Electroreflectance of silicon*

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The major results of this paper are (i) the first high-field flatband-electroflectance data ever taken on silicon and (ii) an analysis with the one-electron theory that shows that the major portion of the direct edge spectrum is an M_0^{2D} from along Λ analogous to the E_1, $E_1+\Delta_1$ structures of germanium and gallium arsenide. The data cover a range of fields from about 77 to 310 kV/cm, and contains more **highly resolved structure than any previously reported results. Specifically, the second, weaker transition at the direct edge has been resolved quite clearly. It is shown that this structure may best be fit with an M_1 line shape, a result both interesting and controversial. A fundamental band parameter has been determined for the first time from the analysis. The transverse mass along Λ, μ_t, has been found to be 0.02m, in conflict with all present calculated values. This result is independent of the model used. In addition, we have obtained values for the energy gaps of the two direct-edge structures and an upper bound has been determined for the matrix element of the Λ transition.**

I. INTRODUCTION

Electroreflectance has passed from the qualitative to the quantitative stage in the last ten years. Early workers in the field had to be content with fairly accurate determinations of gap energies. Today, thanks to the efforts of several theorists, we have a closed-form one-electron theory[1] and a numerical theory[2] incorporating the Coulomb or "exciton" effect. Some debate has sprung up about the relative importance of the latter in interpreting spectra; more will be said later on this subject.

The pioneering experimental work was done on silicon by Seraphin and co-worker.[3] He indicated at that time that the direct edge (roughly 3.1–3.6 eV) was composed of two parts, possibly from different regions of the Brillouin zone. Cardona, Shaklee, and Pollak[4] and later Foreman, Aspnes, and Cardona[5] also performed electroreflectance of silicon.

We elected to do yet another study of silicon for two importance reasons: (i) a true "flatband" set of data has never been published for silicon and (ii) there is current interest in the symmetry of the direct edge. We refer specifically to the Λ-axis–Δ-axis controversy outlined in the paper by Pollak and Rubloff.[6]

We have succeeded in obtaining the flatband data shown in Fig. 1. It is superior to previous electroreflectance data in resolution of structure, especially in the interesting first negative peak. Moreover, the fact that it is flatband data makes it amenable to analysis in the "high-field" limit where more oscillations are present and therefore more accurate parametrizations are possible.

These data have been analyzed via the one-electron theory and fits made to all five fields. The results (a) justify a conclusion, (b) determine a heretofore unmeasured quantity, (c) provoke an interesting but controversial speculation.

First, the conclusion is that the major contribution to the results of Fig. 1 come from a large M_0 along the Λ axis that is best considered two dimensional. It is the analog of the E_1, $E_1+\Delta_1$ doublet of germanium at about 2.1 eV which Koeppen *et al.*[7] analyzed here at the University of Illinois and the similar 2.9-eV structure of GaAs also studied in our laboratory by Pond and Handler.[8] Second, from our fits it has been determined that μ_t, the transverse reduced effective mass along Λ, is about 0.02m, a result in great disagreement with calculated values. Third, we *speculate* that a weak M_1 may be the cause of the residual oscillation in the negative peak of Fig. 1, basing our conclusion strictly on best fits to data shown. We freely admit the unlikelihood of this possibility and would like to emphasize our fits in no way prove the hypothesis.

Despite these misgivings, we feel that our fits are more than just curiosities for no combination of M_0's gave results as consistently good statistically as did the M_0+M_1 we will show. It must be emphasized that our fits cover a broad range of fields

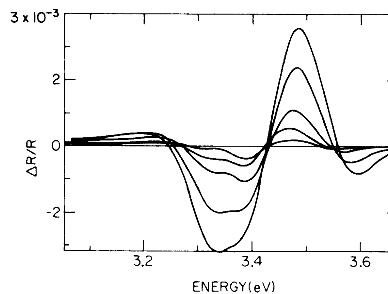

FIG. 1. $\Delta R/R$ vs photon energy at the direct edge of silicon for five applied fields of Table I. The amplitude increases with applied field.

and that at *every* field the M_1 interpretation of the initial region was superior to any other. Such results may not easily be dismissed no matter how farfetched.

Other quantities that have been assigned values from our fits are the fundamental gap energy along Λ, 3.36 eV, the gap of the undetermined transition, 3.28 eV, and an upper limit on the dipole strength of the Λ transition, 0.56 $\hbar/a_0$.

Section II is devoted to experimental details, Sec. III contains results and analysis, and Sec. IV contains a discussion of the results.

II. EXPERIMENTAL

The spectral range we investigated was 3.1–3.6 eV. Other structure exists above here but could not obtain good flatband signals for analysis. The experimental setup has been described elsewhere[7,8] in great detail and will be omitted from the present discussion after these remarks about the electrolyte.

A. Electrolyte

The more or less standard electrolytes for electroreflectance have been K_2SO_4, KCl, and H_2SO_4. Cardona *et al.* reported very little difference in results obtained with any of these. Pond and Handler,[8] however, reported problems with surface contamination of GaAs in solutions other than H_2SO_4. We had similar, more extreme problems with silicon. Though no electrolyte proved very satisfactory, a solution of $1N$ HNO_3 + $0.1N$ HF allowed us to reach flatband and take runs up to 1 h. No other electrolyte that we tried gave results as satisfactory. Whereas Pond found that cooling his samples to 0 °C helped keep currents down and surfaces clean, we found no such effects in silicon. Therefore, the ice bath incorporated in the system of Ref. 8 was not used here. Other than this, our system was the same as that of Fig. 1 in Ref. 8.

B. Flatband

One might ask why we required the flatband condition when low-field[9] electroreflectance could have been done, making this condition unnecessary. We observed that at the fields we required for good signal-to-noise ratio and uniform field profiles[10] (see also Sec. II D) there were always at least four half-oscillations present in the data. It is impossible to be in the low field or asymptotic limit and get a response of more than three half-oscillations (per transition). Furthermore, we observed variations in the size and shape of the response with dc bias when in depletion. Again, this is inconsistent with low-field theory.

Our method of finding flatband was the familiar $2\omega_2$ method outlined in Ref. 8. It proved to be quite satisfactory at the largest negative peak in $\Delta R/R$, but did not work anywhere else in the spectrum.

Some debate has arisen over the accuracy of the determination of flatband via the 2ω method. We would certainly agree that for determinations requiring errors of no more than tens of millivolts, the 2ω method is insufficient, but our modulations ranged from 0.25 to 4.00 V, *orders of magnitude* greater than the probable error voltage.

C. Surface preparation

All the data shown here were taken on n-type samples doped at about 10^{16} cm^{-3}. Lower dopings were also tried as well as p-type samples but the results were less satisfactory. With p-type samples, it was impossible to find flatband. All faces were (111).

Samples were cut to size ($2\times1\times0.2$ cm) and lapped and gold leads were applied eutectically to the unpolished faces. The leads were placed in Teflon caps and the rear and sides of the sample as well as the exposed gold wire were coated with epoxy and Q dope.

Etching the exposed sample faces proved to be the largest hurdle to overcome. The traditional CP-4A etch left a clouded surface with characteristics that prohibited reaching flatband. We found that a slower etch gave a cleaner surface and allowed us to find flatband. This etch was concentrated HNO_3, HF, and $HC_2H_3O_2$ in a volume ratio of 6:1:1.

D. Field uniformity

In electrolyte electroreflectance, the field is normal to the surface as noted earlier but is not precisely uniform. It drops off into the bulk with a characteristic length which is roughly the Schottky barrier length, $L=(2\epsilon V/eN_D)^{1/2}$, where V is the voltage drop, ϵ is the static dielectric constant, and N_D is the donor density. In order that the reflected photons should see a nearly uniform field it can be shown[10] that the parameter β must be small compared to 1, where

TABLE I. Data parameters.

V_{ac}(V)	V_{dc}(V)[a]	F(kV/cm)[b]	β[c]
0.25	0.60	78	0.05
0.50	0.69	110	0.03
1.00	0.58	155	0.02
2.00	0.42	219	0.02
4.00	0.41	310	0.01

[a]About 10% uncertain due to day-to-day fluctuations in the measurement system.

[b]Determined from Schottky-barrier model.

[c]Approximate mean value between 2.8 and 4.0 eV.

$$\beta = (\lambda/2\pi)\ (2\,|n+ik\,|\,L)^{-1}\ . \qquad (1)$$

This condition may be relaxed when $k/n \gg 1$. Since $L \propto V^{1/2}$ this sets a lower limit on V. To keep $\beta < 0.05$ over the energy range we worked with this required $V \gtrsim 0.25$ V. From a Schottky model again this gave $F \gtrsim 75$ kV/cm, approximately, where F is the applied surface field.

At the other end of the range, it was discovered that voltages greater than 4 V ac from flatband began to be clipped. Moreover, at higher ac voltages, net anodic currents were drawn at flatband which quickly corroded sample surfaces.

As a result of the above considerations, the applied fields covered the range from about 75 to 300 kV/cm. In all, data taken at five fields were used for analysis. These are listed in Table I. Also in the table are the β parameters and dc voltages of the five final runs.

The dc voltages listed in the table are the voltages of the saturated KCl-calomel electrode relative to the sample and refer to the potential on the "off" or flatband side of the applied square wave, not the mean or rms dc potential. Increasing the dc potential meant that the samples became more negative. As for the square wave, its sign was always chosen to cause the bands to traverse into depletion. One can see from Table I that the farther the bands were taken into depletion by the ac voltage, the less negative the sample needed to be to arrive at flatband.

III. RESULTS

A. Data

Figure 1 shows the data that were analyzed. The quantity measured is $\Delta R/R$ vs $\hbar\omega$, where

$$\Delta R = R(F) - R(0)\,, \qquad (2)$$

F is the electric field, and R is the reflectance. These data were Kramers-Kronig transformed and $\Delta\epsilon_1$ and $\Delta\epsilon_2$ determined from the optical constants of silicon.[11] Here $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ is the complex dielectric constant and Δ again indicates the change due to the field. Figures 2 and 3 show these results for the applied fields of Table I.

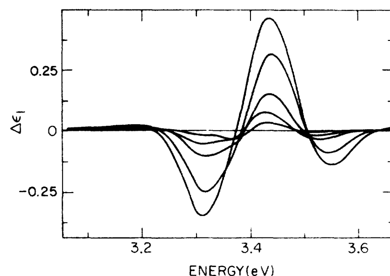

FIG. 2. $\Delta\epsilon_1$ vs photon energy as calculated from the data of Fig. 1. All five fields of Table I are shown with the largest field giving the largest amplitude curve, etc.

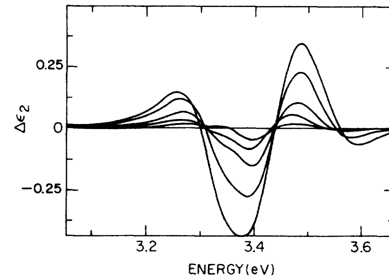

FIG. 3. $\Delta\epsilon_2$ vs photon energy as calculated from the data of Fig. 1. All five fields of Table I are shown with the largest field giving the largest amplitude curve, etc.

It is apparent from these data that there are at least two transitions taking place. This is most obvious in the lowest-field data [Fig. 4(a)], where $\Delta\epsilon_1$ at 77.5 kV/cm is shown. Here the large negative peak is seen to be double with an energy separation of about 0.06–0.07 eV. The dashed line in Fig. 4(a) is a fit to $\Delta\epsilon_1$ using simple M_0^{2D} line shape.[10] Figure 4(b) is the difference between the data and M_0^{2D} fit and it in turn is fit with an M_1^{3D}. Though we do not show them here, similar fits were tried with equal success on $\Delta\epsilon_2$ at 77.5 kV/cm.

It is clear from Fig. 4 that the M_0^{2D} and M_1^{3D} are adequate for fitting the lowest-field data. What justification is there for this choice and is it a unique one? In order to answer these questions, we must consider what is known about the band structure and optical properties of silicon.

It is nearly certain now that the major part of the 3.4-eV structure of silicon comes from transitions along Λ in the Brillouin zone. In 1968, Kline, Pollak, and Cardona[12] demonstrated that the 2-eV structure of germanium coalesced almost perfectly into the 3.4-eV structure of silicon by doing electroreflectance on various alloys of the two materials. It has been accepted fact for some time that the 2-eV region of the germanium spectrum is due to nearly degenerate transitions along Λ.[13] Koeppen, Handler, and Jasperson[7] showed that this region could be interpreted as an M_0^{2D} critical line. Recent high-stress piezoreflectance by Pollak and Rubloff[6] has demonstrated conclusively that the symmetry of the higher-energy part of the spectrum is that of Λ. Moreover, deformation potentials calculated from band-structure calculations[14] are in better agreement with experiment when a Λ transition is assumed than when Δ or other points are tried. Finally, nearly every band-structure calculation ever done on silicon[15–25] shows the Λ_3-Λ_1 bands as nearly parallel and separated by more

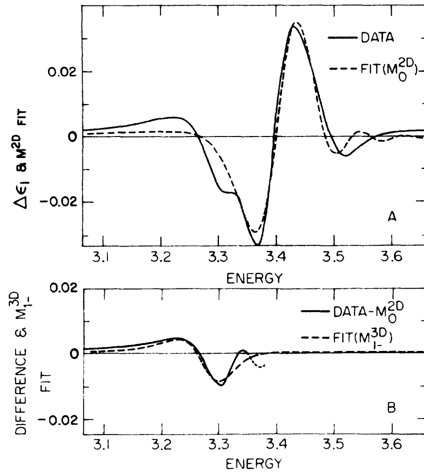

FIG. 4. (a) Lowest-field (78-kV/cm) $\Delta\epsilon_1$ data curve (solid line) and the best fit with an M_0^{2D} line shape (dashed line). (b) The difference between the data and the M_0^{2D} fit of (a) (solid line) and the best fit to this difference with an M_{1-}^{3D} line shape (dashed line). This demonstrates the importance of the second critical point at low fields.

than 3 eV. So an M_0^{2D} is quite a reasonable assumption for the major part of the spectrum.

What about the alleged M_{1-}^{3D}? There is almost no evidence to support this assumption. Some band-structure calculations show clusters[25] of critical points near Γ which contain M_1's but a direct M_1 means there is a direct M_0 below it and none has been observed. It is possible that one may exist with insufficient oscillator strength to be seen. Herein we can only say that the residual structure looks like an M_1 and gives the best fit but we have no additional evidence to offer in support of the claim.

As for uniqueness, we submit that any single fit with an M_0^{2D} can be treated with three-dimensional curves. This was the case with Ge[7] and GaAs[8] and is the case here again. On theoretical grounds, if one mass is larger than the others, as it is here, it is more advantageous to call the critical region two dimensional rather than three dimensional. The reason is that in either case only some sort of amplitude factor can be found from fits. For two dimensions it is proportional to $\mu_t \Delta k$ where Δk is the length of the critical line and μ_t is the mass transverse to the infinite one. For three dimensions the amplitude factor is proportional to $\mu_t \mu_l^{1/2}$, where μ_l is the longitudinal mass. The uncertainty in μ_l can be factors of 10–100, whereas for k it is usually no more than a factor of 2. So obviously it is better to use 2D rather than 3D if one mass is large compared to the others.

It is our claim, therefore, that the fits we will show here are unique only in the sense that no other pair of one-electron functions could do better over the entire range of fields. We cannot claim to have discovered an M_1 in the spectrum of silicon; two half-oscillations are insufficient to characterize any critical point. We only claim that it can best be fit with an M_1 .

B. Fitting procedures

Once it was established that the pair $M_0^{2D} + M_{1-}^{3D}$ could best fit the data it became necessary to systematize the procedure of fitting. We decided initially to ignore spin-orbit effects. This is not a radical assumption since the splitting is so small (about 30 meV [26]) and our signals have such large half-oscillations (width about 125 meV). Neglecting the splitting introduces an uncertainty in the energy gap of about 15 meV and causes us to overestimate the strength of the transitions by about 10%. Since neglecting Coulomb effects has just the opposite effect of the latter, this is not a serious error.

There were five measurements taken at five different fields. From the data we obtained five pairs of curves, $\Delta\epsilon_1$ and $\Delta\epsilon_2$ representing ten semi-independent determinations of band parameters.

Just what are the band parameters referred to here? The functional forms we used contained eight of them, two each of the following: (i) an amplitude factor, proportional to $p^2 \Delta k$ for the M_0^{2D} and to p^2 for the M_1^{3D}, where p is the dipole matrix element for unpolarized light; (ii) an energy gap Eg; (iii) an electrooptic energy $\hbar\theta$ proportional to $F^{2/3}/\mu^{1/3}$, where μ is the reduced mass in the direction of the field F; and (iv) a broadening energy $\hbar\gamma$. The precise expressions used were[10]

$$\Delta\epsilon_1(\omega) = (\hbar\omega)^{-2}\left[A_1 G_2\left(\frac{E_{g1} - \hbar\omega}{\hbar\theta_1}, \frac{\hbar\gamma_1}{\hbar\theta_1}\right) + A_2 G_3\left(\frac{\hbar\omega - E_{g2}}{\hbar\theta_2}, \frac{\hbar\gamma_2}{\hbar\theta_2}\right)\right], \tag{3a}$$

$$\Delta\epsilon_2(\omega) = (\hbar\omega)^{-2}\left[A_1 F_2\left(\frac{E_{g1} - \hbar\omega}{\hbar\theta_1}, \frac{\hbar\gamma_1}{\hbar\theta_1}\right) - A_2 F_3\left(\frac{\hbar\omega - E_{g2}}{\hbar\theta_2}, \frac{\hbar\gamma_2}{\hbar\theta_2}\right)\right], \tag{3b}$$

where F_2 and G_2 are the two-dimensional F and G functions and F_3 and G_3 the corresponding three-dimensional functions as defined in Ref. 13.

The amplitude factors A_1 for the M_0^{2D} and A_2 for the M_{1-}^{3D} are

$$A_1 = 12(2e^2 p^2/m^2)\ \mu_t \Delta k\ , \tag{4a}$$

$$A_2 = d\ \frac{2e^2 p'^2}{m^2}\ \frac{(\hbar\theta)^{1/2}}{\hbar}\ (8\mu_1\mu_2\mu_3)^{1/2}\ , \tag{4b}$$

where p and p' are the polarization-averaged dipole

matrix elements; μ_t is the transverse reduced mass along Λ, μ_1, μ_2, and μ_3 are the unknown reduced masses of the M_1^{3D}; and Δk is the length of the critical level along Λ. The factors 12 and d are the degeneracy factors of the M_0^{2D} and M_{1-}^{3D}, respectively. For the M_0^{2D} it is 12 rather than 16 since the members of the star of k parallel to the field give no contribution. For the M_0^{2D} with the assumption of a transition and field along that direction, one finds

$$(\hbar\theta_1)^3 = \tfrac{1}{2}\hbar^2 e^2 F^2 \frac{8}{9\mu_t} . \tag{5}$$

Therefore, μ_t can be determined from $\hbar\theta_1$. Using (4a), then, one can determine $p^2\Delta k$.

Eight parameters cannot simultaneously be determined from these data sets. However, there is enough information to unambiguously determine five or six and we will report these here.

C. Results of the fits

For the sake of brevity, only the lowest- and highest-field fits are shown in Figs. 5 and 6, respectively. In each the heavy dashed line is the fit and the light dashed lines are the components due to M_0 and M_1. One can see that these are quite good fits. As a measure of goodness, we have chosen the normalized standard deviation σ_n, the standard deviation divided by the rms average of the data set

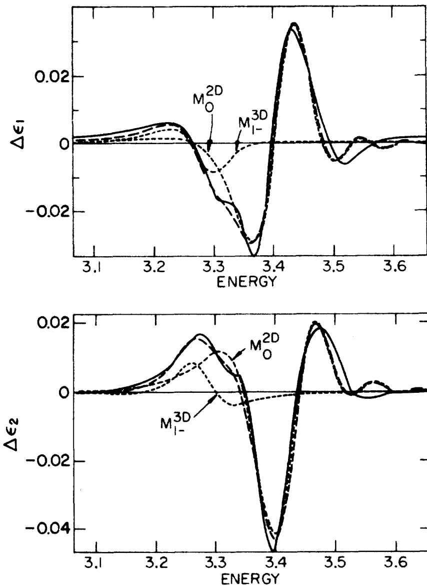

FIG. 5. Data curves and best fits of the lowest-field (78-kV/cm) $\Delta\epsilon_1$ (top) and $\Delta\epsilon_2$ (bottom) data. In each the solid line is the data, the small dashed lines are the contributions of the M_0^{2D} and M_{1-}^{3D} as labeled, and the heavy dashed line is the sum of the latter representing the total fit.

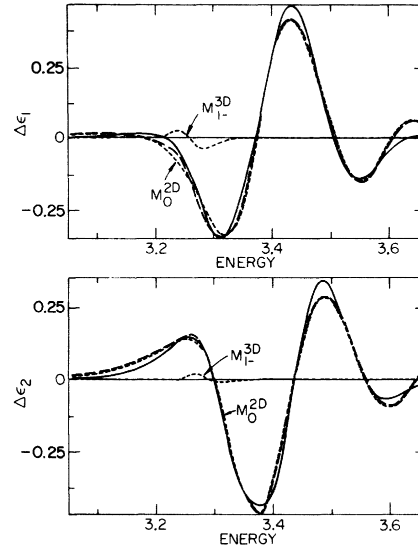

FIG. 6. Data curves and best fits of the highest-field (310-kV/cm) $\Delta\epsilon_1$ (top) and $\Delta\epsilon_2$ (bottom) data. As in Fig. 5, the solid line is the data, the small dashed lines are the M_0^{2D} and M_{1-}^{3D} components, and the heavy dashed line is the total fit.

$$\sigma_N^2 = \sum_i (D_i - F_i)^2 \Big/ \sum_i D_i^2 , \tag{6}$$

where D_i and F_i are data and fit points, respectively.

For Fig. 5, $\sigma_N = 0.181$ for $\Delta\epsilon_1$ and 0.186 for $\Delta\epsilon_2$. For Fig. 6, $\sigma_N = 0.140$ for $\Delta\epsilon_1$ and 0.135 for $\Delta\epsilon_2$. For the other six fits, the values of σ_N obtained were similar, in no case exceeding 0.189. We have found from experience in curve fitting that these are very good values for σ_N. As noted above, we have obtained several numerical values from these fits whose standard deviations are small enough to be meaningful. These values and their standard deviations among the ten fits are: for the M_0^{2D}, $E_g = 3.360 \pm 0.016$ eV, $\hbar\gamma_1 = 53.22 \pm 2.36$ eV, $\mu_t = (0.022 \pm 0.011)m$, $np^2\,\Delta k = (2.80 \pm 0.78)(\hbar/a_0)^2$; for the M_{1-}^{3D}, $E_g = 3.281 \pm 0.007$ eV, $\hbar\gamma_2 = 51.77 \pm 12.86$ eV. The quantity $np^2\Delta k'$ comes from the amplitude factor for the M_0^{2D}; n is the degeneracy factor, assumed to be 12 here; p is the polarization averaged dipole matrix element. $\Delta k'$ is the length of the critical line between Γ and L in units of the distance between Γ and X. Thus, $\Delta k'$ may take on values from 0 to 0.866. As a practical limit, 0 is not very meaningful; a more reasonable estimate might be ~ 0.3. In this case, the upper bound on p is about 0.9. The upper limit on $\Delta k'$, 0.866, gives a lower bound on p of about 0.5. If we assume the bands are parallel for 80% of the Γ-L line, we get $p \sim 0.56\hbar/a_0$ which we will take as

TABLE II. Comparison of numerical results to literature.

Number	Experiment	Literature
$E_g(\Lambda_3 \rightarrow \Lambda_1)$	3.360 eV	3.42 eV[a]
		3.13, 3.37, 3.60 eV[b]
		3.20 eV[c]
$\mu_t(\Lambda_3 \rightarrow \Lambda_1)$	$0.22m$	$0.11m$[b]
		$0.10m$[c]
$p(\Lambda_3 \rightarrow \Lambda_1)$	$0.56\hbar/a_0$	0.45[d]
$E_g(M_{1-}^{3D})$	3.281 eV	none

[a]Reference 27.
[b]Reference 25.
[c]Reference 24.
[d]Reference 21.

our best estimate. The number 80% is reminiscent of the values found for Ge[7] and GaAs.[8]

IV. CONCLUSIONS AND DISCUSSION

In Table II we display the meaningful results of Sec. III and published values from the literature for comparison. There can be little quarrel with the energy gaps since they fall into the specified range. As usual, p is larger than the accepted value. This has always been the case in electroreflectance when Coulomb effects are ignored.[28] Our value of $0.56\hbar/a_0$ must be considered an upper bound. The value for μ_t is disturbingly small, a factor of 5 smaller than those of Saravia and Brust[25] and Dresselhaus and Dresselhaus.[24] We know of no other independent experimental determination of this number and so present it here without further comment.

The shortcomings of the one-electron theory have been well documented and indeed we agree with many of the objections. The excellent results of Dow, Blossey, and others deserve to be incorporated more often than they have been. However, the numerical procedures required in fitting are far more tedious than the closed-form one-electron method and the theory requires the introduction of yet another adjustable parameter, the exciton rydberg. The most reliable parameters obtainable from electroreflectance are μ_F and E_g. For these data, either theory will give the same result. (In private communication, Blossey has shown that even in excitonic theory, the width of the third half-oscillation in $\Delta\epsilon_2$ is very nearly $\hbar\theta$. This gives a result, $\mu_t = 0.021m$ at 310 kV/cm, in fine agreement with our result.) Since the excition rydberg must be assumed small here, it can be presumed that our E_g will be close to the exciton value.

The major objection to the one-electron theory here lies in the determination of p. We have already alluded to this above. Calling our value of 0.56 an upper bound is, we believe, quite reasonable in view of the known effects of the Coulomb interaction.

What sort of conclusions may be drawn from the foregoing analysis? First and foremost, the interpretation of the 3.4-eV structure in terms of nearly degenerate transitions along a Λ critical line is justified but incomplete. There is a second transition taking place at lower energy that is much weaker and may be an M_1. It manifests itself at low fields but is dwarfed by the larger structure at high fields.

It can be concluded that these data are high-field nonasymptotic line shapes unfit for comparison with the low-field theory. In the fits $\Gamma = \hbar\gamma/\hbar\theta$ ranged from a high of about 1.04 to a low of about 0.5 for the M_0^{2D}. This is well outside the strict asymptotic limit of $\Gamma > 3$ and even outside of the marginal limit of $\Gamma \gtrsim 1.5$. Thus flatband *was* a necessary condition.

It would be beneficial now to do some low-temperature electroreflectance on silicon in order to try to resolve the third half-oscillation in the alleged M_1 and to see if there is an M_0 below it. Also, there is structure above 3.6 eV which we were unable to resolve successfully with our system.

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