(1970).
[10]A. Amith, S. B. Berger, and P. J. Wojtowicz, U. S. Air Force Cambridge Research Laboratories Report No. 71-0029, 1970 (unpublished).
[11]A. Amith and L. R. Friedman, Phys. Rev. B 2, 434 (1970).
[12]S. von Molnar, IBM J. Res. Develop. 14, 269 (1970).
[13]M. A. Lampert, RCA Rev. 27, 135 (1966).
[14]R. Bartkowski, J. P. Sage, and R. C. LeCraw, J. Appl. Phys. 39, 1071 (1968).
[15]C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Chap. 4.
[16]A. Many and I. Balberg, in *Electronic Structures in Solids*, edited by E. D. Haidemenakis (Plenum, New York, 1969), pp. 385–416.
[17]G. Weinreich, Phys. Rev. 107, 317 (1957).
[18]N. Bloembergen and S. Wang, Phys. Rev. 93, 72 (1954).

Linearized Third-Derivative Spectroscopy with Depletion-Barrier Modulation

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Low-field (third-derivative) electroreflectance spectra taken on fully depleted space-charge regions are shown to be linear in the modulation potential and free from experimentally induced line-shape distortions due to modulation wave-form, dc bias, or barrier-potential effects. Using a metal-semiconductor (Schottky diode) configuration, accurate threshold energies of the E_0' triplet of Ge are obtained. The observed spin-orbit–splitting energy of the valence band confirms that the highest transition also occurs at Γ.

We report that the quadratic scaling dependence of low-field electroreflectance (ER) spectra[1] upon the electric field can be combined with the square-root dependence of the electric field on the barrier potential in a fully depleted space-charge region to yield third-derivative[2] surface-barrier electroreflectance (SBER) spectra which are linear in the modulation *potential*, rather than the electric field, and therefore are rigorously free from modulation wave-form or dc bias effects. In contrast to high-field ER measurements,[3-5] we show that it is *not* necessary to use square-wave flat-band modulation in order to obtain quantitative spectra accurately representing crystal properties when the low-field depletion barrier conditions are satisfied. This result greatly simplifies experimental procedures and enables third-derivative spectroscopy to be extended to a wide range of materials and temperatures for which quantitative ER measurements are not presently feasible. Since these third-derivative spectra are theoretically the sharpest of all modulation spectra, very precise values of transition threshold energies and broadening parameters can be obtained when they are analyzed by previously developed low-field ER techniques.[6]

In a fully depleted space-charge region of a semiconductor, formed by, e.g., a p-n junction,[7] metal-semiconductor barrier,[7] heterojunction,[7] or semiconductor-electrolyte[8] configuration, minority carriers which diffuse from the bulk and/or are thermally or optically excited in the space-charge region are extracted at the surface, so no inversion layer can form. The electric field $\mathcal{E}$ and the potential φ are related at any point in the barrier by Poisson's equation[7]:

$$\mathcal{E}^2(\varphi) = -(2eN_D/\epsilon_0)(\varphi + kT/e), \tag{1}$$

where N_D is the donor impurity concentration and ϵ_0 is the static dielectric constant. At low fields, the field-induced change in the reflectivity, $\Delta R/R$, is a fourth-rank tensor of the form[1,2]

$$\Delta R/R = \mathcal{E}^2 L(\hbar\omega), \tag{2}$$

where the spectral line-shape function $L(\hbar\omega)$ is determined entirely by the energy band structure and its selection rules through the polarization of the incident light and the direction of the electric field. If $\varphi = V(t)$ is a time-dependent potential, the time-dependent part of $\Delta R(t)/R$ is linearly proportional to the time-dependent part of $V(t)$. The spectrum measured experimentally by phase-sensitive detection is therefore

$$(\Delta R/R)_{\text{expt}} = \Delta R_1/R = -(2eN_D V_1/\epsilon_0)L(\hbar\omega), \tag{3}$$

where ΔR_1 and V_1 are the fundamental harmonic components of $\Delta R(t)$ and $V(t)$, respectively. The measured spectrum is completely independent of

dc bias, internal barrier-potential effects, and the harmonic content of $V(t)$, and depends on experimental conditions only through V_1, N_D, and ϵ_0. The electric field need not be separately determined. For depletion regions on p-type semiconductors, $-N_D$ is replaced by $+N_A$, the acceptor impurity concentration, in Eqs. (1) and (3).

Equation (3) is valid if $|V(t)|$ lies between a lower limit determined either by field inhomogeneity effects[9,10] or by the loss of the fully depleted condition, and an upper limit determined by the breakdown of Eq. (2) at high fields. Approximate theoretical expressions for these limits are easily obtained and show that for carrier concentrations $N \sim 10^{16}$ cm^{-3} or less, the allowed range of $V(t)$ for linear response is at least several volts for higher interband transitions (broadening parameter $\Gamma \sim 50$ meV). Third-rank tensorial (linear ER) effects[11] can also invalidate Eq. (3) in compound semiconductors, but these effects can be eliminated by the proper choice of surface orientation and/or polarization of the incident light. We note that the applicability of the technique and the range of $V(t)$ can (and *should*) be determined directly from the modulation data themselves by first establishing the existence of a fully depleted barrier by, e.g., capacitance measurements (which can also be used to determine N),[7] then measuring the dependence of a spectral feature such as an extremum or zero crossing of $(\Delta R/R)_{\text{expt}}$ as a function of dc bias for a fixed ac modulation. The allowed range of $V(t)$ is that range for which negligible variation of the spectral feature is observed. Alternatively, the real-time wave form, $\Delta R(t)/R$, of the spectral feature can be measured for a triangular modulation wave form[4]; the allowed range of $V(t)$ then corresponds to the linear range of $\Delta R(t)/R$.

The above theory was verified by direct application to the E_1 and $E_1+\Delta_1$ transitions of Ge, where linearized third-derivative SBER line shapes could be compared directly to previously published SBER spectra[5] which were obtained with square-wave flat-band modulation. Our measurements were taken on a ⟨100⟩ surface of an 0.18-Ω-cm n-type Ge crystal [$N_D = (1.30 \pm 0.03) \times 10^{16}$ cm^{-3}] using a standard room-temperature electrolyte technique.[12] Capacitance measurements, and the linearity and bias dependence tests, indicated that linearized third-derivative spectra could be taken with any modulation wave form lying in the range $-0.35\ \text{V} > V(t) > -2\ \text{V}$. The third-derivative spectrum, taken with a 0.500 V peak-to-peak square-wave modulation potential at

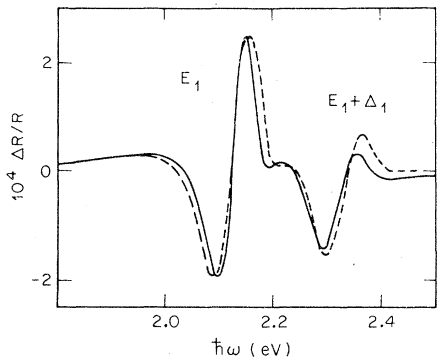

FIG. 1. Linearized third-derivative spectrum of the E_1 and $E_1+\Delta_1$ transitions of Ge (solid line), taken with -0.70 V dc bias and 0.500 V peak-to-peak square-wave modulation. Square-wave flat-band ER spectrum for the same transitions (dashed line), from Ref. 5.

-0.70 V dc bias (surface-field modulating between 42 and 57 kV cm^{-1}) is shown as the solid line in Fig. 1. Identical spectra were obtained from triangular and sinusoidal modulation wave forms with the same fundamental harmonic coefficient V_1, as predicted by the theory. The dashed line is a previously published depletion barrier spectrum taken on a ⟨100⟩ surface of a slightly more heavily doped n-type Ge crystal, using square-wave modulation between flat band and 81 kV cm^{-1}, and has been scaled to bring the positive extremum into coincidence with our results. The agreement between the two spectra provides direct evidence that flat-band modulation is not necessary within the stated conditions. The main differences, a somewhat greater broadening and a discrepancy at the positive peak of the $E_1+\Delta_1$ spectrum, disappear if our surface field is also increased.

We illustrate the capabilities of linearized third-derivative spectroscopy by obtaining threshold and broadening energies of the relatively weak E_0' transitions of Ge, using a Schottky barrier configuration formed by evaporating a 40-Å Ni film on a ⟨100⟩ surface of a Ge crystal of carrier concentration $N_D = 1.49 \times 10^{16}$ cm^{-3}. Sample construction followed the method of Fischer[4] except that the insulating Al_2O_3 layer was omitted. The metal-semiconductor or Schottky barrier configuration is ideal for linearized third-derivative spectroscopy, since it combines the best features of the electrolyte method (direct electrical contact to the space-charge region, elimination of polarization charge buildup at insulating layers with consequent line-shape independence to minority carrier formation and light intensity)

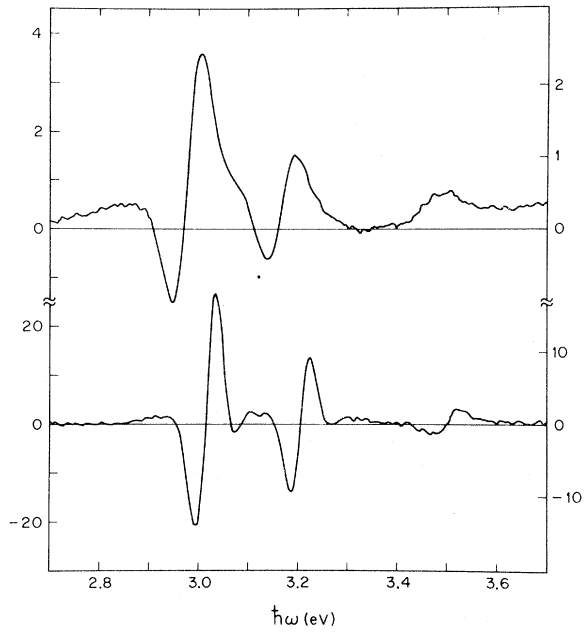

FIG. 2. Linearized third-derivative spectra of the E_0' triplet of Ge at 301°K (top) and 78°K (bottom). Ordinate scales: left, $10^{15}L(\hbar\omega)$, in $cm^2\ V^{-2}$; right, $10^5\Delta R/R$. Note difference of scale factor between top and bottom.

and metal-oxide-semiconductor (MOS) configurations (wide temperature range, general applicability), and eliminates a common sensitivity of both MOS and electrolyte techniques to surface states.

Linearized third-derivative E_0' spectra are shown in Fig. 2. Individual transitions are significantly sharper and better separated than in any previous spectra obtained either by ER[13,14] or first-derivative[15,16] techniques. The 78°K spectrum presents no difficulties due to the well-defined baseline. On the basis of conclusions obtained from E_0 transition spectra,[12] threshold and broadening energies are determined by fitting a two-dimensional low-field line shape[1] to each structure, and the results are shown in Table I. The Seraphin coefficients of the three-phase air-Ni-Ge system (not needed for the threshold and broadening energy analysis[6]) are fortuitously such that the measured line shapes are symmetrical about the baseline, and consequently the same values of E_g would be obtained if a three-dimsional-model line shape were used, although the broadening energies would then be 20% smaller. Estimated uncertainties, obtained from repeating the analysis for a series of such spectra, are also given. The spin-orbit splitting of the conduction bands is determined from these results to be 186 ± 2 meV, as compared with the value 191 ± 5 meV obtained by Fischer.[13,14] A striking demonstration of the resolution obtainable with the third-derivative technique is our ability to measure in addition the spin-orbit splitting of the *valence* bands: Our value of 299 ± 5 meV is in excellent agreement with the value of 295 ± 3 meV previously obtained from the much sharper E_0 and $E_0+\Delta_0$ transitions to the lowest conduction band.[13] This agreement proves conclusively that the previous assignment[13,14] of this structure to the $\Gamma_7^V \rightarrow \Gamma_8^C$ transition is correct.

The room-temperature spectrum contains the broad underlying structure which dominates first-derivative spectra and is attributed to transitions along Δ.[15-17] The values shown in Table I were obtained by assuming that the E_0' structures were symmetric about this background. The threshold energy of the $\Gamma_{8V}^V \rightarrow \Gamma_7^C$ transition, 2.983 ± 0.004 eV, is substantially larger than the value, 2.92 ± 0.05 eV, obtained from photoemission experiments.[14] Consequently, our measured energy shift with temperature, 32 ± 5 meV, is much less than either the value of 84 meV obtained for the E_0 transition[12,13] or the value of 80 meV previously attributed to this transition,[14] and is more consistent with the relative magnitude of the known

TABLE I. Threshold energies E_g, broadening energies Γ, and temperature shifts ΔE_g, for the E_0' triplet in Ge. All numbers are in meV, and were obtained from a two-dimensional model as explained in the text. The symmetry notation corresponds to that of Ref. 16.

Transition	E_g 78°K	E_g 301°K	Γ 78°K	Γ 301°K	ΔE_g (78–301°K)
$\Gamma_{8V}^V \rightarrow \Gamma_7^C$	3015 ± 1	2983 ± 4	41 ± 1	66 ± 2	−32 ± 5
$\Gamma_{8V}^V \rightarrow \Gamma_8^C$	3201 ± 1	3169 ± 4	40 ± 1	64 ± 2	−32 ± 5
$\Gamma_7^V \rightarrow \Gamma_8^C$	3500 ± 4	3470 ± 30	61 ± 5	100 ± 5	(−30?)

pressure shifts of these transitions.[18]

In conclusion, we have shown that quantitative low-field (third-derivative) ER spectra are easily obtainable on fully depleted space-charge regions, with the metal-semiconductor configuration being particularly attractive. This technique should be extremely useful for studying higher interband transitions for a wide range of materials and temperatures. The independence of these spectra to variations of barrier height with surface orientation makes it particularly attractive for the recently proposed signature analysis technique.[19] In addition, since the value of the electric field plays a relatively minor role, linearized third-derivative spectroscopy is remarkably similar to wavelength modulation[15,16] except that third-derivative, rather than first-derivative, spectra can be obtained directly. This suggests that linearized third-derivative spectroscopy will also be useful in studying the effect of secondary perturbations such as stress and hydrostatic pressure.

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[1]D. E. Aspnes and J. E. Rowe, Solid State Commun. 8, 1145 (1970).

[2]D. E. Aspnes and J. E. Row, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U. S. AEC Division of Technical Information, Springfield, Va., 1970), p. 422; D. E. Aspnes, Phys. Rev. Lett. 28, 168 (1972); D. E. Aspnes and J. E. Rowe, Phys. Rev. B (to be published).

[3]B. O. Seraphin, in *Physics of Semiconductors: Proceedings of the Seventh International Conference,* edited by M. Hulin (Academic, New York, 1964), p. 165; M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967); R. A. Forman, D. E. Aspnes, and M. Cardona, J. Phys. Chem. Solids 31, 227 (1970); Y. Hamakawa, P. Handler, and F. Germano, Phys. Rev. 166, 709 (1968); A. Frova and D. E. Aspnes, Phys. Rev. 182, 795 (1969); B. O. Seraphin, Surface Sci. 13, 136 (1969).

[4]J. E. Fischer, Rev. Sci. Instrum. 42, 872 (1971).

[5]S. Koeppen, P. Handler, and S. Jasperson, Phys. Rev. Lett. 27, 265, 1250(E) (1971).

[6]J. E. Rowe and D. E. Aspnes, Phys. Rev. Lett. 25, 162, 979(E) (1970); D. E. Aspnes and J. E. Rowe, Phys. Rev. Lett. 27, 188 (1971); D. E. Aspnes and J. E. Rowe, Bull. Amer. Phys. Soc. 16, 396 (1971).

[7]See, for instance, S. M. Sze, *Physics of Semiconductor Devices* (Interscience, New York, 1969).

[8]See, for instance, V. A. Myamlin and Yu. V. Pleskov, *Electrochemistry of Semiconductors* (Plenum, New York, 1967).

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

[10]S. Koeppen and P. Handler, Phys. Rev. 187, 1182 (1969). Note that for fully depleted space-charge regions, the curves given in Fig. 1 of this reference would continue to decrease monotonically with increasing potential, having no minimum or corresponding "optimum field" value.

[11]D. S. Kyser and V. Rehn, Solid State Commun. 8, 1439 (1970); E. Mohler, Phys. Status Solidi 38, 81 (1970).

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

[13]J. E. Fischer, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U. S. AEC Division of Technical Information, Springfield, Va., 1970), p. 427.

[14]T. M. Donovan, J. E. Fischer, J. Matsuzaki, and W. E. Spicer, Phys. Rev. B 3, 4292 (1971).

[15]R. L. Zucca and Y. R. Shen, Phys. Rev. B 1, 2668 (1970).

[16]D. D. Sell and E. O. Kane, Phys. Rev. B 5, 417 (1972).

[17]J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969); R. N. Cahn and M. L. Cohen, Phys. Rev. B 1, 2569 (1970).

[18]W. Paul, J. Appl. Phys. 32, 2082 (1961); E. Schmidt and K. Vedam, Solid State Commun. 9, 1187 (1971).

[19]B. O. Seraphin, in *Optical Properties of Solids,* edited by E. Haidemenakis (Gordon and Breach, New York, 1970), p. 213; N. Bottka and J. E. Fischer, Phys. Rev. B 3, 2514 (1971).