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Direct Verification of the Third-Derivative Nature of Electroreflectance Spectra

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The electric-field-induced change in the linear dielectric function for the E_1 and $E_1 + \Delta_1$ transitions of Ge, determined from low-field electroreflectance measurements, is shown to be in quantitative agreement with the third derivative of the linear dielectric function measured by high-resolution ellipsometry techniques. This result relates electroreflectance spectra to other types of modulation spectra and provides the first direct verification of the nonlinear optical interpretation of electroreflectance.

We report quantitative experimental verification of the relation between low-field electroreflectance (ER) spectra and the third derivative of the linear dielectric function, predicted by a recent theory^{1,2} which identifies low-field ER as a resonant third-order nonlinear optical susceptibility. This result is obtained by comparing the field-induced change in the linear dielectric function of the E_1 and $E_1 + \Delta_1$ transitions of Ge, as determined from its low-field ER spectrum, with the third derivative of the linear dielectric function, calculated from data taken on the same crystal by high-resolution ellipsometric techniques.³ In addition to being a stringent test of the above theory, this result defines the relationship of ER spectra⁴ to those obtained by first-derivative modulation techniques such as piezoreflectance,⁵ thermoreflectance,⁶ and wavelength-derivative spectroscopy,⁷ and provides a simple qualitative explanation of the fact that ER spectra are sharper and more richly structured than those measured by other modulation techniques.⁸ These results also show that improved ellipsometric methods³ enable the dielectric function to be measured directly with sufficient accuracy to allow the calculation of numerically differentiated spectra whose experimental uncertainties are not significantly larger than those obtained by modulation spectroscopy.

The nonlinear optical approach to ER¹ relates the complex one-electron dielectric function ϵ_0 to its complex field-induced change $\Delta\epsilon_0$ by the ex-

pression

$$\Delta\epsilon_0 = \frac{(\hbar\Omega)^3}{3E^2} \frac{d^3}{dE^3} (E^2\epsilon_0), \quad (1)$$

where E is the energy variable, and $\hbar\Omega$ is the characteristic energy given in terms of the interband energy $E_{cv}(\vec{k})$, or interband reduced mass μ , by

$$(\hbar\Omega)^3 = \frac{1}{8} e^2 (\vec{\mathcal{E}} \cdot \nabla_{\vec{k}})^2 E_{cv}(\vec{k}) = e^2 \hbar^2 \mathcal{E}^2 / 8\mu, \quad (2)$$

where $\vec{\mathcal{E}}$ is the uniform applied electric field. Equation (1) is expected to be valid if $\hbar\Omega$ is nearly independent of E (critical-point transitions between nearly parabolic bands), and if \mathcal{E} is sufficiently small so that $|\hbar\Omega| < \frac{1}{3}\Gamma$, where Γ is the phenomenological broadening parameter. However, correlation effects are not included, and Γ is assumed to be energy independent. Correlation effects can be incorporated to lowest order by simply replacing $\Delta\epsilon_0$ and ϵ_0 in Eq. (1) with their experimentally measured equivalents $\Delta\epsilon$ and ϵ , respectively. This can be proven either from the results of Rees⁹ or from the explicit equations approximating the dominant correlation effect, the electron-hole Coulomb interaction, by a contact potential.^{10,11} Since phenomenological broadening is described by extending the energy E into the complex plane as $E + i\Gamma$, energy dependence of Γ appears after differentiation as a complex prefactor $1 + id\Gamma/dE$, which can be removed (made equivalent to $d\Gamma/dE = 0$) by explicit divi-

sion. If we assume that correlation effects are small and Γ varies linearly with energy, it follows that Eq. (1) can be expressed approximately as

$$\Delta\epsilon \cong \frac{(\hbar\Omega)^3}{3(1 + id\Gamma/dE)^3} \frac{1}{E^2} \frac{d^3}{dE^3} (E^2\epsilon), \quad (3)$$

which may be compared with experiment. Note that Eq. (3) contains two crystal parameters: $d\Gamma/dE$, which determines the amount of line-shape mixing of real and imaginary parts; and μ [see Eq. (2)], which determines the relative amplitude of both sides. These differ from the corresponding parameters, the contact interaction strength and the momentum matrix element, which appear when theoretical models are fitted to experimental ER data.² This suggests that the comparison of ER spectra with other types of optical spectra can yield information not directly obtainable from either spectrum alone.

To compare Eq. (3) to experiment, we have measured $\Delta\epsilon$ by ER and ϵ by ellipsometry for the E_1 and $E_1 + \Delta_1$ transitions of the same 0.18- Ω -cm n -type Ge crystal. These transitions lie in a convenient energy range and involve nondegenerate and nearly parabolic energy bands.^{2,12-14} All measurements were made at room temperature. The ellipsometric measurements were made from 1.9 to 2.6 eV on a Syton-polished (100) surface¹⁵ 2 cm in diameter, and the results are shown in Fig. 1(a). Experimental details and a description of the high-resolution automated scanning ellipsometer are given elsewhere.³ Data were taken in 5-meV increments with a wavelength resolution of 8 Å. The primary source of noise for $E > 2.05$ eV arose from the 0.01° digital resolution of analyzer and polarizer azimuth angles. This noise could be reduced substantially by averaging adjacent data points where necessary. The calculated first, second, and third derivatives of ϵ —in the form $E^{-2}d^n/dE^n(E^2\epsilon)$ with $n = 1, 2,$ and $3,$ respectively—are shown in Figs. 1(b)–1(d), with experimental uncertainties represented by error bars. The first-derivative curves of Fig. 1(b) strongly resemble line shapes obtained in piezoreflectance, thermoreflectance, and wavelength-derivative spectroscopy, as expected.

The field-induced change $\Delta\epsilon$ was calculated from an ER spectrum also taken on a (100) surface, and the results are shown in Fig. 1(e). A standard surface-barrier electrolyte technique¹⁶ was used, and uniform-field conditions were approximated with depletion bias.¹⁷ These spectra correspond to an electric field strength of 38 kV/

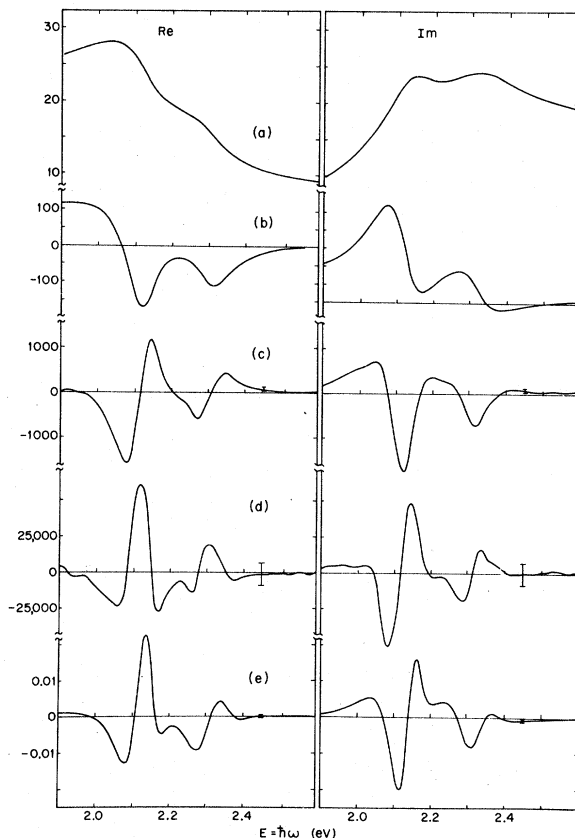


FIG. 1. Real and imaginary parts of (a) ϵ ; (b) $E^{-2} \times (d/dE)(E^2\epsilon)$, in eV^{-1} ; (c) $E^{-2}(d^2/dE^2)(E^2\epsilon)$, in eV^{-2} ; (d) $E^{-2}(d^3/dE^3)(E^2\epsilon)$, in eV^{-3} ; and (e) experimental field-induced change $\Delta\epsilon$ from electroreflectance measurements. Spectra (b)–(d) were evaluated from the experimental ellipsometer data given in (a). Experimental uncertainties are shown for (c), (d), and (e).

cm, well within the low-field limit for these transitions.¹ If Fig. 1(e) is compared with Figs. 1(b)–1(d), it is immediately obvious that the line shapes $\Delta\epsilon$ differ substantially from the first- and second-derivative line shapes of Figs. 1(b) and 1(c), but bear a striking resemblance to the third-derivative curves of Fig. 1(d). There is a one-to-one correspondence of *all* spectral features in the latter case, even extending to the small subsidiary oscillations between the main structures, which is missing completely in Fig. 1(c). We conclude that ER spectra are related to the third derivative of the linear dielectric function, as predicted by theory.

A quantitative comparison of Eq. (3) with experiment was performed by determining μ and $d\Gamma/dE$ from a least-squares fit of a linear combination of the real and imaginary parts of Fig. 1(d) with the imaginary part of Fig. 1(e). The line-

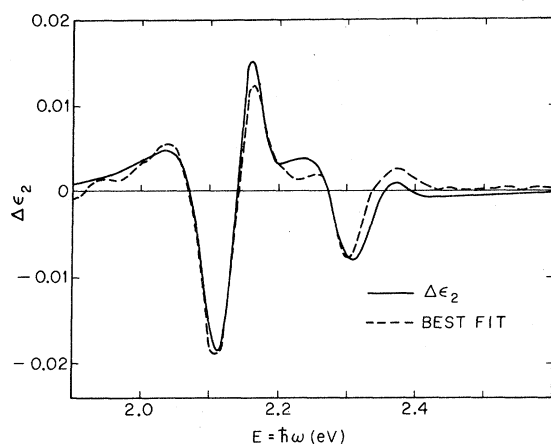


FIG. 2. Best fit of the linear combination of line shapes of Fig. 1(d) (dashed line) with the imaginary-part line shape of Fig. 1(e) (solid line). All energy scales were calibrated against the 5461-Å line of Hg, and no relative shift of energy scales was used in this fit.

shape results are shown in Fig. 2. Despite the assumptions inherent in Eq. (3), the agreement is excellent, being well within the experimental uncertainty. The best least-squares fit was also determined using an arbitrary relative shift of the energy scales as an additional variable, but the only difference was a 2-meV shift of the spectra of Fig. 1(d) to lower energies, which is less than the energy resolution and provides positive verification of the functional energy dependence of Eq. (3). From the fitting parameters and the known value of the $\langle 100 \rangle$ electric field, and its projection angle on the $\langle 111 \rangle$ symmetry axes, we calculated $\mu \cong 0.076m_e$ and $d\Gamma/dE = 0.36$. The value of μ is in good agreement with the theoretical estimate by Dresselhaus and Dresselhaus of $\mu = \mu_t = 0.049m_e$,¹³ which is evidence that the basic theory is quantitatively correct. The value of $d\Gamma/dE$ is larger than the value ~ 0.08 expected from room-temperature estimates¹⁴ of the broadening parameters of the E_1 and $E_1 + \Delta_1$ transitions; this is probably because of the high sensitivity of this parameter to experimental uncertainties through the asymmetry of the line shape. The line-shape differences seen in Fig. 2 are such that $d\Gamma/dE$ would be reduced for the E_1 transition if an individual best fit were made.

A simple physical explanation of the third-derivative behavior can be obtained by noting that, since modulation accounts for one derivative, the real difference between ER and other techniques lies in the appearance of the two extra derivatives. These two derivatives occur because the

electric field interacts by accelerating electrons and holes within one band, and therefore the response must depend directly on the effective mass. The effective mass is given by the second derivative of the band energy with respect to \vec{k} . In the spectral representation, this second derivative can be transformed into two derivatives with respect to E with the resulting appearance of the proportionality constant μ^{-1} as seen in Eqs. (1) and (3). This characteristic dependence of ER upon k -space *gradients* of the band energy is a direct consequence of the symmetry-breaking effect of the perturbation term $-e\vec{\mathcal{E}} \cdot \vec{x}$, which destroys lattice periodicity in the field direction and broadens the density of states.

The above results conclusively link the electric-field-induced change in the dielectric function to the third derivative of the dielectric function, and provide quantitative verification of the perturbation or nonlinear optical approach to ER.¹² The first-, second-, and third-derivative curves of Figs. 1(b), 1(c), and 1(d) clearly define the relationship of ER spectra to first-derivative modulation spectra, and show why ER spectra are sharper and more richly structured than those obtained with other techniques. Since other consequences of the third-derivative nature include better separation of critical points and reduced sensitivity to background effects, this suggests that structure in ER spectra can be related more accurately to the local band-structure properties of specific critical points.¹⁸ The results presented here also demonstrate that the linear dielectric function can be measured sufficiently accurately to permit multiple differentiation; the resulting spectra are suitable for direct comparison with modulation spectra, and the appearance of new scaling parameters indicates that additional information can be obtained by this procedure. Comparison of ER spectra with twice-differentiated first-derivative modulation spectra is also suggested. Finally, we note the interesting possibility of generating fourth- or fifth-derivative spectra by successive differentiation of ER spectra, which may prove useful in the analysis of finer details of critical-point structure.

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Binding to Isoelectronic Impurities in Semiconductors

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The potential produced by isoelectronic impurities is investigated and shown to be critically dependent upon screening. Two methods of calculation of the screened potential are used in this paper, one based on a first-principles wave-function approach and the other using the semiempirical theory of energy bands in semiconductors. The relaxation of the host crystal is also taken into account and shown to be important. The results are in satisfactory agreement with experiment.

Isoelectronic impurities in semiconductors may produce bound states in the forbidden gap,¹ binding a hole (or an electron). Experimental data are now available which suggest that an isoelectronic impurity may bind a hole (electron) only if its electronegativity is smaller (larger) than that of the host atom it replaces. This rule, however, does not indicate which systems will actually have a bound state. It is also found experimentally that only very large atoms (Te and Bi) or very small atoms (N and O) produce bound states (isoelectronic traps). On the theoretical side, the results achieved have been only qualita-

tive^{2,3} and even the binding mechanism is not yet clear. One would like to be able to calculate for a given semiconductor whether a particular isoelectronic substitution will bind a hole (or an electron).

In the present paper we make binding calculations on a model potential for isoelectronic impurities and apply it to the case of isoelectronic donors (i.e., hole traps). The bare impurity potential is assumed to be the difference of atomic pseudopotentials⁴ and is then screened using a dielectric function which reflects the local electron density. The relaxation of the host lattice