High-Resolution Interband-Energy Measurements from Electroreflectance Spectra

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(Received 11 May 1971)

We present a new method for obtaining interband energies to high accuracy from electroreflectance spectra taken under general experimental conditions. The method does not require optical constants or a Kramers-Kronig analysis; hence it is particularly suitable for new materials such as chalcopyrites, binary alloys, and amorphous semiconductors.

It is generally recognized that modulation spectroscopy represents the most accurate method presently available for determining transition energies of interband critical points, being limited by the width of the line shape (typically 100 meV).[1] For many purposes this accuracy has been sufficient. However, recent band-structure calculations, i.e., the dielectric method[2] and improved one-electron techniques,[3] have achieved much higher accuracy. In this Letter we present a new method of obtaining interband transition energies, based on analysis of electroreflectance (ER) spectra, which achieves nearly an order-of-magnitude improvement over the previous technique of assigning the interband transition to the energy of a dominant peak.

Carefully controlled ER measurements have been performed on only a relatively few systems.[4-9] In the great majority of ER experiments it has not been possible to obtain idealized conditions for a variety of reasons. These include experimental difficulties such as obtaining uniform, known fields and square-wave modulation from the flat band or zero-field condition. Other difficulties are intrinsic and involve the electron-hole interaction and a detailed knowledge of the optical constants of the crystal. Nevertheless, experimental ER spectra exhibit a relatively simple line shape which has both positive and negative extrema, where the details (i.e., the subsidiary oscillations of the Franz-Keldysh line shapes) have been averaged out by one or more of the above effects. These experimental line shapes can be approximated quite well by the predictions of a recent perturbation treatment of ER,[10,11] which describes the modulated reflectivity spectra $\Delta R/R$ as

$$\Delta R/R = \mathrm{Re}(Ce^{i\theta}\Delta\epsilon). \qquad (1)$$

The field-induced change in the dielectric function, $\Delta\epsilon$, has the resonant form[10]

$$\Delta\epsilon \sim (E_g - \hbar\omega - i\Gamma)^{-n}, \quad n \geq 2. \qquad (2)$$

The complications mentioned above act mainly to determine the values of C and θ in Eq. (1), which we take to be slowly varying functions of photon energy. For example, we show in Fig. 1 the least-squares fit of Eq. (1) with phase θ, amplitude C, broadening Γ, and energy gap E_g taken as adjustable parameters for $n=3$ for the E_0 transition[12] on a well-characterized ER system: the room-temperature, aqueous electrolyte-Ge interface.[4] Figure 1(a) represents the weak-field limit, where the experimental difficulties mentioned above have negligible ef-

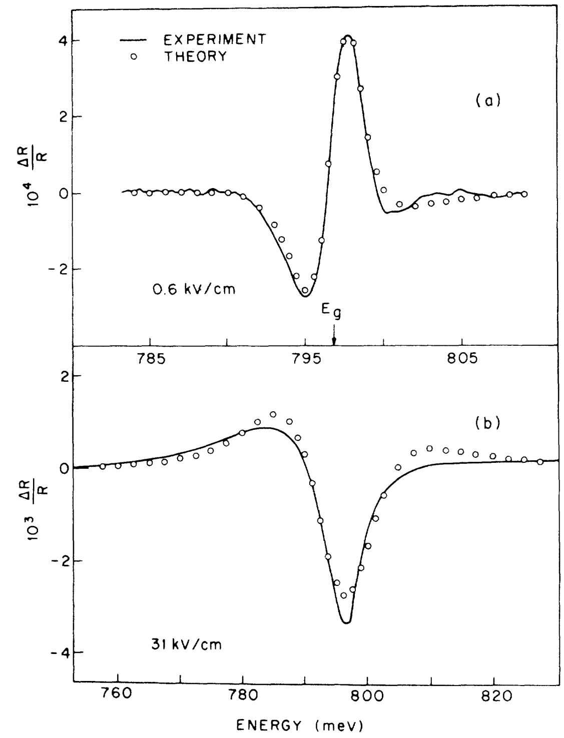

FIG. 1. Least-squares fit of theoretical electroreflectance line shapes to experimental data at the fundamental direct edge of Ge for (a) low and (b) high fields. The values of the surface fields are shown. Note changes in scale between (a) and (b). The energy gap is $E_g = 797 \pm 2$ meV in both cases.

fects. Figure 1(b) represents the same system at very high fields, where field inhomogeneity effects dominate the line shape.[13] The two line shapes represent changes of 154° in the phase θ, a factor of 4 in the broadening Γ, and a factor of 100 in the amplitude C; yet the energy gap E_g differs by less than 3 meV, and the same theoretical line shape $\Delta\epsilon$ fits both spectra reasonably well. This remarkable invariance of E_g is also observed for all intermediate fields: Its value in every case was 797 ± 2 meV in spite of the large changes in the other parameters. This suggests that a least-squares fit of the simple theory of Eq. (2) to ER experimental line shapes is sufficient to determine interband energies to high accuracy.

Since the best-fit parameters depend primarily on the base line and the two dominant peaks, it is expected that a simple three-point fit of theory to experiment will be sufficient to determine E_g. If we define the three-point ratio ρ as

$$\rho = -\Delta R_B/\Delta R_A, \qquad (3)$$

where A and B are the *lower-* and *higher-*energy dominant peaks, respectively, of the $\Delta R/R$ spectrum, then the position of E_g with respect to the energy E_A of peak A is given uniquely in terms of ρ:

$$E_g = E_A + \Delta E f(\rho), \qquad (4)$$

where

$$\Delta E = E_B - E_A. \qquad (5)$$

The scaling parameter $f(\rho)$ is plotted in Fig. 2 for three different values of n in Eq. (2). The value $n = 3$, corresponding to a two-dimensional critical point,[10] is a good description of three-dimensional critical points with large mass ratios[14-16] μ_L/μ_T and fundamental absorption edges modified by the Coulomb interaction.[17] The values $n = 2.0$ and 2.5 describe modulation of discrete excitons and general three-dimensional critical points, respectively.[10,11] Since the curves for all three values of n are nearly the same, it is evident from Fig. 2 that E_g, as determined by the three-point fit, is nearly independent of the physical model chosen to represent the transition. This fundamental requirement of any high-precision method used to determine transition energies is the reason why E_g as determined from Fig. 1 is nearly invariant at both low and high fields.[18]

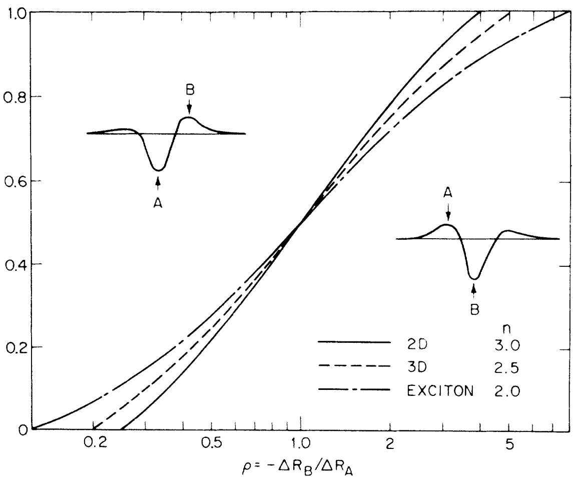

FIG. 2. Three-point scaling parameter $f(\rho)$ as a function of the peak-amplitude ratio ρ for three values of n discussed in the text.

The three-point method should be particularly useful in determining band gaps in new materials such as chalcopyrites, binary semiconductor alloys, layered compounds, amorphous materials, etc., whose optical constants may not be known. We illustrate this point by recalculating the bowing parameter[19] C for the E_1 transition of the binary semiconductor alloy $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ from previously published electrolyte ER data.[20] In Fig. 3, the deviation from linearity of the transition energies E_1, determined by the three-point method and by the previous technique of assignment to the lower-energy peak $E_1(1)$, is plotted as a function of $|x - 0.5|^{1/2}$. By scaling the abscissa in this manner, the expected quadratic deviation appears as two straight-line segments forming a V, as shown, for easy comparison of experiment to theory. It is seen that the three-point transition energies result in significantly less scatter, determining $C = 400 \pm 20$ meV, compared to the previous value of $C = 310 \pm 80$ meV.[21] This more accurate value of C should provide a better test of empirical[2,19] and semiempirical[22] theoretical models of the band structure of semiconductor alloys.

We have demonstrated that highly accurate values of interband transition energies can be obtained from ER data taken under a wide range of experimental conditions. This approach has the particular advantage that a Kramers-Kronig analysis or the optical constants of the material are not required; and, hence, the technique is particularly useful for new materials. These methods can also be used to obtain broadening parameters under similar general experimental conditions. Quantitative spectra, which enable

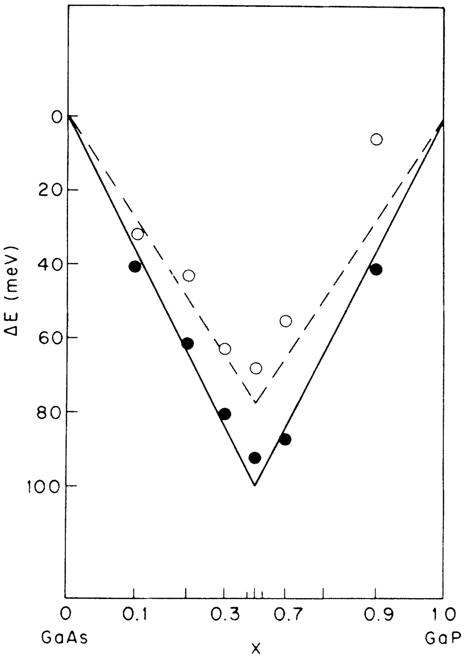

FIG. 3. Deviation from linearity of the E_1 transition energies for the $GaAs_{1-x}P_x$ alloy series as calculated by the three-point method (closed circles) and from the $E_1(1)$ peak (open circles) as used in Ref. (20). The straight lines, determined by a best fit to the data points of the present analysis, correspond to a bowing parameter $C = 400 \pm 20$ meV. The dashed lines represent the bowing parameter $C = 310$ meV determined in Ref. (20).

the phase angle θ to be determined, can be used to obtain in addition the strength of the electron-hole interaction, matrix elements, and critical-point type. These extensions of the theory are the subject of a future publication.

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[18] We have found by direct application to experimental electrolyte ER data for Ge, taken for E_0 and E_1 transitions under a wide range of experimental conditions, that the three-point method determines E_g to within $\pm 0.2\Gamma$, where Γ is the broadening parameter appropriate to the spectrum in question. This uncertainty includes the variation of C and θ with wavelength in Eq. (1).

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