right], \tag{49}$$

where $\tilde{F}=F(\tilde{z})$ and $\tilde{\Theta}_{e,h}=\Theta_{e,h}(\tilde{z})$.

This result is the same as that obtained in a constant electric field equal to $\tilde{F}$. Thus, we have shown that

$$\epsilon(z,z',\omega)=\epsilon_{\mathrm{UF}}(z,z',\omega,\tilde{F}) \tag{50}$$

for $z,z' \gtrsim \Theta_s/F_s$, where ϵ_{UF} is that given by Franz-Keldysh theory. Now, we can write

$$\epsilon(z,z',\omega)=[\epsilon(z,z',\omega)-\epsilon_{\mathrm{UF}}(z,z',\omega,\tilde{F})] + \epsilon_{\mathrm{UF}}(z,z',\omega,\tilde{F}) . \tag{51}$$

The term in square brackets vanishes as z and z' exceed a length Θ_s/F_s, so it is determined only by the surface field F_s. Therefore,

$$\epsilon(z,z',\omega)=\epsilon_s(z,z',\omega,F_s)-\epsilon_{\mathrm{UF}}(z,z',\omega,F_s) + \epsilon_{\mathrm{UF}}(z,z',\omega,\tilde{F}) , \tag{52}$$

where ϵ_s is the dielectric susceptibility computed in a constant electric field equal to F_s and taking into account surface effects.

When the effective dielectric function $\langle\epsilon(\omega)\rangle$ describing reflectivity[20] is considered, we obtain for the change due to the electric field

$$\langle\Delta\epsilon(\omega)\rangle=\Delta\epsilon_s(\omega,F_s)+\Delta\epsilon_{\mathrm{bulk}}(\omega) , \tag{53}$$

where

$$\Delta\epsilon_{\mathrm{bulk}}(\omega)=-2iq\int_0^\infty dz\,\exp(2iqz)\Delta\epsilon_{\mathrm{UF}}(\omega,F(z)) \tag{54}$$

is just the result of Aspnes and Frova.[17] It has been derived neglecting nonlocal effects on the bulk term

$$\int_0^\infty dz\int_0^\infty dz'\exp[iq(z+z')]\epsilon_{\mathrm{UF}}\left(z,z',\omega,F\left(\frac{z+z'}{2}\right)\right) = \int_0^\infty d\tilde{z}\exp(2iq\tilde{z})\int_{-\infty}^{+\infty}dz'\,\epsilon_{\mathrm{UF}}(\tilde{z},z',\omega,F(\tilde{z})) . \tag{55}$$

Therefore, we have decoupled the ER response of a semi-infinite semiconductor in a nonuniform electric field into two terms. The first one describes surface effects and can be computed within the constant-field approach of Ref. 21. The second one is given by the averaging procedure of Ref. 17. Both the decoupling and the Aspnes-Frova result are valid if the condition

$$\frac{1}{F(z)}\frac{dF}{Dz} \ll \frac{F(z)}{\Theta(z)}$$

is fulfilled at any z.

IV. RESULTS AND DISCUSSION

Figure 1 shows an example of calculated nonuniform-field ER line shapes taking into account surface effects. The line-shape function[21] $S(\eta)$, proportional to $\Delta R/R$, is computed for parameters appropriate to the direct gap of intrinsic Ge, taking into account the spatial variation of the field at room temperature. The surface field is 11 kV/cm. Since light holes and electrons have nearly equal masses, the light-hole band contribution is weakly depending on field orientation and is shown only once. The importance of surface effects is clearly recognized in the heavy-hole spectrum. The field reversal asymmetry, namely, the difference between the dotted and dash-dotted curves, is generated by the heavy-hole band contribution and cannot be neglected with respect to the total signal even at this relatively high-field value.

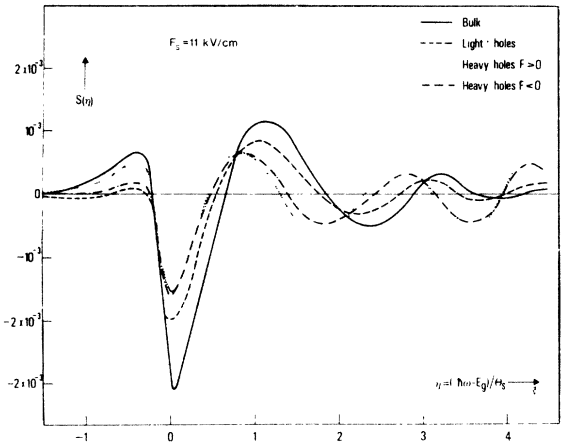

FIG. 1. Computed line-shape function $S(\omega)$, proportional to $\Delta R/R$, is plotted vs $\eta=(\hbar\omega-E_g)/\Theta_s$ at the E_0 edge of Ge for $F_s=11$ kV/cm. The field nonuniformity of intrinsic Ge at room temperature is taken into account, together with a small broadening $\Gamma=1$ meV.

In order to compare theory and experiment, we have computed the odd ER line shape at fixed broadening $\Gamma=2$ meV for a number of field values ranging from 0.9 to 2.3 kV/cm. Two of these line shapes are shown in Fig. 2 as functions of $(\hbar\omega-E_g)/\Theta_s$. Peak positions are the same in the two curves, showing that line shapes depend on $(\hbar\omega-E_g)/\Theta_s$. The main features of the odd spectrum do not change in this electric field range, in agreement with experiment. Minor changes affect only high-energy-side negative peaks, which are more sensitive to the ratio Θ_s/Γ. The results are that line shapes scale almost linearly with the electric field for F values ranging from 900 to 2300 V/cm, as seen in Fig. 3. Measured peak-to-peak values of the odd ER signal are also reported in Fig. 3 as function of F_s. It can be seen that the dependence is linear within 10%, in good agreement with the theoretical results also shown in Fig. 3. The theoretical prediction of linear scaling of line shapes

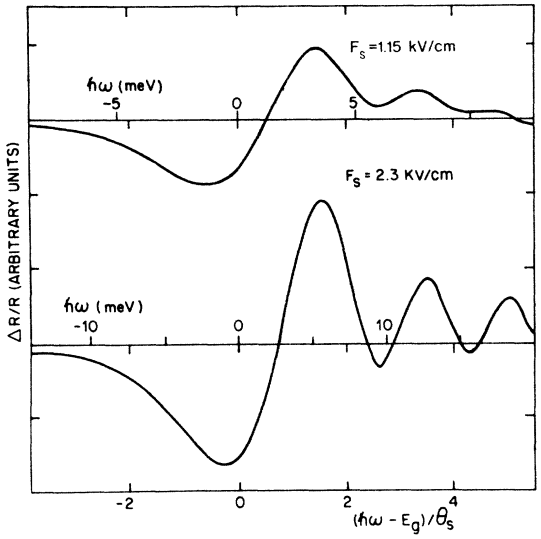

FIG. 2. Theoretical odd ER lineshapes are plotted vs $(\hbar\omega - E_g)/\Theta_s$ for two values of the surface field. Θ_s is computed using the electron heavy-hole reduced mass $\mu = 0.033\, m_e$ (Ref. 21). A realistic value of the broadening, $\Gamma = 2$ meV, is included.

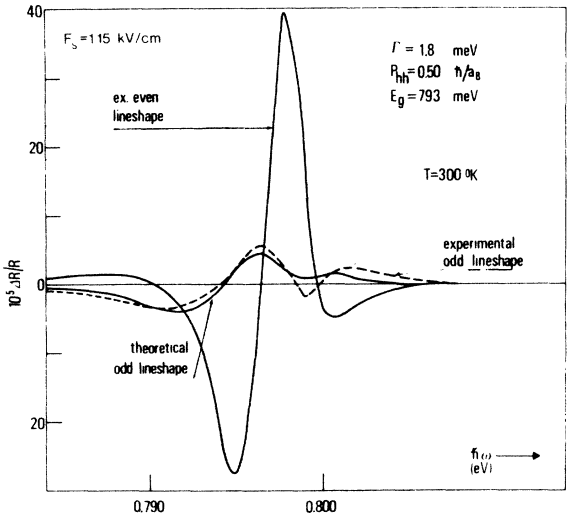

FIG. 4. Experimental even and odd ER components of intrinsic Ge at room temperature. The theoretical odd line shape has been obtained by the present theory of surface effects using the quoted values of parameters.

was necessary, as described in Sec. II, to verify that the "ER flat-band" position was correct for these spectra.

Comparison between theory and experiment is made in Fig. 4. The odd ER component taken at $F_s = 1.15$ kV/cm is well fitted by the theory of surface effects, using as fitting parameters only the broadening Γ, the gap energy E_g, and the heavy-hole matrix element P_{hh}. We get $E_g = 793$ meV, $\Gamma = 1.8$ meV, and $P_{hh} = 0.50\,\hbar/a_B$. Discrepancies at the high-energy side can be produced by the small energy range used in performing numerical Kramers-Kronig transforms. Since both theoretical and experimental line shapes are only weakly dependent on the electric field, and peak-to-peak values agree (see Fig. 3), our fit covers the whole range of measured field values. The values E_g, Γ, and P_{hh} all agree very well with the values $E_g = 793$ meV, $\Gamma = 1.65$ meV, and $P_{hh} = 0.56\hbar/a_B$ obtained by fitting with the present theory[21] Jasperson, Koeppen, and Handler's ER data[8,30] taken with $F_s = 4.6 \times 10^4$ V/cm. We conclude that the present theory of ER including surface effects, though neglecting the Coulomb interaction, is able to give an account of experimental results as a function of the electric field. Furthermore our odd ER measurements allow P_{hh} to be measured independently, since only the heavy-hole band contributes to the odd signal.

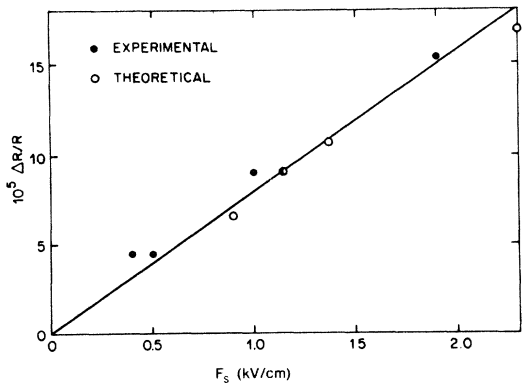

FIG. 3. Comparison of experimental and theoretical peak-to-peak values of the odd ER spectrum as a function of the surface field F_s at the E_0 edge of Ge. The theoretical results were computed as in Fig. 2. Theoretical and experimental values match at $F_s = 1.15$ kV/cm, since theoretical calculations use $P_{hh} = 0.50\ \hbar/a_B$ as determined by fitting the experimental odd spectrum at this field value (see Fig. 4). The straight line has been drawn from the $F_s = 1.15$ kV/cm point to zero to aid in visualizing the linear field dependence of the peak-to-peak values.

The above results provide a good correlation between theory and experiment in the well-controlled case of the E_0 structure of the fundamental absorption edge of Ge, where the broadening is small and the light penetration depth is relatively large. It is of interest to indicate what effects might be expected under other conditions. The similarity of bulk and surface spectra with respect to the period of the Franz-Keldysh oscillations suggests that both even and odd electroreflectance

components will be affected similarly by increasing the broadening parameter. Because higher threshold fields would then be necessary to observe a signal, more broadening would be observed to enhance the even component at the expense of the odd component. But, since larger broadening is typically seen only at higher interband transitions where the light penetration depth is less and surface effects more important, it is possible that the odd term is still significant at these higher-energy transitions, especially since the electron and hole effective masses for higher interband transitions are substantially different, a prerequisite for the observation of an odd term. The odd component would also be enhanced at nearly two-dimensional critical points, as those underlying E_1 transitions in Si, since the relative weight of crystal termination effects, which affect motion in one direction, is increased. It would be of interest to examine these cases experimentally.

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[1]W. Franz, Z. Naturforsch. 13, 484 (1958); L. V. Keldysh, Zh. Eksp. Teor. Fiz. 34, 1138 (1958) [Sov. Phys-JETP 7, 788 (1958)].

[2]D. E. Aspnes and N. Bottka, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1972), Vol. 9, p. 457.

[3]B. O. Seraphin, in *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1972), p. 167.

[4]Y. Hamakawa and T. Nishino, in *Optical Properties of Solids—New Developments*, edited by B. O. Seraphin (North-Holland, Amsterdam, 1975), p. 255.

[5]Y. Hamakawa, P. Handler, and F. A. Germano, Phys. Rev. 167, 709 (1968).

[6]F. Evangelisti and A. Frova, Solid State Commun. 6. 621 (1968).

[7]S. F. Pond and P. Handler, Phys. Rev. B 8, 2869 (1973).

[8]P. Handler, S. Jasperson, and S. Koeppen, Phys. Rev. Lett. 23, 1387 (1969).

[9]D. E. Aspnes and A. Frova, Phys. Rev. B 2, 1037 (1970); 3, 1511 (1971).

[10]D. E. Aspnes, Phys. Rev. 153, 972 (1967).

[11]C. B. Duke and M. E. Alferieff, Phys. Rev. 145, 583 (1966).

[12]R. Enderlein, Phys. Status Solidi 26, 509 (1968).

[13]J. D. Dow and D. Redfield, Phys. Rev. B 1, 3358 (1970); F. C. Weinstein, J. D. Dow, and B. Y. Lao, *ibid.* 4, 3502 (1971).

[14]D. F. Blossey, Phys. Rev. B 2, 3976 (1970).

[15]D. F. Blossey, Phys. Rev. B 3, 1382 (1971).

[16]D. E. Aspnes and J. E. Rowe, Phys. Rev. Lett. 25, 162 (1970).

[17]D. E. Aspnes and A. Frova, Solid State Commun. 7, 155 (1969).

[18]D. E. Aspnes and A. Frova, Phys. Rev. 182, 795 (1969).

[19]E. Yang and A. B. Buckman, Phys. Rev. B 5, 2242 (1970).

[20]R. Del Sole, J. Phys. C 8, 2971 (1975).

[21]R. Del Sole, Solid State Commun. 19, 207 (1976).

[22]D. E. Aspnes, Phys. Rev. 147, 554 (1966).

[23]R. Del Sole and D. E. Aspnes, Nuovo Cimento B 39, 802 (1977).

[24]V. A. Tyagai, V. H. Bondarenko, and O. V. Snitko, Fiz. Tekh. Poluprovodn. 5, 1038 (1971) [Sov. Phys.-Semicond. 5, 920 (1971)].

[25]W. H. Brattain and P. J. Boddy, J. Electrochem. Soc. 109, 574 (1962).

[26]H. A. Antosiewitz, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun, (Natl. Bur. Stand. Appl. Math. Ser. 55 (U.S. GPO, Washington, D. C., 1964), p. 446.

[27]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics; Non-Relativistic Theory* (Pergamon, New York, 1965).

[28]R Del Sole, Internal Report No. 626 of Instituto di Fisica dell'Universita di Roma (1975) (unpublished).

[29]J. A. Appelbaum and G. A. Baraff, Phys. Rev. B 5, 475 (1972).

[30]J. Grover and P. Handler, Phys. Rev. B 6, 3145 (1972).