

Combined Investigation of Nonuniform-Field Electroreflectance and Surface Galvanomagnetic Properties in Germanium

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"Dry" electroreflectance (ER) spectra have been taken near the fundamental edge of intrinsic germanium for comparison with the theory of the Franz-Keldysh effect in nonuniform electric fields. The theory presented by Aspnes and Frova in a previous paper applies quite generally to one-dimensional inhomogeneities induced by any kind of nonuniform perturbation in a medium, and shows that the inhomogeneity causes a mixing of the real and imaginary parts of the dielectric function which results in changes in the line shapes of optical spectra. Typical nonuniform perturbations are space-charge or depletion-region electric fields (which occur in p - n junctions or surface electro-optic effects), gradients in carrier density (such as in photo-reflectance experiments), or gradients in stress, impurity concentration, temperature, etc. For the specific case of surface-barrier ER in an intrinsic semiconductor, the field nonuniformity increases with increasing magnitude of the surface electric field. ER spectra therefore depend drastically on this magnitude and provide a convenient test of the validity of the nonuniform-field theory. The results presented here, obtained with square-wave zero-to-peak modulation, clearly demonstrate that the theory describes the main features of ER in semiconductors. As an example, the measured crossover of the heights of the first and third ER peaks is found to occur almost at the predicted value of the field. The quantitative comparison of theory and experiment requires an accurate measurement of the value of the surface field as a function of electrode voltage. This has been done by performing combined measurements of field-effect-induced changes in the Hall coefficient and conductivity of the sample. Use of the Hall-coefficient data enables the surface mobility to be obtained directly from experiment, so that the excess carrier concentration, and therefore the surface potential and field, can be determined without making assumptions as to the value of the surface mobility. From these data, it has also been possible to obtain information about the nature of the scattering mechanisms which determine the surface mobility. A number of other observations are presented and discussed.

1. INTRODUCTION

THE electro-optic or Franz-Keldysh effect¹ has been used to obtain a great amount of information about solids, such as location and type of critical points in the energy-band structure, effective masses, etc.²⁻⁶ However, the electroreflectance (ER) spectra of semiconductors²⁻⁶ have characteristic line shapes which cannot be accounted for by the one-electron uniform-field theory. In general, satellite oscillations are missing, and the main peaks vary their magnitude, position, and width in a way which is quite different from theoretical predictions. Some authors have pointed out that other effects, such as the Coulomb interaction^{3,5} and collision broadening,² are present and should be properly included in the theory. Several people have also stressed the fact that the field is strongly nonuniform near the surface of a semiconduc-

tor, and Cardona *et al.*³ have suggested that one could treat the problem with the uniform-field theory, provided some suitable average of the ER response is taken over the nonuniform field in the region of penetration of the light.

In order to describe the effect of nonuniform fields, Evangelisti and Frova⁶ calculated a simple weighted average of $\Delta R/R$ for surface-barrier ER at the fundamental direct edge of intrinsic Ge (where collision broadening is relatively unimportant) and compared this with experimental measurements. Although it was easily demonstrated that some of the features observed in the experiment were an obvious consequence of averaging (e.g., the washing out of satellite oscillations by interference), the simple average failed to account for the presence of an unexpectedly large positive peak in the measured ER spectrum below the direct edge, a peak which could not be even qualitatively described by including collision broadening and Coulomb effects in the one-electron theory. Nevertheless, it was shown that the determination of the effective mass from ER spectra is bound to be largely in error in nonuniform fields, and that one should be very careful in trying to get information about fine structure at critical points. Recently, Aspnes and Frova⁷ have proposed a more

¹ See, e.g., D. E. Aspnes, P. Handler, and D. F. Blossey, *Phys. Rev.* **167**, 997 (1968), and references therein.

² B. O. Seraphin, R. B. Hess, and N. Bottka, *J. Appl. Phys.* **36**, 2242 (1965).

³ M. Cardona, K. L. Shaklee, and F. H. Pollak, *Phys. Rev.* **154**, 696 (1967).

⁴ A. K. Ghosh, *Phys. Rev.* **165**, 888 (1968).

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

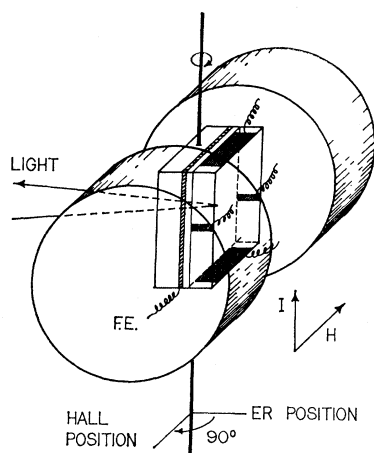


FIG. 1. Sample arrangement. Field-effect package can be rotated 90° for Hall-effect measurements.

accurate averaging procedure, based on an approximate solution of Maxwell's equations for inhomogeneous media, which is valid for any kind of perturbation nonuniform in one dimension. The results, applied to surface-barrier ER at the direct edge in intrinsic Ge, appeared to be in good agreement with the best data available⁶ and, most of all, accounted for the above-mentioned positive peak below the gap in terms of an apparent mixing of the real and imaginary parts of the change of the dielectric function. This mixing effect, not previously recognized, appeared to be of great importance in determining the line shape of spectra obtained through the use of nonuniform perturbations. However, no ER data of sufficient accuracy at the fundamental direct edge were available to allow a direct comparison theory and experiment in this particular case.

The present work was undertaken in order to provide the accurate data needed. These data have to meet the following conditions: (i) The modulation must be *square wave*, to avoid time-averaging effects in the nonlinear ER response; (ii) the modulating field must oscillate between zero and a maximum value; (iii) most importantly, the surface field must be *accurately* known. Previous data^{2,5} at the Ge fundamental edge failed to meet these criteria, especially with respect to the third condition. Evangelisti and Frova⁶ attempted to satisfy the third condition by monitoring the changes in surface conductance produced by the modulating field in a "dry" field-effect system. The determination of the field by this method required assumptions about the mobility of the carriers in the surface region, which is known to be greatly reduced because of additional scattering. If the mobility were known, the surface carrier concentration and thus the surface field could be determined.^{8,9} We have overcome this difficulty by

⁸ R. H. Kingston and S. F. Neustadter, J. Appl. Phys. **26**, 718 (1955).

⁹ C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).

taking combined surface Hall effect and conductance measurements, which enable both carrier mobility and concentration to be directly obtained. ER data have been taken at room temperature in a number of ways, by square-wave modulation and by sine-wave modulation (first and second harmonic), for a wide range of values of the surface electric field, but always requiring that the field vary between zero and its peak value in accordance with condition ii. The results have confirmed that the nonuniform-field theory⁷ accurately describes ER spectra line shapes.

In Sec. 2, a description of the sample preparation and of the experimental method is given. Section 3 gives an account of the galvanomagnetic measurements and the procedure used to determine the surface field and carrier mobility. The results are compared with Schrieffer's theory of the effective surface reduced mobility in terms of random scattering. Effects of hole trapping, resulting in "inverted sign" field-effect mobility, are also discussed. In Sec. 4, a number of ER spectra are shown and a comparison of the experimental peak magnitudes and positions with those expected from the nonuniform-field theory is made. Finally, in the last section, all the results are summarized, with emphasis added to some of the most interesting features observed in the course of the experiment.

2. EXPERIMENT

The experimental apparatus is similar to that described in a number of papers on modulation spectroscopy (see, e.g., Ref. 10). The monochromator was a double-grating Hilger and Watts Model D330/331, the source a Sylvania 1000-W tungsten filament lamp, and the detector a PbS Infracron photoresistor. Samples were cut from a $42\text{-}\Omega\text{ cm}$ (nearly intrinsic) *n*-type germanium crystal and were approximately 20 mm long, 5 mm wide, and 1 mm thick. The face exposed to the incident monochromatic beam was cut along a (111) plane. The surface was mechanically polished to be of good optical quality and then electropolished on soft cloth to remove all damage. Care was taken to have a perfectly flat surface over the entire sample. This was achieved by polishing five closely packed samples and then discarding the outer four. The back surface was left coarse. A modulating electric field of about 100 Hz was applied to the surface by means of a "dry" field-effect package, made by cementing a $12\text{-}\mu$ Mylar film spacer between the germanium sample and a quartz platelet whose inside face had been previously coated with a film of conducting SnO_2 to serve as a transparent electrode. A nearly liquid epoxy resin was used to form the bond, and the various pieces were firmly pressed together while the epoxy was hardening. We believe that the field was reasonably uniform over the whole surface of the sample in the above arrangement, at least in the medium to high-field range. Electrical contacts to the

¹⁰ A. Frova and P. J. Boddy, Phys. Rev. **153**, 606 (1967).

Ge crystal were made to form the field-effect system shown in Fig. 1. The four terminals, soldered by antimony-doped tin, were used for dc and ac (i.e., field-effect-modulated) conductivity and Hall-effect measurements. When the ac Hall voltage was measured, one of the end terminals was grounded; for ac conductivity measurements, one of the Hall terminals was grounded. This, along with the use of differential electronics, allowed automatic cancellation of displacement signals by symmetry and direct display of conductivity and Hall signals versus field-effect voltage on an oscilloscope.¹¹ ER spectra were taken for a number of values of the peak field-effect voltage, both square-wave and sine-wave, along with pictures of the corresponding conductivity curves. After the optical measurements were completed, the sample, located inside the gap of a magnet, was rotated 90° to allow measurement of the Hall effect.

3. TRANSPORT RESULTS AND DISCUSSION

Typical room-temperature field-effect-modulated conductance (per unit area) $\Delta\sigma_{\square}$ and Hall-coefficient ΔR_H results are shown in Fig. 2, for a sinusoidal voltage sweep extending over the entire voltage range used in the experiment. The curves, as they actually appear on the oscilloscope, exhibit a small hysteresis loop owing to competition between generation and recombination of surface carriers. The existence of such a loop in the $\Delta\sigma_{\square}$ curve has been observed in the past and is well understood¹²; the data in Fig. 2 represent an average of the two sides of the loop. A second remark, of greater importance in the discussion of our results, is that both

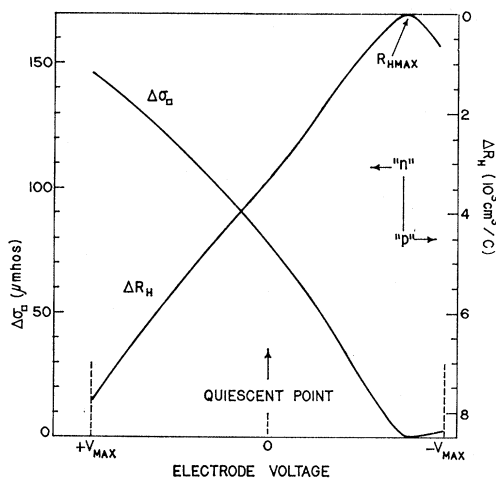


FIG. 2. Oscillographic trace of the excess surface conductance $\Delta\sigma_{\square}$ and Hall effect ΔR_H versus sinusoidal modulating voltage applied to the field-effect electrode. The amplitude was adjusted to scan the entire voltage range used in the ER measurements.

¹¹ A. Balzarotti, G. Chiarotti, and A. Frova, *Nuovo Cimento* **26**, 1205 (1962).

¹² H. C. Montgomery and W. L. Brown, *Phys. Rev.* **103**, 865 (1956); D. R. Frankl, *J. Electrochem. Soc.* **109**, 608 (1962).

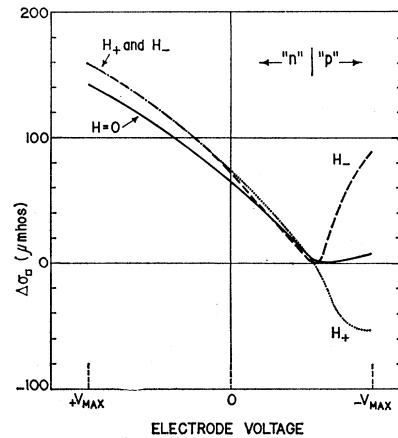


FIG. 3. Excess surface conductance $\Delta\sigma_{\square}$ for zero magnetic field, and for magnetic field applied parallel to the sample surface, with the two possible orientations. H_+ stands for field that deflects a net positive charge towards the front surface.

$\Delta\sigma_{\square}$ and ΔR_H show that the surface is driven only slightly into the p -type region. In fact, for *any* peak-to-peak value of the ac voltage, the $\Delta\sigma_{\square}$ curve relaxes and adjusts itself to reach its minimum when the voltage at the electrode is close to its peak negative value. ΔR_H behaves in a similar way. This relaxation occurs in a time of the order of seconds and can be attributed to the presence of a large density of surface traps for holes which capture carriers as soon as they are created and release them at a slower rate. At the frequency of operation, this effect causes a net storage of positive charge in the surface states and pushes the quiescent point (see Fig. 2) farther into the n region. This behavior, already observed in the past,¹³ was common to all samples prepared by the treatment described above and offered a unique advantage in that it allowed zero-to-peak-field ER measurements without the need to set dc bias, thus automatically satisfying the second condition.

The presence of hole-trapping effects is confirmed by the occurrence of another effect, observed with the magnetic field parallel to the sample surface. Figure 3 illustrates $\Delta\sigma_{\square}$ versus applied voltage for the two possible orientations of the magnetic field, and also for zero field. In this configuration, the Hall voltage is developed between the front and the back surface. The curve labeled H_+ corresponds to the case when a net positive charge is deflected towards the surface facing the transparent electrode. When the electric field is such as to attract holes towards this surface, where they become trapped, there is a net subtraction of carriers from the conduction process. This results in a negative $\Delta\sigma_{\square}$ and the over-all conductivity of the sample drops below its bulk value. The opposite is true when the magnetic field is reversed. On the n side there is no

¹³ G. Dorda, *Phys. Status Solidi* **3**, 1318 (1963); **5**, 107 (19 5); G. Dorda and S. Koch, in *Solid Surfaces*, edited by H. C. Gatos (North-Holland Publishing Co., Amsterdam, 1964), p. 120.

difference between H_+ and H_- because in our case electron trapping is much weaker than hole trapping. The difference between $\Delta\sigma_\square$ with and without magnetic field here is entirely due to magnetoresistance. "Inverted-sign" field-effect mobility $\mu_{FE} = -d\Delta\sigma_\square/dQ_\square$ (with Q_\square = net induced charge per unit area) has been observed in silicon metal-oxide-semiconductor (MOS) structures.¹⁴ In that case, the effect was attributed to a process of repopulation between isoenergetic minima split by the intense electric field. We believe, however, that the trapping-induced inverted-sign mobility described here is a new effect and may deserve further investigation. Its theoretical treatment could be given directly in the framework developed by Greene¹⁵ for the physical description of Fuch's specular reflectivity parameter p (the parameter describing the degree of specular reflection of carriers scattered from a surface, used as an empirical constant in Schrieffer's¹⁶ initial and other later¹⁷ treatments of surface mobility) by relaxing the restriction that all carriers impinging on a surface must be scattered back into conducting states. This carrier-conservation requirement appears to have been included in all theoretical treatments of surface mobility to date. We will restrict all experimental interpretation to n -type surface regions where this effect is not important.

Let us show that the surface field \mathcal{E}_s can be directly determined from the experimental data of Fig. 2. From general surface transport theory,^{18,19} one can derive expressions for the changes in sample conductance and Hall coefficient due to an excess of surface carriers. Hall measurements¹⁹ have shown that, at least for n -type

surfaces, the light hole contribution can be neglected. Taking the experimentally determined bulk values σ_B for σ at the minimum of $\Delta\sigma_\square$ in Fig. 2, and R_{HB} for R_H at the maximum of ΔR_H ,^{18,19} a two-carrier intrinsic model gives

$$\Delta\sigma_\square = e(\Delta n_\square \mu_{ns} + \Delta p_\square \mu_{ps}), \quad (1)$$

$$\Delta R_H = R_{HB} \left(\frac{\sigma_B^2}{\sigma^2} - 1 \right) - \frac{3\pi e}{8 \sigma^2 d} (\Delta n_\square \mu_{ns}^2 - \Delta p_\square \mu_{ps}^2), \quad (2)$$

where Δn_\square and Δp_\square are the surface excess concentrations of electrons and heavy holes per unit area, d is the sample thickness, e the electron charge, and μ_{ns} , μ_{ps} the surface mobilities. As far as our experiment is concerned, we may neglect the terms coming from holes altogether in Eqs. (1) and (2), since the surface is well on the n side (at the lowest applied fields this assumption may lead to some error). In this case, there are only two unknowns in the system of two equations and one has

$$\mu_{ns} = \Delta\sigma_\square / e\Delta n_\square \quad (3)$$

and

$$\Delta n_\square = \frac{8}{3\pi ed} \frac{\Delta\sigma_\square}{(R_{HB}\sigma_B^2 - R_H\sigma^2)} \quad (4)$$

if $|\Delta p_\square| \ll |\Delta n_\square|$. By means of Poisson's equation,⁸ the reduced surface potential $u_s = e\Phi_s/kT$ and the surface field \mathcal{E}_s can be calculated from Δn_\square through the equations

$$u_s = 2 \ln(1 + \Delta n_\square / 2n_i L_D), \quad (5)$$

$$\mathcal{E}_s = (2kT/eL_D) \sinh \frac{1}{2} u_s, \quad (6)$$

which are valid for intrinsic material. In Eqs. (5) and (6), L_D is the Debye length, and n_i is the intrinsic carrier concentration equal to $2.3 \times 10^{13} \text{ cm}^{-3}$ at room temperature (RT). In principle, if μ_{ns} were known, e.g., from theory, one could determine the field from $\Delta\sigma_\square$ alone. This approach was taken in an earlier paper,⁶ but it depends on the assumption that one can exactly predict what kind of mechanism is responsible for the scattering of surface carriers. The random scattering model, first discussed by Schrieffer¹⁶ and later expanded by other authors,¹⁷ may not describe in full what is going on near the surface. Our present approach, therefore, not only allows direct evaluation of the surface field without drastic assumptions, but also provides an experimental determination of the reduced surface mobility of electrons, given by Eq. (3).

Figure 4 shows the surface potential u_s and field \mathcal{E}_s , given by Eqs. (5) and (6), determined as a function of $\Delta\sigma_\square$ from experimental data. Also shown (dashed curve) is the surface field which would have been obtained by Eq. (1) alone, assuming Schrieffer's mobilities.¹⁶ It is seen that the difference between the two methods is not large within the entire range of fields. It is worthwhile to show a direct plot of μ_{ns} versus u_s . From Eqs. (3)–(5) one finds the results shown

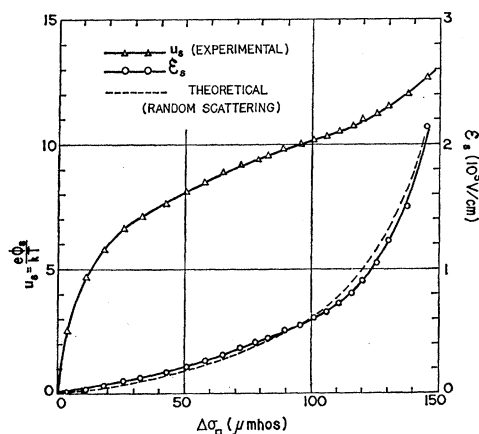


FIG. 4. Surface field \mathcal{E}_s versus excess surface conductance $\Delta\sigma_\square$ as obtained by combined field-effect Hall and conductance measurements (solid curve) and by the use of the theoretical random scattering mobility (see Ref. 16) (dashed curve). Also shown is the experimental reduced surface potential u_s .

¹⁴ F. F. Fang and W. E. Howard, Phys. Rev. Letters **16**, 797 (1966).

¹⁵ R. F. Greene, Phys. Rev. **141**, 687 (1966); **141**, 690 (1966).

¹⁶ J. R. Schrieffer, Phys. Rev. **97**, 641 (1965).

¹⁷ Y. Goldstein, N. B. Grover, A. Many, and R. F. Greene, J. Appl. Phys. **32**, 2540 (1961), and references therein.

¹⁸ R. L. Petritz, Phys. Rev. **110**, 1254 (1958).

¹⁹ J. N. Zemel and R. L. Petritz, Phys. Rev. **110**, 1263 (1958).

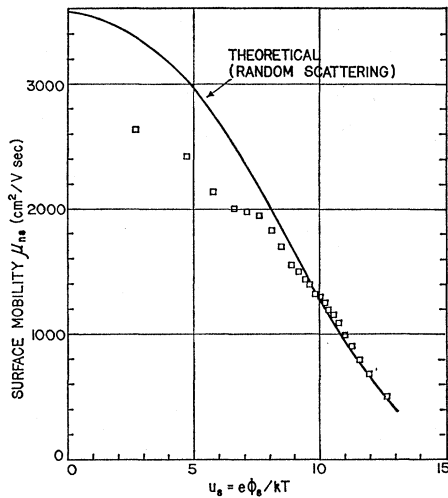


FIG. 5. Comparison between the experimental and theoretical effective mobility of surface electrons versus surface reduced potential u_s .

in Fig. 5. Comparison with Schrieffer's curve¹⁶ indicates that the carriers in the surface region must undergo some other scattering process than just random collisions against the surface.²⁰ We suggest that surface electrons are additively scattered by positively charged impurities, a feature which is again consistent with the existence of a large concentration of hole traps at the surface. The presence of this second scattering mechanism is very evident at low fields where Schrieffer's model predicts little or no mobility reduction. At very high band bending at the surface, instead, random scattering becomes so strong to be completely dominant and to entirely account for the experimental results.

The above considerations indicate that the data shown in Figs. 4 and 5 may not be general, but rather apply to a particular sample and sample treatment. In other words, simultaneous measurements of $\Delta\sigma_{\square}$ and

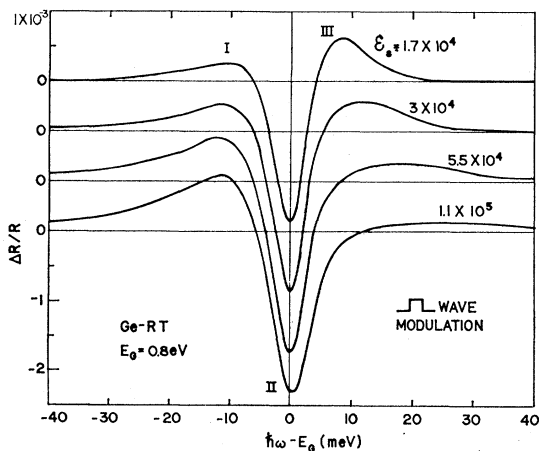


FIG. 6. Square-wave ER spectra for a number of values of the surface field ϵ_s (given in V/cm). During a cycle, ϵ_s varies between zero and peak. ΔR is defined as reflectance at peak field minus reflectance without field. (RT=room temperature.)

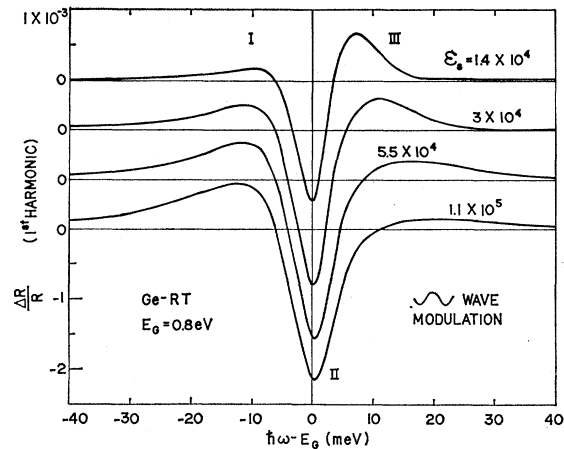


FIG. 7. Sine-wave zero-to-peak ER spectra (first harmonic).

ΔR_H will always be needed to determine surface fields exactly in any given sample. Once these quantities have been measured for all values of surface potential, the knowledge of $\Delta\sigma_{\square}$ alone will give the field (as in Fig. 4), provided the sample behavior does not change in time. Since we have found complete reproducibility of data, both transport and optical, from day to day, we have followed this procedure and have avoided repeating Hall measurements for every ER spectrum. We have already discussed this point in Sec. 2.

4. ELECTROREFLECTANCE RESULTS AND DISCUSSION

Figures 6 and 7 show the relative change in reflectance $\Delta R/R$ near the direct threshold for a number of surface electric fields at room temperature. The figures correspond, respectively, to square-wave modulation (i.e., on-off spectra) and first-harmonic sine-wave modulation. It is seen that the difference between sine-wave and square-wave modulation is not very large, although time-integration effects should be present in the former case, as discussed in Ref. 7. However, the field is sufficiently nonuniform in our system²¹ so as to completely control the line shape of our spectra. For sine-wave modulation, the presence of a second harmonic, down a factor 3 or 4, was observed, as shown in Fig. 8. It should be noted that the second-harmonic spectra resemble closely the energy derivative of the first harmonic. This is particularly true for low fields, as illustrated in

²⁰ For intrinsic materials ($u_B=0$) the surface mobility cusp which appears in the earlier theoretical treatments (see Refs. 16 and 19) is of minor consequence. The explicit consideration of the \hbar dependence of the reflectivity (parameter¹⁶ ρ) does not significantly affect the theoretical mobility in our case, and the Schrieffer results apply.

²¹ The field decays below the surface as

$$\mathcal{E}(z) = \frac{(1-A^2) \exp[-(z_s-z)/L_D]}{1-A^2 \exp[-2(z_s-z)/L_D]} \mathcal{E}_s,$$

where $A = \tanh \frac{1}{2} u_s$. This decay, for large u_s , is very steep, as illustrated by Fig. 2 of Ref. 6.

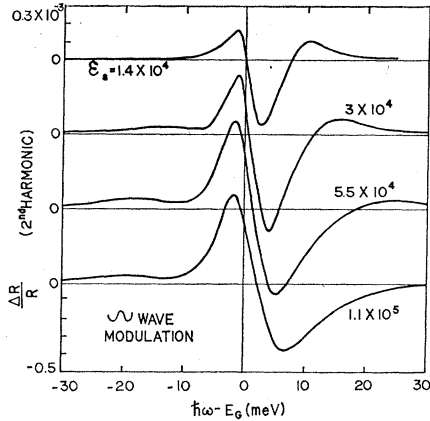


FIG. 8. Sine-wave zero-to-peak ER spectra (second harmonic).

Fig. 9. The physical meaning of the above similarity between field derivatives and energy derivatives of the reflectivity is that the average Franz-Keldysh effect due to nonuniform fields appears to be describable in terms of an “effective-energy-gap shift” towards lower energies. Figure 9 shows that this argument may not apply at some distance below the gap.

Before we proceed to a more detailed comparison with theory, let us briefly comment upon the square-wave data of Fig. 6. The curves shown are among the most representative of the many taken. There is complete reproducibility in any single sample from run to run and very good reproducibility among different samples. The absolute value on the ordinate was carefully checked and corresponds to peak-to-peak values of the difference: R with field minus R without field. The line shape of the spectra presents a number of characteristic deviations from the Franz-Keldysh original theory, which have already been pointed out.⁶ For the sake of understanding, we will briefly recall these features here: (i) Peak I below the gap shows an anomalously large increase with field. (ii) Peak II, the main structure of ER, should increase at least as the $\frac{1}{3}$ power of the field (exactly as the $\frac{1}{3}$ power in the absence of Coulomb effects and collision broadening), but it does

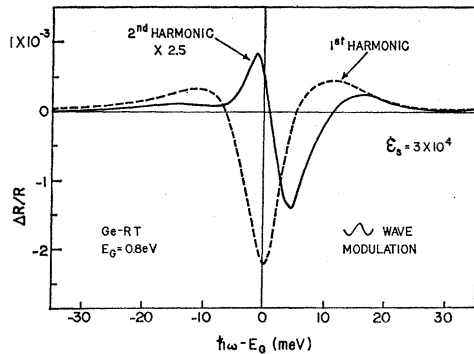


FIG. 9. Comparison between first- and second-harmonic spectra of sine-wave ER for a particular value of the field.

not vary appreciably and its width increases too slowly with field. (iii) Peak III diminishes and tends to vanish at high fields. (iv) The characteristic satellite oscillations above E_G are totally missing. All these features are qualitatively accounted for by the nonuniform-field theory.⁷

The reflectance coefficient of a solid, upon application of a nonuniform perturbation in the region below the surface, is changed by an amount⁷

$$\Delta R/R = \alpha \langle \Delta \epsilon_1 \rangle + \beta \langle \Delta \epsilon_2 \rangle, \quad (7)$$

where

$$\langle \Delta \epsilon \rangle = \langle \Delta \epsilon_1 \rangle + i \langle \Delta \epsilon_2 \rangle$$

$$= -2iK e^{2iKz_s} \int_{-\infty}^{z_s} \Delta \epsilon(z') e^{-2iKz'} dz'. \quad (8)$$

In Eqs. (7) and (8), $\Delta \epsilon$ is the uniform-perturbation change in the dielectric function, α and β are the Seraphin coefficients,²² K is the propagation constant, and z_s is the surface coordinate. When the perturbation is an electric field, neglecting exciton and broadening effects, the change $\Delta \epsilon$ near the gap can be described by $G+iP$, the complex electro-optic function,²³ and the integral in Eq. (8) can be evaluated numerically. If this is done for a number of values of the surface electric field \mathcal{E}_s , using the light-hole effective mass and the field profile given in Ref. 6, which is characteristic of the

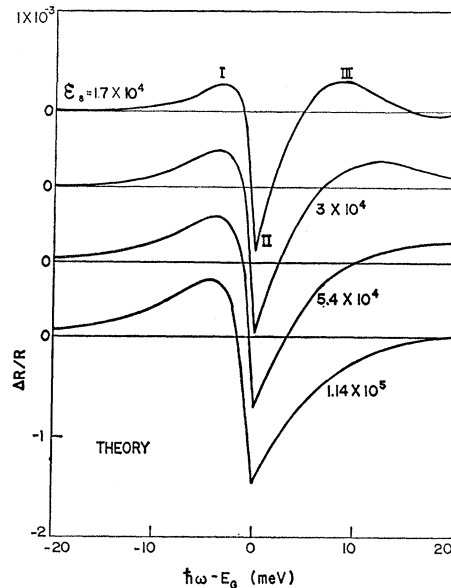


FIG. 10. Calculated ER from the theory of nonuniform-field Franz-Keldysh effect (Ref. 7), for nearly the same values of the electric field shown in Fig. 6. In this instance, the field nonuniformity increases rapidly for increasing values of \mathcal{E}_s . The sharpness of peak II is due to not having included a collision-broadening parameter into the theoretical equations. Exciton effects are also neglected.

²² B. O. Seraphin and N. Bottka, Phys. Rev. 145, 628 (1966).
²³ D. E. Aspnes, Phys. Rev. 153, 972 (1967).

surface space-charge region of an intrinsic semiconductor, one obtains the curves shown in Fig. 10, which contain all the experimental features discussed above. It should be emphasized that the inclusion of collision broadening effects would round off peak II and move it away from I and closer to III. We shall now attempt a more quantitative comparison between theory and experiment.

In Figs. 11 and 12 we have plotted the height and the energy position of the three significant peaks of the ER spectra. The dashed curves are theoretical. The agreement in Fig. 11 is very good in view of the number of approximations inherent to the theory used to describe the electro-optic effect. It should be stressed that the crossover of peaks I and III is a feature which is unique to the inhomogeneous perturbation model, as it can only be obtained by mixing $\Delta\epsilon_2$ and $\Delta\epsilon_1$, and is of basic importance to confirm its validity. In particular, the experimental data cross at 3×10^4 and the theoretical curves at 2×10^4 V/cm, in excellent agreement. It should also be stressed that the asymptotic behavior of all peaks is close to theory, the disagreement being largest at the lowest fields. We have already mentioned in Sec. 3 that there may be some experimental uncertainty, as well as fluctuations along the surface, in the low fields. Some of the approximations in the theory may also be of more drastic nature in the limit of low surface fields, where the sample field should be more nearly uniform.²¹ We also find qualitative agreement between theory and experiment as to the position of the three

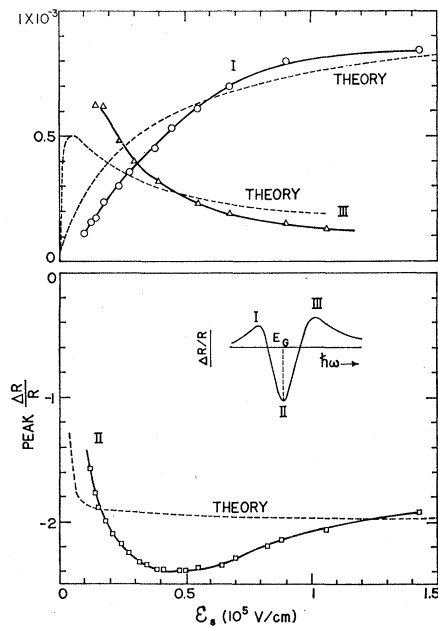


FIG. 11. Magnitude of ER peaks I, II, and III, versus surface field \mathcal{E}_s . The dashed curves are calculated from the theory which neglects exciton and collision-broadening effects. The ordinates of all theoretical curves have been multiplied by the same normalization factor, which equates the theoretical crossover magnitude with the experimental value.

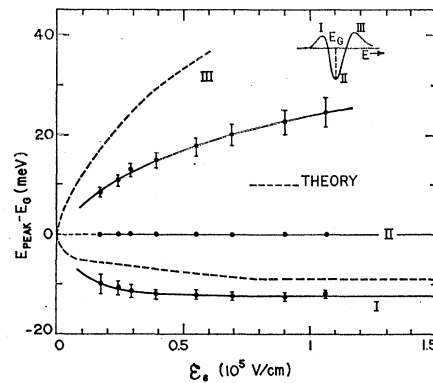


FIG. 12. Energy position of ER peaks I, II, and III versus surface field \mathcal{E}_s . The dashed curves are theoretical for no collision-broadening and exciton effects.

main peaks (Fig. 12). It appears, though, as if peak I should consistently fall closer to peak II than observed, while peak III should be located farther away. We have already pointed out that inclusion of collision broadening alone would actually displace peak II with respect to I and III toward better agreement. Of course, this particular discrepancy, along with other points of quantitative disagreement between theory and experiment, may depend on any of the number of approximations made in the theory.⁷ These include the neglect of exciton effects²⁴ and of lifetime broadening, use of only the light-hole effective mass, etc. Experimentally, there may be a possibility of further improving the precision of the determination of the surface field, in particular at low values, but we believe that neither the spectra of Fig. 6 nor the plots of Figs. 11 and 12 can be made to look appreciably different.

5. CONCLUSION

We have presented ER spectra taken by both sine-wave (first and second harmonic) and square-wave modulation. A characteristic of these results is that the surface field has been accurately determined by combined surface Hall effect and conductivity measurements. Our spectra clearly confirm that the line shape of ER cannot be accounted for in terms of uniform-field Franz-Keldysh theory.

A comparison of the square-wave results with the nonuniform perturbation theoretical model has been made. The qualitative validity of this model is definitely established, and none of the main features of the experimental spectra remains unexplained. In particular, the crossover between peaks I and III, a characteristic

²⁴ The theoretical description of the effect of the electric field on interband optical properties for an isotropic M_0 threshold, where Coulomb effects are included, has been given numerically by H. I. Ralph, *J. Phys.* **C1**, 378 (1968); D. F. Blossey and P. Handler (to be published); J. D. Dow (to be published); and in a closed-form approximation by R. Enderlein, *Phys. Status Solidi* **26**, 509 (1968). For practical computational purposes, however, it is necessary to use the one-electron theory which neglects Coulomb effects (see Ref. 1).

feature of the theory, is found to occur almost at the correct value of the field. A remarkable feature of the data is that for sine-wave modulation at low-fields, the second-harmonic spectra are nearly the energy derivative of the first harmonic. This suggests that photon-assisted tunneling in nonuniform fields can be effectively described by an almost rigid lower-energy shift of the edge.

In addition to an accurate determination of the surface field at any value of the applied electrode voltage, Hall-effect and conductivity data have enabled the direct measurement of the effective reduced mobility of electrons in the surface space-charge region. The results indicate that at large band bendings, the random scattering model discussed by Schrieffer¹⁶ is

the overwhelming factor controlling the motion of electrons near the surface. Closer to the flat band condition, impurity scattering associated with positively charged surface states may be present. A new effect, which we may term inverted-sign field-effect mobility, has been observed and attributed to a strong mechanism of hole trapping. It is believed that the surface presents a very high density of hole traps created by the particular electropolishing treatment applied to the sample.

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Carrier-Concentration Dependence of Electron-Phonon Scattering in Te-Doped GaSb at Low Temperature

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The thermal conductivity K between 5 and 100°K was measured on Te-doped samples with excess donor concentrations n ranging between $\sim 10^{17}$ and 2×10^{18} cm⁻³. At temperatures below that of the peak, K was observed to decrease with increasing n , this behavior being associated to electron-phonon scattering. The dependence of K on n was investigated by calculating the additional thermal resistivity $W_{ep} = 1/K - 1/K_0$ at 6°K, where K and K_0 are, respectively, the experimental and theoretical values of the thermal conductivity. The theoretical conductivity was deduced from the Callaway model, using as parameters the Casimir-boundary mean free path, point-defect scattering calculated from the Klemens relation, and phonon-phonon scattering deduced empirically from the results at higher temperatures. W_{ep} was found to vary approximately as $n_{300^\circ K}^{-1.7}$ or $n^{-0.6^\circ K^{-2.2}}$. The excess thermal resistivity is most likely due to scattering of phonons by an electron gas. On the basis of the Ziman model, it is suggested that the observed $W_{ep}(n)$ behavior may arise from a variation of the effective mass m^* with n , due to the nonparabolic (000) band. Tentatively, an alternative argument is considered. The low-temperature thermal conductivity of undoped p -type samples with hole concentrations of about 1.5×10^{17} cm⁻³ was found to be much lower than that of Te-doped samples with comparable electron concentrations. This indicates that the strength of hole-phonon scattering in undoped material is more pronounced than that of electron-phonon scattering in Te-doped material.

INTRODUCTION

IN doped semiconductors, the decrease of the thermal conductivity K at temperatures below that of the peak, in comparison to boundary¹ and isotope effects,^{2,3} has been shown to arise from electron-phonon scattering. Particularly, the carrier-concentration dependence of K was investigated by Carruthers *et al.*⁴ in p -type german-

ium, by Goff and Pearlman⁵ and by Albany and Laurence⁶ in n -type germanium, and by Challis *et al.*⁷ in p -type InSb. In addition, such a scattering mechanism was found by Vook⁸ and by Albany and Vandevyver^{9,10} to be strongly effective in irradiated germanium. Theoretical works have been carried out by several authors. Ziman's model¹¹ relates to scattering of phonons by an electron gas, and has been applied to highly doped semiconductors where the impurity levels

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