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Differential Electroabsorption*

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Differential-electroabsorption spectra are calculated, using the Elliott theory of optical absorption by excitons, and are compared with experiments by Frova *et al.* at the direct (M_0) edge of Ge. The theory does not fit the data for any reasonable set of values of ϵ_0, μ^*, E_{gap}, Γ, $\langle c|\hat{\epsilon}\cdot\vec{p}|v\rangle$, and applied electric field strength. The discrepancies between theory and experiment can be understood qualitatively as due to nonuniformities in the applied electric field. The physics of electroabsorption is discussed with particular attention paid to the effects of excitons (i.e., the final-state Coulomb interaction) on both quasibound and continuum states of the electron-hole pair. In general, exciton theory predicts three phenomena omitted by the one-electron theory: (i) The excitons enhance the amplitude of the differential absorption both below and above the direct bandgap; (ii) the excitons increase the period of spectral oscillations of the electroabsorption signal above that predicted by Franz-Keldysh theory; and (iii) the first negative peak in the electroabsorption spectrum is due to the broadened zero-field bound-state excitons. The electron-hole interaction is responsible for a differential absorption which is both qualitatively and quantitatively different from that predicted by one-electron Franz-Keldysh theory—even when the applied electric field is so large that the discrete excitons are completely ionized.

I. INTRODUCTION

In recent years, the lock-in amplifier has revolutionized solid-state spectroscopy – giving rise to thermal modulation, strain modulation, wavelength modulation, polarization modulation, and electric field modulation as techniques for probing the changes in the optical properties of solids due to applied fields.[1] Of the various differential spectroscopies, electric field modulation often gives the sharpest signals—suggesting that it may provide the best test for a theory of differential spectra.[2]

Until now, most theories[3] of electroabsorption and electroreflection have assumed (i) the validity of the effective-mass approximation, (ii) the applicability of one-electron theory, (iii) that the linewidths of the observed spectra are adequately described by a single energy-independent broadening parameter Γ, and (iv) that the experimental data with which the theories are compared are uniform-field data.

These theories have been successful in describing the *signatures* of electroreflection and electroabsorption data at M_0 and M_1 critical points in transition-band structures; that is, the theories have succeeded in giving *qualitative* fits to the line shapes, and therefore have led to the determination of the *energies* and the *types* of the various critical points in transition-band structures.

Still, there are no *quantitative* fits to the line shapes of the data; and there is some reason to suspect that the best fits to date may have tended to obscure real discrepancies between theory and experiment, by permitting the fitting parameters to assume unrealistic values.

It is generally believed that many of the discrepancies between existing theories and data can be attributed to the failure of the one-electron approximation and that exciton effects (i.e., correlations in the motions of electron and hole due to final-state interaction) are important. A number of attempts[4–7] have been made to develop a theory which includes exciton effects, with significant contributions made by Duke and Alferieff,[4] Ralph,[5] and Blossey.[6] However, none of those authors have yet calculated *differential* spectra with sufficient accuracy to permit quantitative comparison with experiments.

In this paper, we present the results of calculations of the differential electroabsorption at the direct edge of Ge; these calculations go beyond the one-electron approximation to include exciton effects within the isotropic effective-mass approximation (Elliott theory[8]). These calculations show that the *exciton effects are always significant and often overwhelmingly dominant*. However, the fit we obtain to the experimental data,[9] although better than previous fits, is not good; and it seems impossible to obtain a good fit using any reasonable values of the parameters: experimentally applied field, effective masses, and broadening. We are therefore led to believe that either (i) the simple[10] Elliott theory of optical absorption fails to have sufficient accuracy to adequately describe the small differences measured in electroabsorption; or (ii) screening of the electron-hole interaction by free charges is important; or else (iii) experimental difficulties associated with nonuniform applied fields are responsible for the remaining discrepancies. In any case, our calculations indicate that the measured differential absorption spectra generally are particularly sensitive to energy-dependent broadening processes.

If the Elliott theory actually fails to describe differential spectra, the implications are quite serious. Since its conception the Elliott theory has been the simplest and the most successful many-body theory of solid-state physics; its failure would force a complete revision of the theories of optical properties of insulating solids. For these reasons, we consider it to be extremely important that the electroabsorption at the direct edge of Ge be remeasured, using the recently developed flat-band[11] and selective-doping[12] techniques, in order to insure a uniform applied electric field and a low density of free carriers in the sample.

For the moment we prefer to adopt the viewpoint that the Elliott theory is applicable and ascribe the discrepancies to field inhomogeneities (according to the theory of Aspnes and Frova[13]), while noting that the experimentalists seem to be making considerable progress toward solving the extremely difficult problem of obtaining and measuring a uniform field in a semiconductor.

Section II of this paper discusses the model on which our calculations are based; Sec. III treats the effects of the Coulomb interaction between electron and hole; while Sec. IV is devoted to a presentation of our results. The paper is summarized in Sec. V.

II. MODEL

The starting point of our calculations is the Elliott theory of direct optical transitions to Wannier-Mott exciton states,[8] which gives the prescription that the imaginary part of the dielectric function $\epsilon_2(\omega)$ and the absorption coefficient $\alpha(\omega)$ are both proportional to the transition density of states $S(E)$ times the probability $|U(0)|^2$ that the final-state electron and hole are in the same unit cell:

$$\epsilon_2(\omega) \propto \alpha(\omega) \propto |U(0)|^2 S(E) \ . \tag{1}$$

Here we have $E = (\hbar\omega - E_{\text{gap}})/R$, where $\hbar\omega$ is the photon energy; E_{gap} is the direct band gap; the unit of energy is the exciton Rydberg $R = e^2/2\epsilon_0 a$; the unit of length is the exciton radius $a = \hbar^2\epsilon_0/\mu^* e^2$; μ^* is the reduced effective mass of the electron and the hole; and ϵ_0 is the static dielectric constant. Henceforth, we shall refer to $|U(0)|^2 S(E)$ as the *absorption strength*.

In uniform applied electric field $\vec{F} = F\hat{z}$ directed along the z axis, the relative-motion wave function $U(\vec{r})$ solves the effective-mass equation

$$(-\nabla^2 - 2/r + fz)\, U(\vec{r}) = E U(\vec{r}) \ . \tag{2}$$

Here $f = |e| Fa/R$ is the applied potential-energy drop across the radius of the exciton divided by the exciton binding energy; i.e., the electric field strength in units of exciton rydberg $R = e^2/2\epsilon_0 a$; the per exciton radius. Qualitatively, for fields such that f exceeds unity, the exciton is field ionized. For $f < 1$, quasibound exciton states exist, giving rise to the characteristic exciton peaks in the optical-absorption spectrum.

The calculation of the differential absorption occurs in five steps: (i) The applied field f is determined and the effective-mass equation (2) is solved numerically[14] for the wave function at $\vec{r} = 0$, $U(0)$, and the density of states $S(E)$[15]; (ii) the absorption strength is evaluated using the Elliott formula (1); (iii) the zero-field absorption strength[16] is subtracted from this giving the differential-absorption strength

$$\Delta[\,|U(0)|^2 S(E)] \ ; \tag{3}$$

(iv) this differential absorption is appropriately broadened[17,18]; and (v) the contributions to the differential absorption from both light- and heavy-hole bands are added with the weights of each contribution determined by the value of $|\langle c|\vec{\epsilon}\cdot\vec{p}|v\rangle|^2/Ra^3$ for the bands.[19] The central part of this procedure is the solution of the effective-mass equation which is done numerically in order to achieve an *exact* solution. The exact solution is necessary for this problem because the usual perturbation expansions or classical approximations fail.

An exciton in an arbitrarily weak uniform electric field has no bound states. Therefore, perturbation expansions (in powers of the field f) of the wave functions and the energies are *divergent asymptotic* series. The reason for this is that the potential energy associated with the applied field

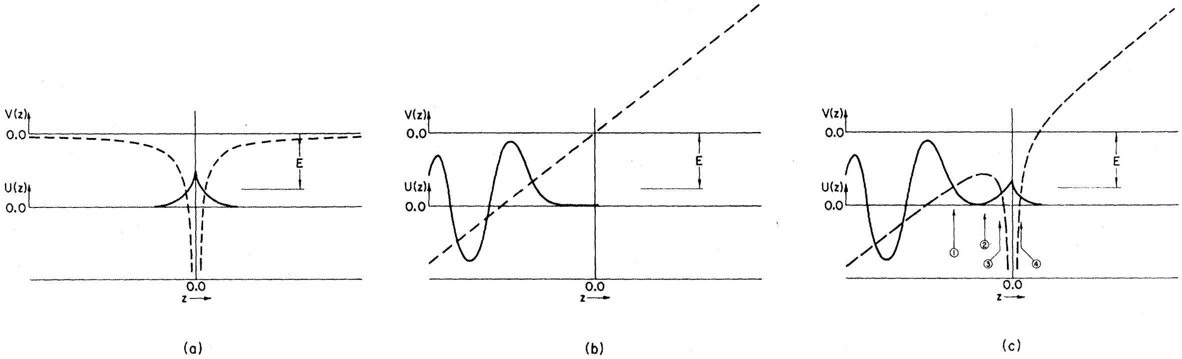


FIG. 1. (a) Sketch of the potential energy (dashed line) and the envelope wave function (solid line) for the final-state electron relative to the hole (at $z=0$) viewed along the direction of the applied field (*a*) with zero applied field and nonzero electron-hole Coulomb interaction (excitons: $f=0$, weak-coupling limit); (b) with nonzero applied field and zero Coulomb interaction (no excitons: $f \gg 1$, strong-coupling one-electron Franz-Keldysh theory); (c) nonzero applied field and nonzero Coulomb interaction (excitons: f finite, present theory). Note the qualitative differences in the wave functions in each of the three cases. In (c), the classical turning points are "1", "3", and "4", and the relative maximum of the potential is "2".

is unbounded: $V=-eFz=fz$. This failure of perturbation theory is physically obvious because the stationary states of the field-perturbed exciton are qualitatively different from the unperturbed states: An electron initially localized in a quasibound state near the hole ($\vec{r}=0$) will eventually tunnel out to $z=-\infty$ [see Figs. 1(a) and 1(c)]. No finite order of perturbation theory will result in wave functions qualitatively different from the initial wave functions.

The large fields f often used in electroabsorption and electroreflection experiments suggest that a suitable zero-order approximation to the wave function might be to neglect the Coulomb interaction completely and then to improve on this by developing a perturbation series in powers of the Coulomb interaction (i.e., in powers of $f^{-1/3}$). However the electron-hole interaction is also unbounded (below) and causes the Coulomb-perturbed wave functions to be qualitatively different from the Airy-function eigenstates of the uniform-field Hamiltonian [see Figs. 1(b) and 1(c)]. Hence, perturbation series in powers of the electron-hole interaction are likewise doomed to divergence difficulties; the expansion parameter of these series is $f^{-1/3}$, so that there is little hope of an adequate *asymptotic* approximation of the Coulomb effects for fields smaller than $f=10^3$ (i.e., $f^{-1/3}=0.1$).

For electric fields between 10^4 and 10^6 V/cm, the dimensionless field f takes on values between 10^{-2} and 200 for typical semiconductors (see Table I). Therefore, an adequate theory of excitons in uniform electric fields of such magnitude must be a *nonperturbative intermediate-coupling* theory in order to avoid the divergences associated with the asymptotic expansions about the strong- and weak-field limits. In the case of hydrogenic excitons in a uniform electric field an *exact* solution of the effective-mass Schrödinger equation can be achieved by numerically integrating the separated equations of motion in parabolic coordinates.[20] In addition to circumventing the divergence difficulties associated with perturbation theory, the exact solution has the advantage that it avoids whatever errors might be associated with any approximation scheme. Remember that the quantities being calculated are small differences between large numbers (that is why the experiments are performed using phase-sensitive detection); any error in the evaluation of the absorption coefficient would be greatly amplified in a calculation of differential absorption.

III. EFFECTS OF COULOMB INTERACTION

The experiments of interest in this paper were all performed in the strong-field regime ($f>1$) so that the applied field ionizes the exciton. Previous theories of these experiments were based on the one-electron Franz-Keldysh theory which neglects the Coulomb interaction between the electron and the hole. The exciton theory predicts three effects which the Franz-Keldysh theory overlooks and all three of these effects manifest themselves in experimental spectra[21]: (i) The Coulomb interaction greatly *enhances the magnitude* of the differential electroabsorption both below and above the band-gap.[22] (ii) The spectral oscillations of the differential-electroabsorption coefficient have a *longer period* than those predicted by one-electron theory.[23] (iii) The (broadened) zero-field exciton peak manifests itself as a large narrow *negative peak* in the differential spectrum which is temperature dependent but insensitive to the applied field strength.[24]

The Coulomb enhancement can be easily understood by considering the wave functions depicted

TABLE I. Relevant properties of excitons. Values of the exciton rydberg $R = m^* e^2/2\epsilon^2\hbar^2$ and radius $a = \hbar^2\epsilon/m^* e^2$ are calculated from the measured values given for the static dielectric constant ϵ and electron effective mass m^*/m. Calculated values of our dimensionless field strength f corresponds to an applied field of 10^4 V/cm.

Substance	(m^*/m) [a]	ϵ [b]	R(eV)	a(Å)	f
Ge (direct)	0.033	16	0.0018	250	14
	0.0195	16	0.0010	430	40
C (diamond)	(1)	5.8	0.40	3.1	0.00078
GaP	0.34	10	0.044	16	0.036
GaAs	0.067	12	0.0061	94	1.5
InSb	0.015	18	0.00067	620	93
CdS	0.20	8.9	0.035	23	0.065
ZnO	0.24	7.9	0.053	17	0.033
ZnS	0.28	8.3	0.055	16	0.028
ZnTe	0.15	9.7	0.020	35	0.17
PbS	0.16	170	0.000072	575	8000
Cu_2O	0.80	10	0.10	6.9	0.0070
AgCl	0.35	9.5	0.052	14	0.028
AgBr	0.24	11	0.029	23	0.080
TlCl	0.32	38	0.0031	62	2.0
TlBr	(1)	31	0.015	16	0.10
MgO	(1)	9.8	0.14	5.2	0.0037
LiF	(1)	9.0	0.16	4.8	0.0029
NaCl	(1)	5.9	0.39	3.1	0.0008
KCl	0.50	4.5	0.33	4.8	0.0014
RbCl	0.52	4.6	0.33	4.7	0.0015
CsCl	(1)	7.2	0.26	3.8	0.0015

[a] If no value of m^*/m was available, it was taken to be unity.

[b] Sources for m^*/m and ϵ are listed in Ref. 7.

(along the direction of the field) in Figs. 1(b) and 1(c) and by recalling that the absorption is proportional to $|U(0)|^2$. The uniform-field Airy function [Fig. 1(b)] oscillates with increasing frequency (the electron's momentum is increasing) and decreasing amplitude (the time the electron spends in a given region decreases as its speed increases) as z tends to negative infinity. To the right of the classical turning point the electron's wave function dies out exponentially. The exciton wave function [Fig. 1(c)] is similar to a phase-shifted Airy function to the left of the classical turning point "$\underline{1}$," and also dies out exponentially from there to the point "$\underline{2}$" where the potential has a Coulomb-induced relative maximum. *The Coulomb potential is responsible* for an exponential rise in the wave function from "$\underline{2}$" to the classical turning point "$\underline{3}$"; the wave function is fairly flat near the origin (but cusped at $z = 0$), then decays to the right of the classical turning point "$\underline{4}$." Note, in particular, that the Coulomb interaction causes the wave amplitude at the origin to be *exponentially* larger than it would have been in the absence of the electron-hole interaction.[25] And since the absorption is proportional to $|U(0)|^2$, we see that the Coulomb force is responsible for an *exponential enhancement* of the absorption by states well below the lowest-energy zero-field exciton peak. Recalling that the zero-field absorption is zero in this region, we see that the differential electroabsorption has a first positive peak which is *exponentially* larger than Franz-Keldysh theory predicts.

While the above argument strictly holds only for energies below the relative maximum at "$\underline{2}$" in the potential, another argument indicates that the Coulomb interaction is responsible for considerable enhancement in the amplitude of the differential electroabsorption above the zero-field energy gap: Consider a state with $E > 0$ (Fig. 2), and conceptually integrate its wave function from $z = +\infty$ to the origin. Throughout this spectral region, the Coulomb-plus-applied potential (solid line in Fig. 2) is always less than the potential associated with just the uniform field (dashed line in Fig. 2). *Qualitatively* we could represent the *average effective potential* in this region by the straight dotted line in Fig. 2. Note that the "*effective uniform field* f_*" is somewhat larger than the applied field f. The larger effective field will give a larger differential absorption, as we know, from the Coulomb-free uniform-field case[26]; for example, for $E \gg f^{2/3}$, the exciton-free differential absorption is

$$\Delta\alpha \propto (f/16\pi^2 E)\cos\tfrac{4}{3}E^{3/2}/f. \qquad (4)$$

This effect can also be seen in Fig. 2 as an increase in the amplitude of the wave function in the neighborhood of $z = 0$ due to the Coulomb potential. The increased amplitude of the wave function is equiva-

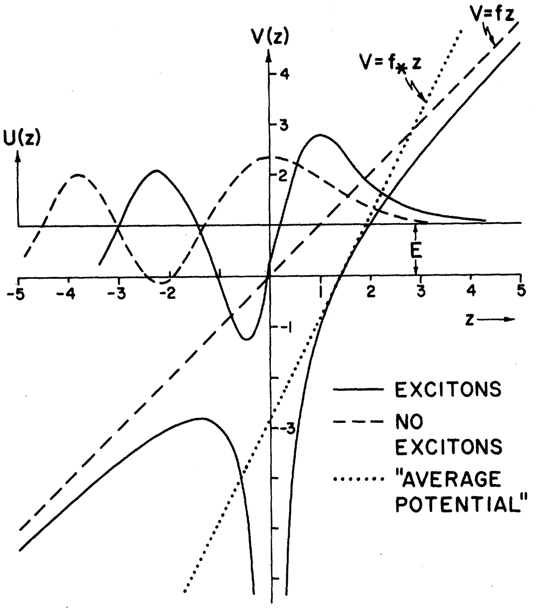


FIG. 2. Wave function $U(z)$ for a continuum state ($E>0$) and potential $V(z)$ associated with (a) uniform applied field (i.e., no excitons) denoted by dashed lines; and (b) uniform applied field plus electron-hole scattering (i.e., excitons) denoted by solid lines. The "average potential" associated with the larger effective field f_* is denoted by a dotted line. Note the larger amplitude and smaller period of spatial oscillation for the exciton wave function.

lent to an increased amplitude of the differential absorption by virtue of the Elliott formula (1).

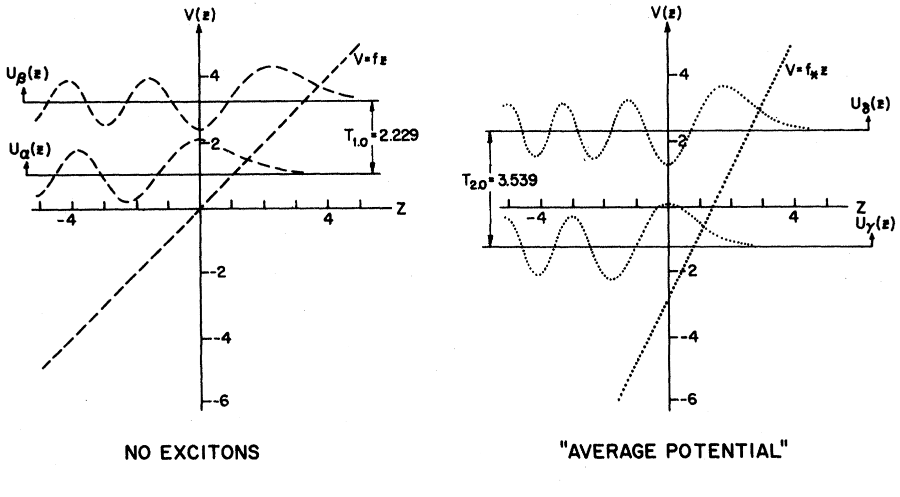
The second effect of the Coulomb interaction is to prolong the period of oscillations of the differential spectrum. This can be understood also in terms of a larger Coulomb-induced effective field f_*, which causes a longer period $T(T \propto f_*^{2/3})$. Another way to see how this arises is to note that *long periods of spectral oscillations in the absorption can be associated with rapid spatial oscillations in the wave function.* This fact is obvious in the uniform-field case, where the uniform-field wave function is

$$U(z) \propto \mathrm{Ai}\,(f^{1/3} z - E/f^{2/3}) , \qquad (5)$$

so that it oscillates more rapidly (as $f^{1/3}$) as a function of z (the electron has more momentum) owing to a larger field f, but $U(0)$ and the absorption strength oscillate more slowly with energy (as $f^{-2/3}$). The Coulomb interaction clearly accelerates the electron when it nears the hole, giving the wave function $U(z)$ more kinks and more rapid spatial oscillations than it would have otherwise. This effect shows up in the differential spectra as the longer oscillation period.

The fact that the spectral-oscillation period is longer for a larger effective field is illustrated in Fig. 3, where the potential energy and wave functions are plotted for an electron in the applied field [Fig. 3(a)] and in the "average" uniform field [Fig. 3(b)] depicted in Fig. 2. The wave functions are plotted for energies corresponding to adjacent maxima in the differential absorption [i.e., $|U(0)|$ is a relative maximum]. Note that the separation T of these maxima is smaller for the applied field than for the "average" field.

Turning to the third exciton effect, we note that the first negative peak in electroabsorption is due to the zero-field exciton states and its exact shape



NO EXCITONS

"AVERAGE POTENTIAL"

FIG. 3. Uniform-field potentials V and wave functions U (along the direction of the field) for the case of no excitons (dashed lines; $V=fz$) and "average potential" due to excitons (dotted lines; $V=f_*z$). Note that the energies of the wave functions were chosen to correspond to adjacent maxima in the differential absorption (i.e., wave functions have extrema at $z \approx 0$). Larger effective field due to excitons causes a larger period, $T_{2,0}=3.539$, than the corresponding period of $T_{1,0}=2.229$ for just the applied field. The values used here for f and f_* are 1.0 and 2.0, respectively, and are the same as in Fig. 2. The energies E_α, E_β, E_γ, and E_δ are 1.019, 3.248, -1.211, and 2.328, respectively.

is quite sensitive to broadening mechanisms. In the idealized case of zero broadening (Fig. 4), the differential-absorption spectrum below the direct gap should have a broad positive peak (associated with absorption by broad field-ionized excitons) with many sharp negative peaks (corresponding to the discrete exciton series at $E=-R/n^2$, $n=1$, 2, 3, etc.)[27]; above the gap, the oscillations in the differential absorption are due to Franz-Keldysh-type oscillations in the absorption coefficient. The primary effect of finite broadening ($\Gamma \neq 0$) is to spread the discrete exciton states out over a spectral region of order Γ, so that if the broadening is larger than the exciton binding ($\Gamma \gtrsim R$) there is only one negative peak in the differential spectrum.[28] The shape of the negative peak depends primarily on temperature (through Γ) and not on f, since the peak corresponds to the zero-field excitons. In contrast, the field-perturbed excitons are well ionized by the electric field ($f \gg 1$); therefore their contribution to the absorption is relatively smooth and quite unaffected by the broadening in most cases where $fR \gg \Gamma$.[29]

Once more, we emphasize that *the electron-hole Coulomb interaction cannot be neglected* in any quantitative theory of differential electroabsorption, *even for electric fields much larger than the ionization field of the exciton.* Excitons are responsible both for a large enhancement of the amplitude of differential absorption oscillations and also for a prolongation of the period of the oscillations. These effects are apparent not only in the region of the bound exciton states but also well up into the continuum of unbound excitons.

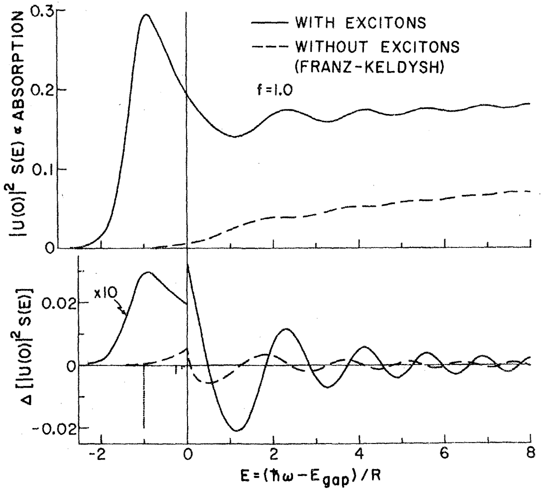


FIG. 4. One-electron and exciton theoretical optical-absorption strength and differential-absorption strength $\Delta[|U(0)|^2 S(E)]$ for a field of $f=1$. The differential absorption by excitons is *not* plotted for negative E since it is the difference between $|U(0)|^2 S(E)$ and a sum of δ functions:

$$\sum_{n=1}^{\infty} n^{-3}\delta(E+n^{-2}).$$

However, the total absorption strength by field-perturbed excitons, scaled down by a factor of 10 (i.e., the value at the peak is 0.3) is plotted for $E<0$, along with the first few zero-field exciton lines (dotted). Note that the total oscillator strengths under the field-perturbed and field-free curves for $E<0$ differ by only a few percent for $f=1$. The excitonic differential absorption for $E<0$ actually joins continuously to that for $E>0$.

IV. RESULTS

The results of the calculations described in Sec. II are presented in Fig. 5. The solid lines are the theoretical curves with excitons included, the dashed lines are the one-electron theory,[9] and the dotted lines are the measurements[9] of the differential electroabsorption at the direct edge of Ge.[30] The theoretical curve is the sum of contributions from the light- and heavy-hole bands, assuming that the transition matrix elements are equal. The reduced exciton masses are taken to be 0.0195 and 0.033 electron masses, respectively. Since the static dielectric constant is 15.8, the exciton binding energies are 1.062 and 1.80 meV, respectively. The unbroadened theoretical differential absorption was convoluted with various different broadening functions in order to obtain good agreement between theory and experiment.[18] In general, Lorentzian broadening, where

$$\Delta\epsilon_2(\omega,\Gamma)=\frac{\Gamma\hbar}{\pi}\int_{-\infty}^{\infty}\frac{1}{\hbar^2(\omega-\omega')^2+\Gamma^2}\times\Delta\epsilon_2(\omega',\Gamma=0)\,d\omega' \qquad (6)$$

produced better agreement, especially at lower energies, than could be obtained with Gaussian broadening. (Below the edge, Gaussian broadening caused a downward curvature of the exponential tail.) The fit was best for Lorentzian widths such that $\Gamma \approx 1.062$ meV.[31]

The agreement between theory and experiment is, in our opinion, poor. While we were able to achieve qualitative and even semiquantitative agreement (especially at the higher temperatures), we were generally unable to obtain a satisfactory fit to the first positive peak—which was always larger in magnitude and smaller in width than theory predicted. (Be careful to note that the differential absorption is plotted on a logarithmic scale which makes the theory appear to be in deceptively close agreement with experiment.) Consideration of the arguments of Sec. III and Fig. 5 indicate that this unduly sharp narrow positive peak *cannot* appear in a uniform-field electroabsorption measurement if the simple isotropic-mass Elliott theory is valid, if the applied field is uniform, and if the field is sufficiently strong that f exceeds unity. The reasoning goes as follows: (i) A positive peak in the

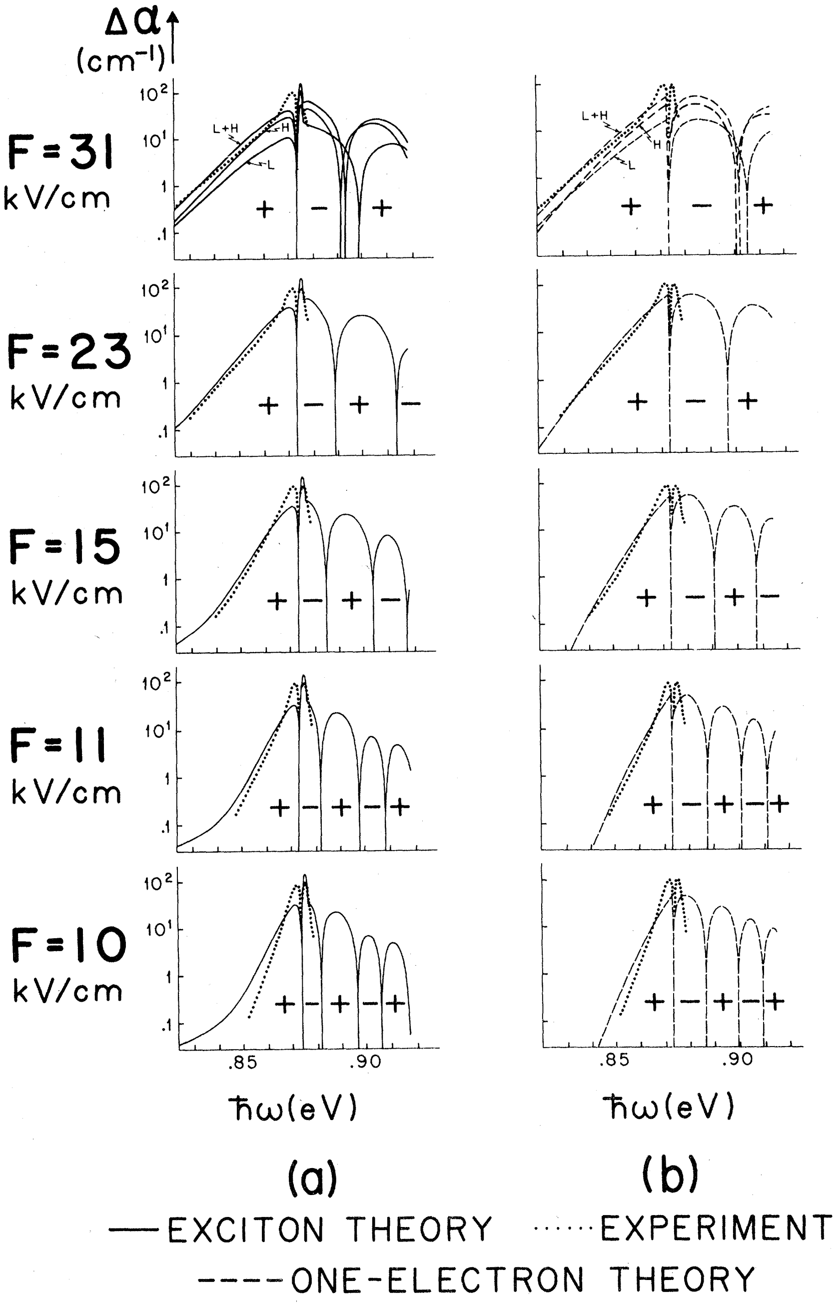


FIG. 5. Differential absorption $\Delta\alpha$ (in cm^{-1}) vs photon energy (in eV) at the direct edge of Ge for applied fields F of 31, 23, 15, 11, and 10 kV/cm, respectively, and at a temperature of of 123 °K. Dotted line: experiment of Ref. 9. Solid line: Lorentzian-broadened exciton theory ($\Gamma = 1.062$ meV). Dashed line: one-electron (Franz-Keldysh) theory. Columns (a) and (b) present a comparison between experiment and (a) exciton theory and (b) one-electron theory, respectively. For $F = 31$, the contributions to the differential absorption from the light- and heavy-hole bands are denoted by L and H, respectively; the sum is denoted $L+H$. The signs of the various peaks are denoted under them.

differential absorption necessarily comes from a peak in the optical absorption in the electric field and not from the zero-field absorption[7]; (ii) at fields such that $f > 1.0$ no well-defined peak such as that found in the experiment exists in the theoretical absorption; and (iii) no matter what (reasonable) broadening may occur, the differential absorption for fields $f \approx 100$ will be the (broadened) difference between two curves such as those plotted in Fig. 6. The first positive peak in the differential absorption is due to the exponential edge in the field-perturbed absorption, which is *rising smoothly* (with no abrupt change in curvature) up to the first peak above the band gap. Clearly, no reasonable broadening of the field-perturbed absorption will cause it to *rise abruptly* near $E = 0$, giving the theoretical differential absorption the observed shape.

We believe that the peak structure can be attributed to nonuniformities in the applied field. Aspnes and Frova[13] have shown that one of the effects of a nonuniform field is to mix the real and the imaginary parts of the dielectric function. Therefore, if uniform fields are present, then $\delta\Delta\epsilon_2$, the difference between the calculated and the measured differential-

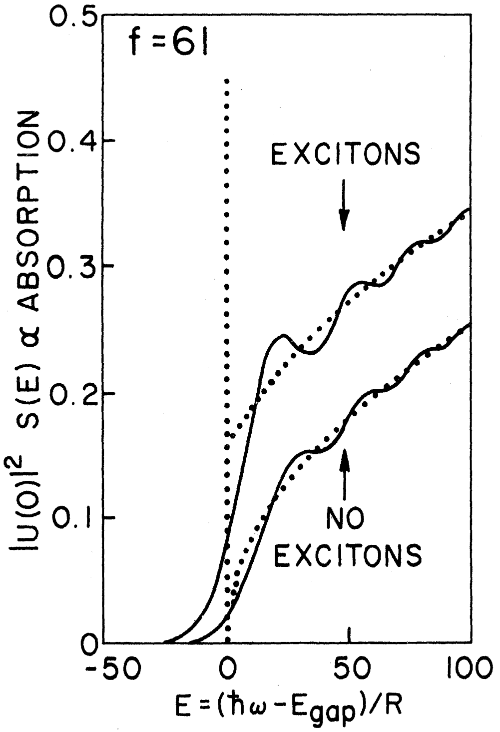


FIG. 6. Unbroadened theoretical absorption strength $|U(0)|^2 S(E)$ (i) for an applied field of $f = 61$ (solid lines) and (ii) in zero applied field (dotted lines). The upper curves are for excitons; the lower, for free-electron-hole pairs (Franz-Keldysh theory). The theoretical differential-absorption strength in each case is the difference between the solid and the dotted lines.

absorption curves, should have the shape of $\Delta\epsilon_1$, the change in the real part of the dielectric function. In Fig. 7, we plot both $\Delta\epsilon_2(\omega)$ and $\delta\Delta\epsilon_2(\omega)$ for the case $F = 31$ kV/cm. Note that the curve of $\Delta\epsilon_2$ vs ω has the same shape as $\Delta\epsilon_1$ vs ω, having nodes near the maxima of $\Delta\epsilon_2$ and zeros near the half-maxima of $\Delta\epsilon_2$.[32] Therefore, we conclude that the data of Ref. 9 were probably taken with a somewhat nonuniform electric field in the sample, and we hope that the electroabsorption at the direct edge of Ge will be measured again under uniform-field conditions, such as those which are becoming available now with flat-band[11] and selective-doping[12] techniques.

It should be emphasized that while we feel the agreement of theory with experiment is poor, it is in fact much better than previous "good" one-electron-theory fits (See Fig. 5). We are unhappy with the fit because we expect the Elliott theory to be capable of a much more precise description of the data. The agreement between theory and experiment achieved here is, at best, qualitative.

In fact, the theory may be in much worse agreement with experiment than the curves of Fig. 5 indicate, for the transition matrix elements were taken to be parameters in the fitting procedure. The transition matrix elements extracted from the fitting procedure seem to be about a factor of three smaller than the generally accepted values ($0.222\hbar$ Å^{-1} vs an experimental value of $0.7\hbar$ Å^{-1}; Franz-Keldysh theory gives a fitted value of $0.253\hbar$ Å^{-1}). That is, the theoretical differential absorption is almost an order of magnitude larger than the measured values. A simple way to explain this discrepancy is to assert that the measured electric fields were appreciably larger than the actual fields seen by the excitons (probably due to surface effects[11, 33]) and that broadening played a dominant role in reducing the amplitude of the differential-electroabsorption signal. The first of these explanations suggests that the technology of securing uniform electric fields in the bulk of a semiconductor may still be in its infancy. The sensitivity of differential absorption to broadening is documented in Fig. 8 (for the case of energy-independent broadening). The primary effect of increased broadening is to reduce the amplitude of the differential absorption without significantly altering the phase. The factor-of-3 discrepancy in the matrix element could be removed by arbitrarily increasing the broadening by about a factor of 10. This sensitivity to broadening suggests that a complete understanding of modulation spectra may only come after the broadening mechanisms (and perhaps their dependences on energy) are fully understood. However, if an accurate first-principles theory of broadening were available and if uniform-field experiments were possible, then theoretical fits to electroabsorption

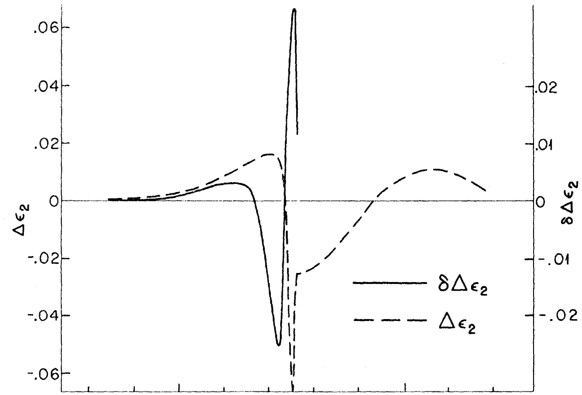
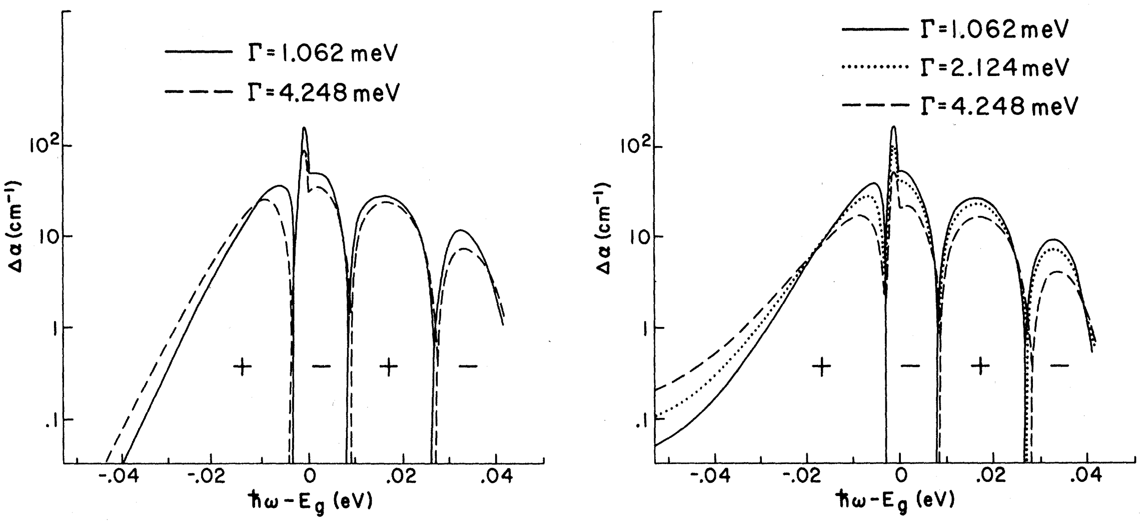


FIG. 7. $\Delta\epsilon_2$, the (theoretical) change in the imaginary part of the dielectric function with uniform applied field and $\delta\Delta\epsilon_2$, the difference between the (exciton) theoretical and experimental values of $\Delta\epsilon_2$, as a function of photon energy $\hbar\omega$ for Ge at 123 °K in an applied field of $F = 31$ kV/cm with Lorentzian broadening $\Gamma = 1.062$ meV. Note that qualitatively $\delta\Delta\epsilon_2$ has the general shape of the $\Delta\epsilon_1$ curve for Ge, in agreement with the predictions of Ref. 13. Note the different scales for $\Delta\epsilon_2$ and $\delta\Delta\epsilon_2$.



(a) (b)

FIG. 8. $\Delta\alpha$, the field-induced change in the optical-absorption coefficient for (a) Gaussian and (b) Lorentzian broadening. The solid, dotted, and dashed lines correspond to $\Gamma = 1.062$, 2.124, and 4.248 meV, respectively. The photon energy $\hbar\omega$ is measured relative to a value of $E_g = 0.872$ eV. Note that for $\Gamma > R$ and $f \gg 1$, the effect of increased broadening is to reduce the amplitude of the electroabsorption oscillations without significantly changing the phase.

data should yield very precise information about matrix elements, bandgaps, broadening mechanisms (such as exciton-phonon scattering), and effective masses (including the energy dependence of μ^*, which would manifest itself as energy dependences in f and R). The information which can be extracted from modulation spectra once these difficulties are overcome is sufficiently great to warrant a renewed experimental and theoretical effort to solve these problems.

V. SUMMARY

We have calculated the differential-absorption coefficient $\Delta\alpha$ at the direct edge of germanium, and have compared our results with the experiments of Ref. (9). The exciton effects are important, and change some qualitative features of $\Delta\alpha$, but some discrepancies between theory and experiment (which were previously thought to be due to excitons) still remain. Some of the remaining discrepancies may be understood qualitatively as due to nonuniformities in the applied electric field. However, a complete quantitative understanding of the rich structure in electromodulation spectra may be possible only after the details of broadening mechanisms are understood. In any case, we would discourage experimentalists from fitting their modulation spectra with one-electron theory because we feel such fits may retard the advancement of the understanding of these spectra. The exciton theory predicts sufficiently different amplitudes and periods of differential absorption that a good "fit" to one-electron theory can often be achieved only by forcing the fitting parameters (E_{gap}, f, R, Γ, and $\langle c | \hat{\epsilon} \cdot \vec{p} | v \rangle$) to assume unrealistic values. Our criteria for a good fit of exciton theory to experimental data are that (a) E_{gap} must agree with the experimental data within $\pm R$; (b) the effective mass and static dielectric constant (which affect f and R) must be independently determined; (c) f must agree with the value calculated from the applied field F within 15%; (d) Γ must agree with a calculated value within 100%; and (e) the transition matrix element extracted from the fit must agree with the empirical value within 50%.

Considerably more theoretical and experimental work will be necessary before electroabsorption spectra yield their quantitative information about band gaps, matrix elements, electron correlations, and electron-phonon interactions.[34]

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[10] We have not accounted for the possible mixing of the valence bands by the electric field. This effect is important in CuCl; see E. Mohler, Phys. Status Solidi 38, 81 (1970).

[11] For a discussion, see Ref. 2, Sec. 5.5.

[12] S. Koeppen and P. Handler, Phys. Rev. 187, 1182 (1969).

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

[14] The necessity of an exact (numerical) solution is discussed below.

[15] For a detailed discussion of mathematical and physical aspects of electroabsorption, see Ref. 7.

[16] In the units used here, the zero-field absorption strength is

$$\sum_{n=1}^{\infty} (n^3\pi)^{-1}\,\delta(E+n^{-2}) + \Theta(E)\,(2\pi)^{-1}\,(1-e^{-2\pi E^{-1/2}})^{-1},$$

where $\Theta(E)$ is the unit step function.

[17] In broadening the difference between absorption with and without applied field, we assume that the field does not allow any broadening processes to occur which were forbidden in zero field.

[18] The broadening was performed using both Lorentzian and Gaussian broadening functions $B(\omega, \Gamma)$:

$$\Delta\epsilon_2(\omega, \Gamma) = \int_{-\infty}^{\infty} B(\omega-\omega', \Gamma)\,\Delta\epsilon_2(\omega', 0)\,d\omega',$$

where

$$B(\omega,\Gamma) = \frac{\Gamma}{\pi}\,\frac{\hbar^{-1}}{\omega^2+\Gamma^2/\hbar^2} \qquad \text{(Lorentzian)}$$

$$= \frac{\hbar}{(2\pi)^{1/2}\Gamma}\,e^{-(\hbar\omega)^2/2\Gamma^2} \qquad \text{(Gaussian).}$$

[19] Assuming $|U(0)|^2 S(E)$ is unitless, then

$$\Delta\epsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2} \sum_i \langle v_i \,|\, \hat{\epsilon}\cdot\vec{p} \,|\, c\rangle \frac{1}{R_i a_i^3} \times \Delta\{|U(0)|^2 S[(\hbar\omega - E_{\text{gap}})/R_i]\},$$

where i runs over the light- and heavy-hole valence bands.

[20] See Ref. 4 for references to early work on the field ionization of atomic hydrogen.

[21] A conclusive statement that these effects *do* show up in the spectra will be possible only after quantitative agreement has been obtained between theory and experiment. Until then, we adopt (on theoretical grounds) the attitude that the exciton theory is generally superior to one-electron theory.

[22] This effect seems to have manifested itself in electroreflection; see D. E. Aspnes and A. Frova, Phys. Rev. B 2, 1037 (1970); and F. C. Weinstein, J. D. Dow, and B. Y. Lao, Phys. Status Solidi 43, K105 (1971); and (unpublished).

[23] This effect is apparent in indirect electroabsorption spectra, see B. Y. Lao, J. D. Dow, and F. C. Weinstein, Phys. Rev. Letters 26, 499, (1971); and (unpublished).

[24] This effect seems to show up in the spectra analyzed here (Ref. 9).

[25] This argument implicitly assumes that the amplitude of the wave function as it nears the turning point "1" is nearly independent of the presence of the Coulomb potential—a fact which follows from the continuum nature of the state, so that virtually all the contribution to the normalization comes from the asymptotic region, $z \to -\infty$.

[26] This argument is, of course, somewhat oversimplified, and depends on the notion that, for $z<0$, the primary effect of the Coulomb interaction is to give the wave function a phase shift. Still, one can show, by examining the potential energy in parabolic coordinates (Ref. 7), that the effect of the Coulomb potential is to create an effective field $f_* = f + 8\zeta^{-2}$, where $\zeta \equiv r - z$ is a parabolic coordinate. So, while the idea of a larger effective field is valid, the notion that it affects the wave function primarily at positive z is not.

[27] Here we are considering the strong-field case $f \gg 1$. For small fields ($f \ll 1$) the primary effect of the field is to shift and broaden the zero-field lines, leading to a relatively sharp absorption by the field-perturbed excitons; in this latter case the differential spectra should be particularly rich in structure.

[28] Wavelength modulation or other higher-derivative measurements on such negative peaks should reveal structure due to the discrete excitons.

[29] In order to minimize the uncertainties due to broadening, it may be useful to measure differential spectra between *two different* fields such that $fR \gg \Gamma$, instead of between one field and zero. That is, measure

$$\Delta\epsilon_2(\omega, f_1, f_2) = \epsilon_2(\omega, f_1) - \epsilon_2(\omega, f_2)$$

rather than

$$\Delta\epsilon_2(\omega, f) = \epsilon_2(\omega, f) - \epsilon_2(\omega, 0).$$

If the fields f_1 and f_2 can be precisely determined, or if f_1/f_2 can be precisely determined, then it should be possible to obtain a good fit of theory to experiment.

[30] Note that the infinite slope of $\Delta\alpha$ at $E=0$ (which was due to the square-root threshold in the zero-field absorption) is no longer present when excitons are included in the calculation. However the unbroadened (theoretical) $\Delta\alpha$ does have δ-function singularities for $E<0$ corresponding to the zero-field exciton states.

[31] No attempt was made to obtain an optimal fit in a least-squares sense—such a procedure would have been unduly expensive, and would not have significantly improved the quality of the final fit.

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[33] R. H. Kingston and S. F. Neustadter, J. Appl. Phys. 26, 716 (1955); C. G. B. Garrett and W. H. Brattain,

Phys. Rev. 99, 376 (1955).

[34] *Footnote added in proof.* Recent calculations have yielded such quantitative information. See Weinstein *et al.* (Ref. 22 and Ref. 23.)

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Optical Absorption, Reflectivity, and Electrical Conductivity in GeAs and $GeAs_2$[†]

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Single-crystal samples of two germanium arsenides were prepared: monoclinic-type GeAs and orthorhombic-type $GeAs_2$. Measurements are described for optical absorption and reflectivity in the neighborhood of the fundamental absorption edge at 300 °K and electrical resistivity over the temperature range 77–400 °K. Analysis of the optical data indicates the following: GeAs has a possible indirect band gap at 0.65 eV and direct band gaps at 1.01 and 1.65 eV; $GeAs_2$ has a possible indirect band gap at 1.06 eV and direct band gaps at 1.77 and 1.10 eV. The tailing of the absorption edge in both materials in the low-absorption region prevents a clear understanding of band structure details at the minimal band gap. Analysis of the electrical measurements for $GeAs_2$ indicates an activation energy of 0.36 eV which is associated with extrinsic behavior, carrier concentrations of the order 10^{17} cm^{-3}, and mobilities of 60 cm^2/V sec at 300 °K. All measurements are correlated with crystallographic orientation in these anisotropic materials.

I. INTRODUCTION

The use of arsenic as a doping agent to produce an *n*-type extrinsic semiconductor of germanium has been extensively studied by many workers. There are, however, two stoichiometric binary compounds GeAs and $GeAs_2$ which are known to exist and which have received very little attention in the literature. The present investigation is concerned with these two compounds.

The initial phase-diagram–composition identification of the germanium-arsenic system was proposed by Stöhr and Klemm.[1] The crystal systems were reported by Schubert *et al.*[2] to be monoclinic for GeAs and orthorhombic for $GeAs_2$. A complete structure determination was made for $GeAs_2$ by Bryden.[3] The silicon-arsenic, silicon-phosphorous, and germanium-phosphorous systems also have compounds that have the same two basic structure types.[4] From various studies of the general geometrical bonding arrangement of the atoms in the crystal structures of many compounds, Hulliger and Mooser[5] and Pearson[6] suggested that both GeAs and $GeAs_2$ should exhibit semiconducting electrical properties.

Very little is known about any of the properties of the compounds belonging to these structure types. The identification of the presence of GeAs and $GeAs_2$ in the surface layers of germanium crystals into which a large amount of arsenic, in comparison to normal extrinsic doping amounts, has been diffused was described by Waring *et al.*[7] Recent studies at this laboratory with the isotypic SiAs, primarily by optical-absorption measurements, demonstrated that the prediction for semiconducting behavior was correct for this structure type.[8] The present paper now continues this work to both optical and electrical measurements on the germanium arsenides.

II. EXPERIMENTAL

A. Sample Preparation

Ingots of both GeAs and $GeAs_2$ were prepared by the same procedure. The stoichiometric mixture of the elements[9] was heated in a sealed quartz tube that had been evacuated to a pressure of 10^{-4} Torr or less. To prevent a fracture of the quartz tube during synthesis, 14-mm-o.d. tubing with 2-mm-thick walls was employed. The temperature was increased to 750 °C over an 8-h interval, maintained at this point for 12–24 h, then slowly increased to 900 °C and held at that temperature for 3 h. The tube was then allowed to slowly cool to room temperature over a period of 12 h. The same temperature cycle was used to prepare both compounds because the melting points are nearly the same (737 °C for GeAs, 732 °C for $GeAs_2$).[1]

The introduction of one stage of zone melting as the last step in the synthesis process was found to promote the growth of larger single-crystal regions in the ingots. The ingot was cooled to just below the melting point and then passed (at a rate of 1.5 cm/h) through a narrow higher-temperature zone which was just sufficient to melt a portion of the ingot. Because the molten zone was not narrow enough to produce efficient zone refining and the