OPTICAL STUDIES OF THE INTERNAL ACCEPTOR STATES IN BORON-DOPED SILICON

by

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We accept this thesis as conforming to the required standard

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ABSTRACT

The introduction of boron into a silicon crystal lattice produces two sets of acceptor impurity states: (i) the "external" states (which include the acceptor ground state) which are associated with the $p_{3/2}$ valence band maxima and are the usual impurity states lying in the forbidden gap, (ii) the "internal" states which are associated with the $p_{1/2}$ valence band maximum and are degenerate with $p_{3/2}$ continuum states. The energies of the transitions from the ground state to the so-called $2p'$, $3p'$ and $4p'$ internal acceptor states are such that the $2p'$, $3p'$ and $4p'$ internal absorption peaks are seen in the infrared.

Three different experiments are performed to study the "internal" spectrum of boron-doped silicon.

(i) The stress-perturbed behavior of the $2p'$ and $3p'$ absorption peaks is studied with the use of calibrated uniaxial stress ($\leq 10^9$ dynes/cm$^2$) and polarized light.

From these data it is deduced that the ground state has a $\Gamma_8$ symmetry while the $2p'$ and $3p'$ internal states each have a $\Gamma_6$ symmetry. In addition the deformation potential parameters of the ground state are calculated to be: $b' = -0.66 \pm 0.04$ eV. and $d' = -2.1 \pm 0.2$ eV. These calculated parameters for the ground state are used to obtain indirectly some information about the deformation potential parameters of the $p_{3/2}$ valence band edge.
(ii) For the temperature range \(5^\circ\text{K} \leq T \leq 60^\circ\text{K}\) the temperature dependences of the breadths of the \(2p'\) and \(3p'\) peaks are measured.

These temperature dependences are attributed to phonon broadening. The phonon broadening mechanism for the \(2p'\) and \(3p'\) peaks is shown to be primarily due to a lifetime effect caused by electron-phonon coupling of the \(2p'\) and \(3p'\) states to the \(p_{3/2}\) valence band states.

(iii) For the impurity concentration range \(2.6 \times 10^{15}\) boron/cm\(^3\) \(\leq N \leq 4.5 \times 10^{17}\) boron/cm\(^3\) the \(2p'\) absorption peak is measured. With increasing concentration this peak is observed to broaden and become very asymmetrical.

Explanations to the above data are presented.
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CHAPTER I - INTRODUCTION

1.1 GENERAL INTRODUCTION

When an atom from Group III of the periodic table replaces an atom in the crystal structure of silicon or germanium a hole is loosely bound to the impurity site (Kohn, 1957). The energy states which this hole can occupy are called the "acceptor states." At low temperatures far infrared absorption peaks are seen due to the photon-induced excitations of this hole from the acceptor ground state to acceptor excited states. From the observed energy positions of these absorption peaks (Burstein et al., 1953; Zwerdling et al., 1960a) the acceptor states in boron-doped silicon have been associated with the $p_{3/2}$ and $p_{1/2}$ valence band maxima. (These acceptor states are shown in figure 1.1. Note that one distinguishes between "external" and "internal" acceptor states. That spectrum which is associated with transitions from the ground state to the external states will be called the "external" spectrum. Similarly, that spectrum which is associated with transitions from the ground state to the internal states will be called the "internal" spectrum.)

Previous optical studies of the acceptor states in boron-doped silicon have been mainly devoted to the external states. The experiments on the external spectra include: the Zeeman-effect measurement (Zwerdling et al., 1960b), the temperature and concentration dependences of the line breadths (Colbow, 1963; White, 1967a and b), the electrical (Stark) effect (White, 1967a and c), and the effect of uncalibrated uniaxial
Figure 1.1 The Approximate Energy Positions of the Boron Impurity States and the Valence Band States in Silicon.
stress (Skoczylas and White, 1965; Fisher and Ramdas, 1965; Onton et al., 1967; Fisher et al., 1966). The theory used to explain these measurements was based on the Effective Mass Theory of Acceptor States (see Kohn (1957) for a detailed description).

The existence of the internal acceptor states in boron-doped and aluminum-doped silicon was first confirmed by Zwerdling et al. (1960a) who observed the associated internal spectra. Zwerdling et al. also performed the Zeeman effect measurements on these spectra. Recently, Onton et al. (1967) and Fisher et al. (1966) completed a comprehensive study of the internal spectra of boron, aluminum, gallium and indium in silicon with and without uniaxial stress and polarized light. Using symmetry arguments, Onton et al. and Fisher et al. were able to deduce the symmetries of the 2p' and 3p' states.

Unlike the external acceptor states the internal states are degenerate with valence band states (see figure 1.1). The effect of this degeneracy has been theoretically considered by Peterson (1964) and Kaplan (1963). Their results indicate that a hole initially in an internal acceptor state will be localized near the impurity site for some time, but will eventually propagate away to a $p_{3/2}$ Bloch state which is degenerate (or nearly degenerate) with this internal state. Therefore, in their description, the internal states are non-stationary and a lifetime (which will be called the
"non-stationary lifetime") is associated with this eventual decay into a $p_{3/2}$ valence band.

1.2 THE PURPOSE AND OUTLINE OF THIS THESIS

The main purpose of this thesis is to understand more clearly the internal acceptor states in boron-doped silicon by an experimental study of the $2p'$ and $3p'$ internal spectrum (i.e. those absorption peaks which are associated with photon-induced transitions from the ground state to the $2p'$ and $3p'$ internal states seen in figure 1.1). A secondary purpose of this thesis is to obtain information about the stress-induced ground state splitting which will enable a calculation of the deformation potential parameters of the ground state and the $p_{3/2}$ valence band edge.

Three sets of experiments were performed.

(i) The boron-doped silicon samples were compressed uniaxially along the $<001>$ or $<111>$ direction and the $2p'$ and $3p'$ spectrum observed for radiation polarized perpendicular and parallel to the stress direction. These experiments were used to deduce the symmetries (and degeneracies) of the ground state and the $2p'$ and $3p'$ internal states. In addition the data were used to calculate deformation potential parameters.

(ii) In the second set of experiments the temperature dependence of the half-widths (the full peak width at half-maximum) of the $2p'$ and $3p'$ peaks was measured. The sample temperature range was $5^\circ K \leq T \leq 60^\circ K$. These experiments were used to understand the temperature dependence of the broadening of these internal peaks.
(iii) The 2p' absorption peak was observed for impurity concentrations in the range $2.6 \times 10^{15}$ boron/cm$^3 \leq N \leq 4.5 \times 10^{17}$ boron/cm$^3$. These experiments were used to examine the concentration dependence of the half-width and the concentration-dependent asymmetry of the 2p' peak.
CHAPTER 2 - THEORY OF ACCEPTOR STATES

2.1 REVIEW OF THE EFFECTIVE MASS THEORY FOR ACCEPTOR STATES

In a perfect lattice each valence electron moves in a periodic potential \( V(r) \) which is produced by the ion cores and the charge densities of all other electrons. The Hamiltonian \( H_0(r) \) for each valence electron is

\[
H_0 = \frac{p^2}{2m_0} + V(r)
\]  

(2.1)

The periodicity of \( H_0(r) \) gives rise to energy bands \( E_m(\kappa) \), where \( m \) is the band index and \( \kappa \) is the wavevector. The one-electron wavefunctions which satisfy \( H_0(r) \) are the Bloch functions \( \Phi_{m\kappa}(r) \). These functions can be written as

\[
\Phi_{m\kappa}(r) = \frac{1}{\sqrt{V}} \; e^{i\kappa \cdot r} \; \psi_{m\kappa}(r)
\]  

(2.2)

where \( \psi_{m\kappa}(r) \) has the periodicity of the lattice.

To theoretically treat acceptor states in boron-doped silicon one can consider a single, positively charged hole moving in the periodic potential of the pure crystal plus a perturbing coulomb-like potential \(-e^2/\kappa_{0}r\) (where \( \kappa_{0} \) is the static dielectric constant of the pure crystal) produced by a negatively charged acceptor ion (Kohn, 1957). In this model the Hamiltonian \( H(r) \) for the (acceptor) hole is

\[
H(r) = H_0(r) - \frac{e^2}{\kappa_{0}r}
\]  

(2.3)

Equation 2.3 will be a good approximation for the true acceptor Hamiltonian at large distances from the impurity site. However, the actual acceptor potential deviates from \(-e^2/\kappa_{0}r\) at small \( |r| \) (Kohn, 1957).

Since the functions \( \Phi_{m\kappa}(r) \) form a complete set, the
acceptor wavefunctions $\psi^\lambda(r)$ of $H(r)$ can be expanded as

$$\psi^\lambda(r) = \sum_m \sum_\omega A^\lambda_m(\omega) \phi^\lambda_m(r)$$  \hspace{1cm} (2.4)

where the summations are over all energy bands and all wavevectors in the first Brillouin zone.

The "effective-mass theory" can be used to obtain approximate solutions for the above coefficients $A^\lambda_m(\omega)$. The important assumptions of this theory are enumerated below (Kohn and Luttinger, 1955)

(i) The acceptor potential (which is assumed to be $-e^2/\kappa_0 r$) is assumed to be weak so that first order perturbation theory can be used. In other words the impurity is said to be a "shallow" impurity.

(ii) The acceptor potential is assumed to be slowly varying over several lattice spacings.

(iii) The periodic Hamiltonian $H_v(r)$ is replaced by an effective Hamiltonian involving an effective mass tensor.

In the effective mass theory $|A^\lambda_m(\omega)|$ is expected to be large only for small $|\omega|$ (i.e. in a Taylor expansion of $A^\lambda_m(\omega)$, terms to order $\omega^2$ need be considered). Therefore, the functions $\phi^\lambda_m(r)$ in equation 2.4 are approximated by

$$\phi^\lambda_m(r) \simeq 1/\sqrt{V} e^{i \mathbf{k} \cdot \mathbf{r}} \Upsilon^\lambda_{m\omega}(r)$$  \hspace{1cm} (2.5)

Defining the envelope functions $F^\lambda_m(r)$ as

$$F^\lambda_m(r) \equiv \sum_\omega A^\lambda_m(\omega) e^{i \mathbf{k} \cdot \mathbf{r}}$$  \hspace{1cm} (2.6)

one can write the effective mass acceptor wavefunctions as

$$\psi^\lambda(r) = \sum_m F^\lambda_m(r) \phi^\lambda_m(r)$$  \hspace{1cm} (2.7)

where the summation over $m$ only includes the valence bands, and $\phi^\lambda_m(r)$ is defined as
\[ \phi_m(r) \equiv \frac{1}{\sqrt{v}} U_{m0}(r) \]  

(2.8)

Compared to \( \phi_m(r) \), the envelope functions \( F_m^3(r) \) are slowly varying. Locally, therefore, \( \psi^1(r) \) of equation 2.7 appears like a Bloch function. Over many lattice sites, however, \( \psi^1(r) \) is slowly modulated by the functions \( F_m^3(r) \) (which is a result of the weak coulomb-like attraction \(-e^2/\epsilon_0 r\) of the acceptor hole to the impurity site).

Since optical absorption peaks are of interest in this thesis (section 1.2), consider the transition probability for electric-dipole transitions from the acceptor ground state \( |g\rangle \) to an excited state \( |\mu\rangle \). This probability is proportional to \( |(\psi^\mu / q \cdot \mathbf{r} / \psi^3)|^2 \), where \( q \) is a unit vector in the direction of the light polarization. Since the \( F_m^3(r) \) are slowly varying compared to \( \phi_m(r) \), one obtains

\[ |(\psi^\mu / q \cdot \mathbf{r} / \psi^3)|^2 \approx \left| \sum_m (F_m^\mu(r) / q \cdot \mathbf{r} / F_m^3(r)) \right|^2 \]  

(2.9)

It is noted that equation 2.9 does not require a knowledge of the Bloch function \( \phi_m(r) \). This result is the practical aspect of the effective mass theory for acceptor states since the envelope functions \( F_m^3(r) \), unlike the Bloch functions \( \phi_m(r) \), can be (approximately) evaluated.

2.2 THE SIMPLE BAND SOLUTION

In the situation in which the valence bands are simply a spin-degenerate parabolic band, Kohn (1957) has shown that the envelope functions \( F_m^3(r) \) are modified hydrogenic wavefunctions. For a simple band, therefore, the effective mass acceptor wavefunctions can be categorized as 1s, 2s, 2p, 3s, etc.
In addition the eigenvalues of these simple band solutions obey a modified Rydberg series

\[ E_n = E_{v,\beta} - \frac{m^*}{2(\pi\hbar)^2} \left( \frac{e^2}{\epsilon_0} \right)^2 n = 1, 2, 3, \ldots \]  

(2.10)

where \( E_{v,\beta} \) is the energy position of the valence band maximum, and \( m^* \) is the effective mass of the valence band (note, energies refer to energies of the bound hole).

Since the ground state wavefunction is associated with the 1s envelope function, equation 2.9 predicts that the strongest optical absorption peaks should be those corresponding to transitions from the ground state to p-like excited states.

2.3 THE EXTERNAL ACCEPTOR WAVEFUNCTIONS IN SILICON

The \( p_{3/2} \) and \( p_{1/2} \) valence band maxima of silicon seen in figure 1.1 are 4-fold and 2-fold degenerate, respectively. Denoting the Bloch functions at these band edges by \( \phi_{m}^{3/2}(\xi) \) (\( m = -3/2, \ldots, 3/2 \)) and \( \phi_{m'}^{1/2}(\xi) \) (\( m' = -1/2, 1/2 \)), respectively, the effective mass wavefunctions for the external acceptor states are (from equation 2.7)

\[ \Psi_{\pm}^{\lambda}(\xi) = \sum_{m = -3/2}^{3/2} F_{\pm}^{\lambda, m}(\xi) \phi_{m}^{3/2}(\xi) + \sum_{m' = -1/2}^{1/2} F_{\pm}^{\lambda, m'}(\xi) \phi_{m'}^{1/2}(\xi) \]  

(2.11)

where \( F_{\pm}^{\lambda, m}(\xi) \) and \( F_{\pm}^{\lambda, m'}(\xi) \) are the envelope functions which modulate \( \phi_{m}^{3/2}(\xi) \) and \( \phi_{m'}^{1/2}(\xi) \), respectively. For silicon these envelope functions satisfy a system of coupled partial differential equations (Kohn and Luttinger, 1955)

\[
\sum_{j' = \frac{3}{2}, \frac{1}{2}} \sum_{m' = -\frac{3}{2}}^{\frac{3}{2}} \{ H_{j, m, j', m'} - \frac{e^2}{\epsilon_0 \hbar} \delta_{j, j'} \delta_{m, m'} \} F_{j, m}^{3/2}(\xi) = F_{j, m}^{3/2}(\xi)
\]  

(2.12)
where $H_{j,m, j', m'}$ is the effective mass Hamiltonian for the valence bands. Since $H_{j,m, j', m'}$ is invariant under inversion and $-e^2/\hbar c r^3$ has spherical symmetry, the functions $F_{j,m}^\lambda(r)$ are eigenfunctions of definite parity.

For the external acceptor states in silicon Schechter (1962) obtained approximate solutions to equation 2.12. He expanded the functions $F_{j,m}^\lambda(r)$ in spherical harmonics

$$F_{j,m}^\lambda(r) = \sum_{\ell' \geq 0} \sum_{m'_{\ell'}} f_{j,m}^{\lambda \ell} (r) Y_{m'_{\ell'}}(\theta, \varphi)$$

(2.13)

Schechter cut off this expansion over $\ell'$ after a few terms and chose the simple form $c_{j,m}^{\lambda \ell} r^{\ell} e^{-r/a_{\ell'}}$ for the $f_{j,m}^{\lambda \ell}$. Using symmetry arguments, he minimized the number of $Y_{m'_{\ell'}}(\theta, \varphi)$ appearing in the expansions. Finally, he solved for the $c_{j,m}^{\lambda \ell}$ and $a_{\ell'}$ using variational techniques. For silicon he showed that the $p_{1/2}$ valence band contribution in equation 2.11 is small (but not negligible) compared to the $p_{3/2}$ contribution. [The external acceptor wavefunctions are said to be primarily "associated" with the $p_{3/2}$ valence band edge.]

[For acceptor states in germanium the $p_{1/2}$ valence band contribution in equation 2.11 can be neglected (Kohn, 1957; Schechter, 1962). Mendelson and James (1964) used a more complete variational method than that of Schechter to calculate the external acceptor wavefunctions of impurities in germanium. Although their method could be extended to handle the problem for silicon, they did not consider this case.]
2.4 THE INTERNAL ACCEPTOR WAVEFUNCTIONS IN SILICON

Zwerdling et al. (1960a) deduced that the eigenvalues of the observed 2p', 3p' and 4p' internal states very nearly obey the modified Rydberg series which one calculates by assuming that these three states are the 2p, 3p and 4p simple band states, respectively, which are associated with the split-off p_{1/2} valence band edge (see section 2.2). In other words the energy eigenvalues of the 2p', 3p' and 4p' states are in close agreement with those eigenvalues of the effective mass simple band wavefunctions

\[ \Psi_{np'}^{(r)} = \sum_{m'=-\frac{1}{2}}^{\frac{1}{2}} F_{nm',m'}^{p'}(r) \phi_{m',m'}^{p'}(r) \quad [n = 2, 3, 4] \quad (2.14) \]

(The summation is only over the spin states)

In equation 2.14 the p_{3/2} Bloch functions are neglected in the expansion of the internal wavefunctions. As mentioned in section 1.1, however, Peterson (1964) and Kaplan (1963) have predicted that the degeneracy of the internal and p_{3/2} band states will cause a "non-stationary lifetime" of a hole initially in an internal state. [The mechanism which scatters this hole from an internal state to a Bloch state is the impurity-potential (-e^2/κ_r).] Therefore, in equation 2.14 additional terms, which involve the p_{3/2} Bloch functions, must be included to describe this lifetime effect.

The non-stationary lifetime causes lifetime-broadenings of the internal absorption peaks. However, it does not significantly affect the energy eigenvalues of the internal acceptor states. Therefore, the above experimental and theo-
Theoretical results suggest that the $2p'$, $3p'$ and $4p'$ wavefunctions given by equation 2.14 can be used when the non-stationary lifetimes can be ignored.

Estimates of the non-stationary lifetime have been made by Peterson and Kaplan. Applying their results to the present investigation, one would expect a non-stationary lifetime of $10^{-8}$ to $10^{-10}$ seconds for the internal acceptor states in silicon. As it will transpire, this estimated non-stationary lifetime is long compared to another lifetime (phonon-lifetime). Therefore, in the interpretations in this thesis the non-stationary lifetimes were neglected and the np' wavefunctions of equation 2.14 used.
CHAPTER 3 - EXPERIMENTAL DETAILS

3.1 GENERAL APPARATUS

A Perkin Elmer (Model 98G) monochromator equipped with a Bausch and Lomb grating blazed at 16 microns in the first order was used to produce quasi-monochromatic infrared radiation. Light from a globar source was chopped at 13 cycles per second near the entrance slits, and the transmitted radiation detected with a Reeder CsI window vacuum thermocouple. Stray radiation was kept to less than 1% by means of a Perkin Elmer interference filter. Polarized radiation was produced with a Perkin Elmer wire grid polarizer which had a nominal polarization ratio of 525. The amplified signal was displayed on a Honeywell chart recorder.

The spectrometer was calibrated by measuring atmospheric carbon dioxide absorption (Tables of Wavenumbers for the Calibration of Infrared Spectrometers, 1961). From the calibration spectra the resolving power of the spectrometer was observed to be approximately 1000. During the experiments the spectrometer was continuously flushed with nitrogen gas which effectively removed all traces of atmospheric carbon dioxide absorption. (In the photon energy range of interest, 80 to 90 meV., only the carbon dioxide absorption was observed in the atmospheric absorption)

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† The "Polarization Ratio" (P.R.) is defined as $P.R. = \frac{I_\parallel}{I_\perp}$, where $I_\parallel$ and $I_\perp$ are the transmitted intensities through two polarizers (both identical to the one used) for parallel and perpendicular polarization positions, respectively.
Two metal liquid helium dewars were used. One was a temperature controlled dewar operating in the range 5°K to 100°K; the other, a calibrated uniaxial stress dewar which could produce a maximum compressive stress of $10^9$ dynes/cm$^2$ in the silicon samples.

The temperature controlled dewar was constructed and described in detail by McPherson (1965). Modifications, however, were made. The dewar sample holder was redesigned (see figure 3.1a) to hold each sample by only one end. In this manner strain-free sample mounting was achieved (White, 1967a). A small amount of grease was used to improve the thermal contact. The sample temperature was assumed to be very nearly that of the dewar tail (i.e. within one degree Kelvin). This assumption seemed reasonable since the effect of bolting the sample less tightly to the dewar tail did not change the observations (which would be the case for good thermal contact between the sample and sample holder). A Solitron germanium resistance thermometer, which was calibrated by the manufacturer to $\pm 0.1^\circ$K in the temperature range 4.2°K to 100°K, was tightly screwed into the dewar tail (see figure 3.1a). To minimize temperature gradients near the sample-region of the sample holder, the heater which varied the sample temperature (McPherson, 1965) was removed from the sample holder and repositioned on the stainless steel tube leading to the liquid helium container (see figure 3.1a).

A metal stress dewar was constructed. Lower and upper yokes were used to retain the sample which was to be compressed
Figure 3.1 Sketches of the Sample Holders for (a) the Temperature Controlled Dewar, and (b) the Uniaxial Stress Dewar.
uniaxially. Sample compression was obtained by tension on a stainless steel wire which rotated four pulleys attached to the yokes (see figure 3.1b). The sample was tightly held in a vise-arrangement which was part of the upper yoke (figure 3.1b). Since the lateral sample stress due to this vise-arrangement was very much greater than the calibrated uniaxial stress, the thermal contact between the sample and the dewar tail was dependent only on the former stress (i.e. not the calibrated uniaxial stress). Therefore, a sample temperature which was nearly independent of the calibrated uniaxial stress was achieved. This sample temperature was not measured, however, a comparison of the breadth of absorption peak $3\nu'$ for zero-stress with that measured with the temperature controlled dewar indicated that this temperature was less than $15^\circ$K. (The breadth of the $3\nu'$ peak was used rather than that of the $2\nu'$ peak because the former peak begins to broaden at a lower temperature than the latter one, see section 4.2 and figure 4.5) The stress produced by the vise-arrangement was not transmitted into the sample region where the infrared beam passed. To check the performance of the stress dewar samples of cross-sectional areas in the range $0.04 \text{ cm}^2$ to $0.12 \text{ cm}^2$ were used. For each sample the same stress results were obtained. Therefore, negligible sample buckling and pulley friction was indicated.

3.2 SAMPLES

All samples were cut from float-zoned boron-doped silicon ingots which were purchased from Semi-Elements Inc. All but one ingot had nominally $5.0 \times 10^4$ dislocation lines per cm$^2$. 
The remaining ingot was special in that it had a low dislocation count \( \approx 10^3 \) lines/cm\(^2\).

Surface damage due to sample cutting was removed by grinding and polishing. The thick samples (>0.01 cm thick) were ground with \#600 mesh carborundum on glass and then polished with \#600 carborundum on Astromat cloth† to a mirror finish. The thin samples (<0.01 cm thick) were prepared more carefully by using \#800 mesh grinding compound on glass, \#800 compound on Astromat cloth and, finally, 0.1 micron micropolish on silk. (This sort of sample polishing has also been used by White (1967a) in his investigations of the external absorption spectra.)

The ingots were oriented to ±1 degree using Laue X-ray techniques. Using a jig, the ends of the samples for the stress experiments were ground flat with \#600 mesh carborundum on glass.

3.3 MEASUREMENT AND CALCULATION OF ABSORPTION COEFFICIENTS

In all experiments the absorption coefficient, \( \alpha(\nu) \), of the extrinsic sample under investigation was desired. When the temperature controlled dewar was used an intrinsic sample was always mounted so that the extrinsic transmission, \( T_{ex} \), could be compared to the intrinsic transmission, \( T_{in} \), by

† Astromat cloth is a Precision Scientific Instruments product. It is a durable cloth with a very short nap, for polishing surfaces.
rotating the extrinsic and intrinsic samples in and out of the light beam. From the quotient transmission $T_{ex}/T_{in}$ the extrinsic absorption coefficient ($\alpha(\nu)$) was calculated using the formula

$$\frac{T_{ex}}{T_{in}} = \frac{e^{-\alpha(\nu)d}}{(1 - R^2 e^{-2\alpha d'})} \frac{(1 - R^2 e^{-2\alpha d'})^{d'}}{R^2 e^{-2\alpha d'}},$$

(3.1)

where $\alpha_{in}(\nu)$ is the intrinsic lattice absorption (Collins and Fan, 1954), $R$ is the reflectivity, and $d$ and $d'$ are the extrinsic and intrinsic sample thicknesses, respectively. The surface reflectivity ($R$) in the photon energy range 80 to 90 meV. is $0.34 \pm 0.02$ (McCarthy, 1963; White, 1967a). Within experimental error, the reflectivity for both the intrinsic and extrinsic silicon remained constant over the photon energy and temperature ranges of interest. The advantage of calculating $\alpha(\nu)$ from $T_{ex}/T_{in}$ (equation 3.1) is that the calculation is not sensitive to the uncertainty in $R$. Equation 3.1 assumes parallel sided samples. Care was taken to prepare samples with uniform thicknesses. Little error ($<1\%$), however, was introduced by using a non-parallel sided sample since $\alpha d', d'$ and $\alpha d$ were always $>0.1$.

The stress dewar did not permit a direct comparison of the extrinsic and intrinsic transmissions. However, with no applied stress the extrinsic transmission of the stress-sample was scaled to equal that obtained using the temperature controlled dewar. In this way the extrinsic transmission from the stress dewar was matched-up with the appropriate intrinsic transmission obtained from the temperature controlled dewar.
and equation 3.1 (again) used to calculate $\alpha(\nu)$.

The intrinsic lattice absorption ($\alpha^{\text{int}}(\nu)$), which was used in equation 3.1, was measured by comparing the transmissions of intrinsic samples of different thicknesses (see figure 3.2 for these results). For each sample negligible change in $\alpha^{\text{int}}(\nu)$ was observed for the temperature range 6°K to 60°K.

The extrinsic absorption coefficient ($\alpha'(\nu)$) is the combined result of the impurity and lattice absorption mechanisms. Assume that

$$\alpha'(\nu) = \alpha^{\text{imp}}(\nu) + \alpha^{\text{int}}(\nu) \tag{3.2}$$

where $\alpha^{\text{imp}}(\nu)$ is the "impurity absorption coefficient" which is defined as the extrinsic absorption coefficient when the radiation-lattice interaction (i.e. that which gives rise to $\alpha^{\text{int}}(\nu)$) is ignored. Some arguments were made to justify equation 3.2. However, since the mechanism of lattice absorption is not clearly understood (see for example, Gielisse et al., 1964; Johnson, 1959; Lax and Burstein, 1955; Collins and Fan, 1954), the value of these arguments was thought too doubtful for reproduction here. Instead, therefore, equation 3.2 is taken to be a hopeful assumption.

In figure 3.3 typical plots of $\alpha^{\text{imp}}(\nu)$ are seen. One can see that $\alpha^{\text{imp}}(\nu)$ consists of absorption peaks on a background absorption. Suppose that this background absorption, which will be denoted by $\alpha_{\text{b}}(\nu)$, is extrapolated across the 2$p'$, 3$p'$ and 4$p'$ peaks. Define $\alpha^{\text{np'}}(\nu)$ by

$$\alpha^{\text{np'}}(\nu) = \alpha^{\text{imp}}(\nu) - \alpha_{\text{b}}(\nu) \quad [n = 2, 3, 4] \tag{3.3}$$
Figure 3.2 The Intrinsic Lattice Absorption of Silicon for Sample Temperature $6^\circ K \leq T \leq 60^\circ K$. The Error Bars Indicates the Root Mean Square Deviation for Three Experiments.

Away from the peaks (eg. $h\nu = 80.0$ or $84.0$ meV. in figure 3.3) $\alpha_K'(\nu)$ is attributed only to photon-induced transitions from the ground state of the bound hole to $p_{3/2}$ valence band states (see figure 1.1). This photon absorption mechanism will be called the "ionization absorption mechanism."

In this thesis the ionization absorption mechanism is assumed$^\dagger$ to be independent of the presence of the internal

$^\dagger$ In Appendix (A) this assumption is shown to be consistent with the conclusions of this thesis.
Figure 3.3 The Internal Acceptor Absorption Spectrum of Boron-Doped Silicon

\( N = 2.6 \times 10^{15} \text{ boron/cm}^3 \)

observed spectra
(slit width = 0.30 mm)
acceptor states. This assumption implies that the background absorption \( \alpha_{\text{b}}(\nu) \) would be equal to \( \alpha_{\text{imp}}(\nu) \) if the internal acceptor states were not present. Therefore, \( \alpha_{\nu}(\nu) \) is attributed to the increase in \( \alpha_{\text{imp}}(\nu) \) due to the presence of the internal acceptor states. \( \left[ \alpha_{\eta}(\nu) \right. \) and \( \alpha_{\eta}(\nu) \) will be called the "ionization absorption coefficient" and "internal absorption coefficient", respectively. In this thesis, which is an optical study of the internal acceptor states, the \( \alpha_{\eta}(\nu) \) is of interest.
CHAPTER 4 - EXPERIMENTAL RESULTS

4.1 BEHAVIOR OF THE 2p' AND 3p' SPECTRUM UNDER CALIBRATED UNIAXIAL STRESS

Measurements of the 2p' and 3p' spectrum were made for calibrated uniaxial stress in the <001> and <111> directions. In all stress experiments the radiation propagated in a direction which was equivalent to the <110> direction and perpendicular to the stress direction. The sample temperature was less than 15°K and very nearly independent of the stress (section 3.1).

Figure 4.1 shows this perturbed spectrum for stress in the <111> direction and "unpolarized" (neglecting polarization effects of the grating) radiation. Within experimental error identical results were obtained for stress in the <001> direction. Under the available stresses (≤10^9 dynes/cm^2) the 2p' and 3p' peaks were observed to split into only two components.

In figures 4.2 and 4.3 the effects of polarized light on the 2p' and 3p' stress-perturbed spectrum are shown.

In figure 4.4 the peak positions of the stress-induced components of the 2p' and 3p' peaks are plotted against the stress.

4.2 TEMPERATURE DEPENDENCE OF THE TRUE BREADTHS OF THE 2p' AND 3p' PEAKS

The 2p' and 3p' spectrum was measured for the temperature range 5°K to 60°K and then the extrinsic absorption coefficients were corrected for instrumental broadening (see Appendix B).
Figure 4.1 The 2p' and 3p' Spectrum under Uniaxial Stress. The Vertical Arrows Indicate the Zero-Stress Peak Positions. The Radiation Is Unpolarized. The Error Flags Represent the Reproducibility of Four Runs Through the Peaks.
STRESS IN $\langle001\rangle$
DIRECTION (3.1 x 10^8 dynes/cm^2)

$N = 2.6 \times 10^{15}$ boron/cm^3

$T \leq 15^\circ K$

observed spectrum
(slit width = 0.45mm)

Figure 4.2 The $2p'$ and $3p'$ Spectrum under Uniaxial Stress in the $\langle001\rangle$ Direction and with Polarized Radiation. The Vertical Arrows Are the Zero-Stress Peak Positions. The Error Flags Indicate the Reproducibility of Four Experiments.
Figure 4.3 The 2p' and 3p' Spectrum under Uniaxial Stress in the <111> Direction and with Polarized Radiation. The Vertical Arrows Are the Zero-Stress Peak Positions. The Error Flags Indicate the Reproducibility of Four Experiments.
Figure 4.4 Stress-Induced Splitting of the 2p' and 3p' Spectrum. Solid Lines Represent Stress Parallel to (111) Direction; Dashed Lines Represent Stress Parallel to (001) Direction. Each Straight Line Was Obtained by a Least Square Fit. The Standard Errors for the 2p' Straight Line Fits Are Represented by Error Flags I. The Random Error Associated with the Individual Data Points Are Indicated by the Error Flags Ⅰ. T < 15°K
Using the approximations given by equations 3.2 and 3.3, the background lattice and ionization absorptions were subtracted and the 2p' and 3p', internal absorption peaks $\alpha_{2p'}(\nu)$ and $\alpha_{3p'}(\nu)$ plotted. These peaks were approximately Lorentzian in shape. For the above temperature range (5°K ≤ T ≤ 60°K) the true half-widths $h_{2p'}(T)$ and $h_{3p'}(T)$ of the $\alpha_{2p'}(\nu)$ and $\alpha_{3p'}(\nu)$ peaks, respectively, were measured. In figure 4.5 these half-width results are shown for the impurity concentration equal to 2.6 x 10$^{15}$ boron/cm$^3$. Increasing the concentration from 2.6 x 10$^{15}$ boron/cm$^3$ to 1.2 x 10$^{16}$ boron/cm$^3$ resulted in an increase in $h_{2p'}(T)$ and $h_{3p'}(T)$ of less than 0.04 meV. for the above temperature range. In addition, experiments were attempted on samples with impurity concentrations 1.0 x 10$^{15}$ boron/cm$^3$ and 5.0 x 10$^{14}$ boron/cm$^3$. At these low concentrations, however, $\alpha_{lat}(\nu)$ is approximately equal to $\alpha_{imp}(\nu)$ and thick samples (≈ 0.8 cm) were cut to yield well defined internal spectra. Since the strong background lattice absorption considerably reduced the transmitted radiation, increased signal amplification was necessary. Considerable amplifier noise resulted so that good quantitative measurements for these low concentrations were not possible.

The results obtained from a low-dislocation sample (< 10$^3$ dislocation lines/cm$^2$) were similar to those obtained from the above samples with approximately 5 x 10$^4$ dislocation lines/cm$^2$. Taking the experimental errors into account, the dislocation broadening $h_d^{2p'}$ of the $\alpha_{2p'}(\nu)$ peak was estimated.
Figure 4.5 Temperature Dependence of the True Half-Widths of (a) the 3p′ Absorption Peak, and (b) the 2p′ Absorption Peak. The Error Flags Indicate the Reproducibility of Four Experiments.
to be (Kohn (1957) describes this broadening)

$$h_{d}^{2p'} \lesssim 0.05 \text{ meV. (for } 5 \times 10^{4} \text{ disl. lines} / \text{cm}^{2})$$ (4.1)

The weak $4p'$ absorption peak was observed only for temperatures less than $10^0K$.

4.3 CONCENTRATION DEPENDENCE OF THE $2p'$ PEAK

In figure 4.6 the effect of increasing the impurity concentration from $2.6 \times 10^{15}$ boron/cm$^3$ to $4.5 \times 10^{17}$ boron/cm$^3$ on the normalized $2p'$ internal absorption peak ($\alpha_{2p'}(\nu)$) is seen. The sample temperature was $6.5 \pm 1.5^0$K. Extreme care was taken in preparing the sample surfaces and mounting the samples in a strain-free manner (section 3.2). In table 4.1 the integrated absorption cross-sections for the peaks in figure 4.6 are tabulated. [For impurity concentrations greater than $4 \times 10^{16}$ boron/cm$^3$ the weak $3p'$ internal absorption peak was not well defined. Therefore, no similar measurements of the concentration behavior of the $3p'$ peak were possible.]

<table>
<thead>
<tr>
<th>N (boron/cm$^3$ x 10$^{16}$)</th>
<th>.26$^{\dagger}$</th>
<th>1.3$^{\dagger}$</th>
<th>4.3$^{\dagger}$</th>
<th>8.8$^{\dagger}$</th>
<th>45.1$^{\dagger}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sum_{2p'}/N$ (cm$^2$ meV. x 10$^{-15}$)</td>
<td>4.0$^{\dagger}$</td>
<td>3.6$^{\dagger}$</td>
<td>4.0$^{\dagger}$</td>
<td>3.9$^{\dagger}$</td>
<td>5.1$^{\dagger}$</td>
</tr>
</tbody>
</table>

$^{\dagger}$ four-point probe measurements at $300^0K$. estimated error 10%

$^{\dagger}$ estimated error 20%

$^{\dagger}$ estimated error 40%

$^{\star}$ $\sum_{2p'} \equiv h \int_{0}^{\infty} \alpha_{2p'}(\nu) d\nu$, where $h$ is Planck's constant.
Figure 4.6  The Concentration Behavior of the 2p' Absorption Peak. The $2.6 \times 10^{15}/\text{cm}^3$ and $8.8 \times 10^{16}/\text{cm}^3$ Curves Each Represent Two Different Experiments on Different Samples. The Error Flags Respresent the Reproducibility of Four Runs Through the Spectrum.
CHAPTER 5 - INTERPRETATION OF THE UNIAXIAL STRESS RESULTS

In this chapter the experimental data on the 2p' and 3p' stress-perturbed spectrum are analyzed (figures 4.1, 4.2, 4.3, and 4.4). The main purpose of this stress investigation is to deduce the symmetries of the wavefunctions for the ground state and the 2p' and 3p' (non-stationary) states. The secondary purpose is to obtain the deformation potential parameters for the ground state and the p_{3/2} valence band edge.

[Kohn (1957) first suggested the use of stress perturbations in the study of impurity spectra.]

5.1 ZERO-STRESS SYMMETRY PREDICTIONS

This section considers the theoretical symmetries of the wavefunctions of the acceptor ground state and the 2p' and 3p' non-stationary states. In part (a) below, the symmetries of the associated effective mass wavefunctions are considered. In part (b), corrections to the effective mass formulation are discussed and the theoretical "true" symmetries obtained.

\[\text{\textsuperscript{+}}\]

\[\text{\textsuperscript{+}}\] This chapter considers the stress-induced splittings of acceptor energy levels and the selection rules and relative intensities for electric-dipole transitions which are associated with the stress-perturbed internal spectra for polarized light. Since the non-stationary lifetimes of the internal states do not affect these phenomena (i.e. lifetime effects primarily broaden absorption peaks), the symmetries of the "non-stationary" 2p' and 3p' wavefunctions are of importance here.
(a) Symmetries of the Effective Mass Wavefunctions

Since the approximate acceptor potential $-e^2/k_0r$ has spherical symmetry, the acceptor Hamiltonian $H(\varepsilon)$ in equation 2.3 has the symmetry group of the crystal Hamiltonian $H_0(\varepsilon)$. This symmetry group is the full cubic group $\overline{O}_h$ (group theoretical notation will be that of Koster et al., 1963). Under $\overline{O}_h$ the effective mass wavefunctions given by equation 2.7 transform as the representation product

$$\Gamma_\alpha = \Gamma_F \times \Gamma_\phi$$ (5.1)

where $\Gamma_F$ and $\Gamma_\phi$ are the representations of $\overline{O}_h$ which are generated by the envelope functions $F_{m(\varepsilon)}^{\lambda}$ and the Bloch functions $\phi_{m(\varepsilon)}$, respectively.

Now, consider the symmetry of the effective mass wavefunctions $\Psi_\alpha(\varepsilon)$ for the ground state. From equation 2.11 these wavefunctions are given by

$$\Psi_\alpha(\varepsilon) = \sum_{m=3/2}^{5/2} F_{m(\varepsilon)}^{3/2} \phi_{m(\varepsilon)}^{3/2} + \sum_{m'=3/2}^{11/2} F_{m(\varepsilon)}^{11/2} \phi_{m'(\varepsilon)}^{11/2}$$ (5.2)

The envelope functions $F_{m(\varepsilon)}^{3/2}$, which modulate the $p_{3/2}$ Bloch functions $\phi_{m(\varepsilon)}^{3/2}$, are finite at $r=0$ (Schechter, 1962). In equation 2.13, therefore, the expansion of $F_{3/2(\varepsilon)}^{3/2}$ in spherical harmonics $Y_{l',m'}(\theta, \phi)$ must contain $l'=0$ terms. Since $\Psi_\alpha(\varepsilon)$ transforms as the identity representation $\Gamma_1^+$, the representation generated by $F_{3/2(\varepsilon)}^{3/2}$ must contain $\Gamma_1^+$ (Bir et al., 1963). Since the $p_{3/2}$ Bloch functions $\phi_{m(\varepsilon)}^{3/2}$ transform as $\Gamma_8^+$ under $\overline{O}_h$, therefore, one obtains from equation 5.1

$$\Psi_\alpha(\varepsilon) \sim \Gamma_1^+ \times \Gamma_8^+ = \Gamma_8^+ \text{ under } \overline{O}_h$$ (5.3)

for the effective mass wavefunctions of the acceptor ground
Now, consider the symmetries of the effective mass wavefunctions for the non-stationary $2p'$ and $3p'$ states. As section 2.4 explained, these wavefunctions are given by equation 2.14. Under $\bar{O}_h$ the envelope functions $F_{\mu_m}(r)$ for the $np'$ states transform as $\Gamma_7^-$; while the $p_{1/2}$ Bloch functions $\Phi_{m,\ell}^{1/2}(r)$, as $\Gamma_7^+$. Therefore, from equation 5.1 one obtains

$$\psi_{np'}(r) \sim \Gamma_7^- \times \Gamma_7^+ = \Gamma_7^- + \Gamma_7^+ \text{ under } \bar{O}_h$$

for the effective mass non-stationary $np'$ wavefunctions.

(b) Symmetries of the True Acceptor Wavefunctions

Since the approximate acceptor Hamiltonian given by equation 2.3 is invariant under inversion, the effective mass wavefunctions are associated with parity. However, the true acceptor Hamiltonian is not invariant under inversion. The true acceptor symmetry group is that of the impurity site - the full double tetrahedral group $\bar{T}_d$ (Dresselhaus, 1955; Parmenter, 1955). \[ \text{Note: } \bar{O}_h = T_d \times C_i \text{, where } C_i \text{ is the group of the inversion (Koster et al., 1963)} \]

To obtain the "true" symmetry predictions for the wavefunctions of the ground state and the $2p'$ and $3p'$ states, a correction perturbation with symmetry $\bar{T}_d$ must be added to the approximate Hamiltonian of equation 2.3. The effective mass wavefunctions, therefore, can be considered as the acceptor wavefunctions to zero-order in this correction perturbation. For the symmetry reduction $\bar{O}_h \rightarrow \bar{T}_d$, Koster et al. (1963) give $\Gamma_7^- \rightarrow \Gamma_7$ and $\Gamma_7^+ \rightarrow \Gamma_7$. Therefore,
one obtains from equations 5.3 and 5.4

\[ \psi^\Lambda_{\alpha}(c) \sim \Gamma^\Lambda \ \text{under } \overline{T_d} \]

(5.5)

and

\[ \psi^{m'}(c) \sim \Gamma^6 \ \text{or } \Gamma^8 \ \text{under } \overline{T_d} \]

(5.6)

for the predicted "true" symmetries. As equation 5.6 indicates this correction perturbation splits the effective mass \((\Gamma_7^- + \Gamma_8^-)\) level into one \(\Gamma^6\) level and one \(\Gamma^8\) level. These symmetries for the np' internal states were first deduced by Onton et al. (1967).

It is noted here that the true degenerate acceptor wavefunctions, which correspond to a particular energy level, must transform as one of the extra irreducible representations \(\Gamma^6, \Gamma^7\) or \(\Gamma^8\) of \(\overline{T_d}\). Since \(\Gamma^6, \Gamma^7\) and \(\Gamma^8\) are 2-, 2-, and 4-dimensional representations, respectively, the possible degeneracy (including spin) of an acceptor energy level is 2 or 4.

5.2 OBSERVED STRESS-INDUCED SPLITTINGS OF THE 2p' AND 3p' PEAKS

In this section the symmetry of the wavefunctions for the ground state in boron-doped silicon is established.

Consider figure 4.1. Under uniaxial stress both the 2p' and 3p' absorption peaks split into two components. With increasing stress, furthermore, the intensities of the higher photon energy components increase, while those of
the lower ones decrease.

These stress-induced splittings of the 2p' and 3p' peaks are attributed to a splitting of the ground state. As the arguments below will show, this interpretation is established by the change in relative intensities of the stress-induced components with stress.

In figure 5.1 the relative integrated absorption coefficients $\frac{\Sigma_{\text{low}}}{\Sigma_{\text{high}}}$ for the low and the high photon energy components of the 2p' peak are plotted on semi-log scales against the stress-induced splitting $\xi$ of this peak. The good straight line fit for the data in this figure indicates that

$$\frac{\Sigma_{\text{low}}}{\Sigma_{\text{high}}} \propto e^{-\xi/C}$$  \hspace{1cm} (5.7)

where $C$ is independent of stress. For a ground state splitting $\Delta$ and a sample temperature $T$ the relative populations of the ground state sublevels are described by the Boltzmann factor $e^{-\Delta/kt}$. Since the sample temperature in the present investigation is very nearly independent of the stress (section 3.1), a ground state splitting $\Delta$ which is equal to the splitting $\xi$ of the 2p' peak would be associated with

$$\frac{\Sigma_{\text{low}}}{\Sigma_{\text{high}}} \propto e^{-\Delta/kt} = e^{-\xi/kt}$$  \hspace{1cm} (5.8)

---

$^\dagger$ To obtain the integrated absorption coefficients of the individual components the perturbed 2p' profiles of figure 4.1 were "peeled apart." This method of separating composite profiles into individual peaks has been described by Colbow et al. (1962). The "peeling apart" is achieved by assuming a symmetric profile for each individual component.
With $C = k\tau$ the theoretical result of the above equation is identical to the empirical result of equation 5.7. The agreement of these results establishes the stress-induced splitting of the ground state.† [From the slope of the line in figure 5.1 and using equation 5.8 one calculates a sample temperature of $T = 8.3 \pm 2.5^\circ K$. This temperature agrees with that $T < 15^\circ K$ which was estimated in section 3.1.]

Qualitatively, under uniaxial stress the weaker $3p'$ peak behaved the same as the $2p'$ peak. This similar behavior is consistent with the above interpretation since the de-

† Polarization of the light by the grating does not affect the slope of the curve in figure 5.1. Polarization only changes the zero-stress extrapolation.
population effects in the split ground state is reflected in the relative intensities of the stress-induced components of both perturbed absorption peaks.

Since the possible zero-stress degeneracy of an acceptor energy level is 2 or 4 (section 5.1), the stress-induced splitting of the ground state requires a 4-fold degeneracy for this state. Hence, these stress results indicate a $\Gamma_2$ symmetry for the wavefunctions of the ground state (section 5.1). This symmetry result is consistent with the theoretical prediction given by equation 5.5.

Fisher et al. (1966) and Onton et al. (1967) have also reported the features of the stress-perturbed 2p' and 3p' spectra which were discussed in this section. Furthermore, they were first to suggest that the change in relative intensities of the stress-induced 2p' and 3p' components with stress indicates temperature depopulation effects which are associated with a splitting of the ground state. Unlike the present investigation, however, they did not show quantitatively (i.e. in the manner of figure 5.1) the dependence of these relative intensities on the Boltzmann factor $e^{-\Delta / kT}$.

5.3 THE EFFECT OF POLARIZED LIGHT ON THE STRESS-PERTURBED 2p' AND 3p' SPECTRUM

The purposes of this section are to deduce the symmetries of the wavefunctions for the 2p' and 3p' non-stationary states and to determine the ordering of the stress-induced sublevels of the $\Gamma_2$ ground state.

In the previous section the observed stress-induced splittings of the 2p' and 3p' peaks were attributed to the
ground state splitting. Since only two components were observed for both the stress-perturbed \(2p'\) and \(3p'\) peaks (section 4.1), one might tentatively assume that the \(2p'\) and \(3p'\) states are only spin degenerate and transform as \(\Gamma_6\) or \(\Gamma_7\) under \(T_d\). Since this failure to observe a further stress-induced splitting is not a good criterion to assign degeneracies, the effect of polarized radiation on the stress-perturbed internal spectra has been considered.

As figures 4.2 and 4.3 show, the intensities of the components of the stress-perturbed \(2p'\) and \(3p'\) spectra are very sensitive to the direction of the polarization of light. In particular, for parallel polarization (i.e. for light polarized in a direction which is parallel to the stress direction) the low photon energy components are not observed in either figure. These features of the stress-perturbed internal spectra have been also reported by Fisher et al. (1966) and Onton et al. (1967). The relationship of the present investigation to that of Fisher et al. and Onton et al. will be discussed at the end of this section.

For uniaxial stress in the \(\langle 001\rangle\) direction the symmetry group of the acceptor site is reduced from \(\bar{T}_d\) to \(\bar{D}_{2d}\). Similarly, for stress in the \(\langle 111\rangle\) direction this symmetry group is reduced from \(\bar{T}_d\) to \(\bar{C}_{3v}\). Figure 5.2 shows the allowed electric-dipole transitions for the stress-perturbed \(\Gamma_8 \rightarrow \Gamma_5\), \(\Gamma_8 \rightarrow \Gamma_7\) and \(\Gamma_8 \rightarrow \Gamma_8\) transitions (Koster et al., 1963). Now assume that the apparent absences of the low photon energy components for parallel polarization in figures 4.2
Figure 5.2 Allowed Electric-Dipole Transitions for the Stress-Perturbed Internal Acceptor Spectra. Solid Lines Indicate That the Radiation Is Polarized Parallel to the Stress Direction; Dashed Lines, Perpendicular to the Stress Direction.
and 4.3 are due to electric-dipole selection rules. If the ordering of the stress-induced sublevels of the ground state is that shown in figure 5.2, one can see that these empirical selection rules are explained by the forbidden electric-dipole transitions for the stress-perturbed $\Gamma_0 \rightarrow \Gamma_6$ transitions. For this ordering of the ground state sublevels, therefore, a $\Gamma_6$ symmetry for the 2p' and 3p' wavefunctions is deduced. However, for a reversed ordering of the ground state sublevels for stress in the <001> direction (see figure 5.2) one can also see that a $\Gamma_7$ symmetry for the 2p' and 3p' wavefunctions is deduced. Since the ordering of the ground state sublevels cannot be determined from the present experimental data alone, therefore, both symmetry results are possible here

$$\psi^{n'}(\xi) \sim \Gamma_6 \text{ or } \Gamma_7 \text{ under } \overline{T_d} \text{ (empirical)} \quad [n=2,3] \quad (5.9)$$

However, in section 5.1b $\psi^{n'}(\xi)$ was theoretically predicted to transform as $\Gamma_6$ or $\Gamma_8$ under $\overline{T_d}$ (equation 5.6). Combining these experimental and theoretical results, one obtains

$$\psi^{n'}(\xi) \sim \Gamma_6 \text{ under } \overline{T_d} \text{ (empirical \& theoretical)} \quad [n=2,3] \quad (5.10)$$

With this symmetry assignment for the 2p' and 3p' wavefunctions the ordering of the stress-induced sublevels of the ground state is that shown in figure 5.2.

The empirical symmetry result of equation 5.9 can be checked by considering the relative integrated absorption coefficients of the 2p' stress-induced components. Dickey and Dimmock (1967) and Onton et al. (1967) have calculated $^+$

$^+$ This calculation is described in Appendix C.
the relative transition probabilities (also called "relative intensities") for the allowed electric-dipole transitions which are associated with the stress-perturbed \( \Gamma_8 \rightarrow \Gamma_6 \) and \( \Gamma_8 \rightarrow \Gamma_7 \) transitions (see figure 5.2). For the components of the stress-perturbed \( \Gamma_8 \rightarrow \Gamma_6 \) transition they calculated relative intensities of 3:1:4 for \( (\Gamma_5 + \Gamma_6 \rightarrow \Gamma_6')_\perp : (\Gamma_4 \rightarrow \Gamma_4')_\perp : (\Gamma_4 \rightarrow \Gamma_4')_\parallel \) in \( \bar{C}_{3v} \) (stress in the \( \langle 111 \rangle \) direction), and \( (\Gamma_7 \rightarrow \Gamma_6)_\perp : (\Gamma_7 \rightarrow \Gamma_6)_\parallel \) in \( \bar{D}_{2d} \) (stress in the \( \langle 001 \rangle \) direction). The subscripts \( \perp \) and \( \parallel \) denote the direction of the polarization of light. The intensity ratios of the components of the stress-perturbed \( \Gamma_8 \rightarrow \Gamma_7 \) transition are the same as for the corresponding transitions for \( \Gamma_8 \rightarrow \Gamma_6 \). \(^\dagger\) A similar calculation of the relative intensities is not possible for the stress-perturbed \( \Gamma_8 \rightarrow \Gamma_8 \) transition (see Appendix C). For \( \psi^{2p(\Gamma)} \) transforming as \( \Gamma_6 \) or \( \Gamma_7 \), therefore, one obtains (section 5.2)

\[
\begin{align*}
\sum_{\text{low}}^{\perp} : \sum_{\text{high}}^{\perp} &= 3.0 e^{-\Delta/\kappa T} \\
\sum_{\text{low}}^{\parallel} : \sum_{\text{high}}^{\parallel} &= 4.0
\end{align*}
\]

\[
\text{for stress in the } \langle 001 \rangle \text{ or } \langle 111 \rangle \text{ direction}
\]

where \( \sum_{\text{low}} \) and \( \sum_{\text{high}} \) are the integrated absorption coefficients (defined in section 5.2) of the components of the stress-perturbed \( 2p' \) peak, \( \Delta \) is the stress-induced ground state splitting, and \( \perp \) and \( \parallel \) denote the polarization. For a

\(^\dagger\) Thus, the relative intensities of the components cannot be used to decide whether \( \psi^{2p(\Gamma)} \rightarrow \Gamma_6 \) or \( \psi^{2p(\Gamma)} \rightarrow \Gamma_7 \).
finite \( \Delta \) the above ratio \( \Sigma_{low}^t / \Sigma_{high}^t \) is sensitive to the temperature depopulation effects in the ground state sublevels (section 5.2). However, as figure 5.1 suggests these temperature depopulation effects can be corrected for by extrapolating \( \log \left( \frac{\Sigma_{low}^t}{\Sigma_{high}^t} \right) \) to \( \Delta = 0 \). This extrapolation is carried out in figure 5.3. Since approximately the same ground state splitting is obtained for stress in the \( \langle 001 \rangle \) and \( \langle 111 \rangle \) directions (see figure 4.4), the data for both stress orientations were superimposed in the extrapolation in figure 5.3.] The final measurements of the relative integrated absorption coefficients are summarized in table 5.1.

Table 5.1 Comparison of the Theoretical and Experimental Relative Integrated Absorption Coefficients for the 2p' Stress-Induced Components

<table>
<thead>
<tr>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\Sigma_{low}^t}{\Sigma_{high}^t} )</td>
<td>3.0</td>
</tr>
<tr>
<td>( \frac{\Sigma_{low}^<em>'t}{\Sigma_{high}^</em>'t} )</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*for uniaxial stress in the \( \langle 001 \rangle \) or \( \langle 111 \rangle \) direction

Since these theoretical and experimental results are in agreement, therefore, the relative intensities of the components are compatible with the \( \Gamma_6 \) or \( \Gamma_7 \) symmetry assignment (equation 5.9) for the 2p' wavefunctions.

The experimental errors and the weak intensities associated with the stress-perturbed 3p' peak (see figures 4.2 and 4.3) did not permit a meaningful quantitative relative intensity analysis for this peak.
Figure 5.3 Extrapolation of $\frac{\Sigma_{\text{low}}}{\Sigma_{\text{high}}} \Delta \rightarrow 0$ to Zero-Stress for the 2p' Stress-Induced Components. ($T < 15^\circ K$)
Using uncalibrated uniaxial stress, Fisher et al. (1966) and Onton et al. (1967) recently studied those features of the 2p' and 3p' stress-perturbed spectrum of boron-doped silicon which were considered in this section. They have discussed in detail the selection rules and relative intensities of the stress-induced components for polarized radiation. Using these selection rule arguments and the symmetry predictions of the effective mass theory, they deduced in the manner of this section a \( \Gamma_6 \) symmetry for the 2p' and 3p' states. They indicated qualitative agreement of the theoretical and empirical relative intensities of the stress-induced components.

The investigations of this section, therefore, repeat the measurements of Fisher et al. and Onton et al. as a function of stress. In addition, the present studies have made a quantitative comparison of the theoretical and experimental relative intensities of the stress-induced components of the 2p' peak (i.e. table 5.1).

With the use of polarized light Onton et al. have also observed the 2p' and 3p' stress-induced spectra of aluminum-, gallium-, and indium-doped silicon. For these spectra they observed features which were identical in most details to those exhibited by the internal spectrum of boron-doped silicon.

5.4  CALCULATION OF DEFORMATION POTENTIAL PARAMETERS

The effects of stress on the acceptor ground state in boron-doped silicon can be described in terms of the deformation potential parameters \( a', b' \) and \( d' \) for the ground state. These parameters are analogous to the familiar deformation
potential parameters $a$, $b$ and $d$ for the $p_{3/2}$ valence band edge. These two sets of parameters are described in Appendix D.

In section 5.2 the stress-induced splittings of the $2p'$ and $3p'$ peaks were attributed to the stress-induced splitting of the ground state. Since calibrated stress was used, therefore, the data of figure 4.4 can be used to calculate the splitting parameters $b'$ and $d'$ for the ground state (Appendix D).

In figure 4.4 consider only the $2p'$ data which are associated with smaller experimental errors. Denote the stress-induced splittings of the $2p'$ peak for stress in the $\langle 001 \rangle$ and $\langle 111 \rangle$ directions by $\xi$ and $\xi'$, respectively. With the above discussions and the ordering of the ground state sublevels (see figure D.1b), one obtains from equations D.8 and D.9

$$\xi = 2 b' S (s_{11} - s_{12})$$

and

$$\xi' = \frac{d'}{2} S s_{\gamma\gamma}$$

Using the following elastic compliances (Huntington, 1958)

$s_{11} = 0.768 \times 10^{-12}$, $s_{12} = -0.214 \times 10^{-12}$ and $s_{\gamma\gamma} = 1.256 \times 10^{-12}$ in units of cm$^2$/dyne, figure 4.4 and the above two equations give

$$b' = -0.66 \pm 0.04 \text{ eV. (electron-volts)}$$

$$d' = -2.1 \pm 0.2 \text{ eV.}$$

If the ordering of the ground state sublevels were not known, the results would be $\xi = 2 b' S (s_{11} - s_{12})$ and $\xi' = 1 d' S s_{\gamma\gamma}/2$, so that only the absolute values of $b'$ and $d'$ could be determined.
The shift of the center of gravity of the peak positions of the stress-induced components of the 2p' (or 3p') peak is the net result of the stress-induced shift of the ground state (see Appendix D) and the shift of the 2p' (or 3p') state. As the straight line fits in figure 4.4 show, this shift for the 2p' components is observed to be approximately equal to the experimental errors. Taking these errors into account and assuming that the stress-induced shift of the 2p' state is negligible compared to that of the ground state, figure 4.4 and equations D.8 and D.9 give

\[ 1\sigma' < 0.59 \text{ eV.} \]  

(5.16)

for the shift parameter \( a' \) of the ground state in boron-doped silicon (Appendix D).

The effective mass wavefunctions \( \varphi_n^{m'}(\xi) \) of the ground state are expressed as a linear combination of the Bloch functions \( \varphi_n^{m}(\xi) \) and \( \varphi_n^{m}(\xi) \) as

\[ \varphi_n^{m'}(\xi) = \sum_{n=3s}^{\infty} F_{n, n'}^{m}(\xi) \varphi_n^{m}(\xi) + \sum_{n, \nu} F_{n, \nu}^{m}(\xi) \varphi_n^{\nu}(\xi) \]  

(5.17)

[the above equation is a reproduction of equation 5.2] In terms of the envelope functions \( F_{n, \nu}^{m}(\xi) \), Bir et al. (1963) have related \( b' \) and \( d' \) to \( b \) and \( d \) through the equation

\[ (H_{\xi})_{m, m'} = \sum_{n, n'} (H_{\xi}^{m', m})_{n, n'} (F_{n, n'}^{m}(\xi) | F_{n, n'}^{m}(\xi)) \]  

(5.18)

where \( H_{\xi} \) and \( H_{\xi}^{m', m} \) are the strain Hamiltonians introduced in Appendix D. Using the approximate numerical results of Schechter (1962) [see section 2.3] Bir et al. evaluated equation 5.18 and obtained

\[ 0.77 \leq b'/b \leq 0.84 \]  

(5.19)

\[ 0.82 \leq d'/d \leq 0.93 \]  

(5.20)
The lower and upper bounds in the above equations were obtained by using Schechter's wavefunctions for infinite and zero spin-orbit splittings of the valence bands, respectively. As Bir et al. also explained, in the effective mass theory the stress-perturbed ground state is assumed to shift with the $p_{3/2}$ valence band edge, so that

$$ a = a' $$

(5.21)

Combining the above three theoretical relationships with the empirical results of equations 5.14, 5.15 and 5.16, one obtains

$$ |a| < 0.59 \text{ eV.} $$

(5.22)

$$ 0.74 \text{ eV.} \leq -b \leq 0.91 \text{ eV.} $$

(5.23)

$$ 2.0 \text{ eV.} \leq -d \leq 2.8 \text{ eV.} $$

(5.24)

for the deformation potential parameters of the $p_{3/2}$ valence band edge in silicon. The experimental errors associated with $b'$ and $d'$ are included in the above inequalities for $b$ and $d$.

5.5 CHANGE IN THE STRESS-PERTURBED BACKGROUND ABSORPTION WITH THE DIRECTION OF LIGHT POLARIZATION

Figures 4.2 and 4.3 show that the stress-perturbed background absorption near the internal absorption peaks of boron-doped silicon is dependent on the direction of the polarization. This observation is also reported by Onton et al. (1967).

In section 3.3 the extrinsic background absorption was attributed to ionization and intrinsic lattice absorption. Since a stress experiment on an intrinsic sample indicated no significant change in the lattice absorption for different directions of the polarization of light, the observed change in background absorption is attributed to a stress-induced change in the
ionization absorption.

Since the $p_{3/2}$ valence bands are quite warped (see figure 1.1), the controlling factor which produces this change in ionization absorption might be the density of final states for the corresponding electric-dipole transitions.

5.6 RELATING THESE RESULTS TO OTHER REPORTED RESULTS

(a) Stress-Perturbed External Spectrum

Skoczylas and White (1965) and Fisher et al. (1965) independently investigated the effect of uniaxial stress on the external spectrum of boron-doped silicon. [Fisher et al. used polarized light.] They observed stress-induced splittings of the external absorption peaks. From these data they deduced a stress-induced splitting of the ground state, which is consistent with the result of section 5.2 in the present investigation.

Onton et al. (1967) and Fisher et al. (1966) report detailed studies of this stress-perturbed external spectrum with the use of polarized light. They observed selection rules for the corresponding electric-dipole transitions and established the ordering of the stress-induced sublevels of the ground state seen in figures 5.2 and D.1b. This ordering, therefore, unambiguously requires $I_6$ symmetry for the $2p'$ and $3p'$ states (see section 5.3).
(b) Zeeman Splitting of the Internal Absorption Peaks

In their Zeeman effect measurement Zwerdling et al. (1960a) observed that the 2p' peak splits into 4 components and the 3p' peak splits into 2 components with the magnetic field. Since the present stress results indicate a $^6$ symmetry, and consequently, a 2-fold degeneracy of the 2p' state, part of the Zeeman splitting of the 2p' peak is probably due to the Zeeman splitting of the ground state. However, before anyone can seriously attempt to reconcile these Zeeman and stress measurements one should make a comprehensive Zeeman study of the stress-perturbed internal spectra with the use of polarized light and a high resolution spectrometer. These experiments should indicate selection rules for the magnetic- and stress-perturbed spectra so that the symmetry of the 2p' state can be checked. In addition, a detailed experimental and theoretical study of the effect of the Landau levels of the valence bands (as suggested by Zwerdling et al.) on the 2p' state should be made.

(c) Deformation Potential Parameters of the $p_{3/2}$ Valence Band

Using cyclotron resonance, Hensel and Feher (1963) calculated the deformation potential parameters of the $p_{3/2}$
valence band edge. In the analysis of their results, however, they neglected certain important correction terms. Balslev and Lawaetz (1965) made these corrections and obtained (they used the $D_u$, $D_u'$ notation, see Appendix D)

\[
\begin{align*}
    b &= -2.3 \pm 0.4 \text{ eV.} \\
    d &= -5.1 \pm 0.9 \text{ eV.}
\end{align*}
\tag{5.25}
\]

Comparing equations 5.23 and 5.24 with those equations above, one sees that the results for $b$ and $d$ in the present investigation are at variance with the results obtained from cyclotron resonance. This discrepancy is probably due to the effective mass wavefunctions for the ground state which were used by Bir et al. (1963) to relate $b'$ and $d'$ to $b$ and $d$ (see section 5.4). Since the effective mass wavefunctions for the ground state have large amplitudes at the impurity site where the acceptor potential deviates significantly from $-e^2/\kappa_0 r$, they are poor approximations for the true ground state wavefunctions. They are not expected, therefore, to yield accurate results.

It is noted, however, that the ratio $d/b$ in equations 5.23 and 5.24 is in fair agreement with that ratio of equation 5.25

\[
\frac{d}{b} = 2.2 \pm 0.9 \quad \text{[cyclotron resonance]} \tag{5.26}
\]

\[
2.7 \leq \frac{d}{b} \leq 3.1 \quad \text{[this thesis]} \tag{5.27}
\]

It is also noted that the signs of $b$ and $d$ obtained here are in agreement with those obtained by cyclotron resonance.

6.1 INTRODUCTION

The theory of acceptor states in Chapter 2 neglected (i) the interaction of the bound holes with lattice vibrations, and (ii) concentration effects. In other words, the model of this theory was that for a single acceptor impurity in a silicon crystal with negligible electron-phonon interactions (Barrie and Nishikawa, 1963). These additional effects are usually included as perturbations on the acceptor Hamiltonian of equation 2.3. These additional perturbations have been used to explain the broadening of the external acceptor absorption peaks.

These broadening effects for the external spectrum have been observed and discussed by many researchers. The results of recent comprehensive investigations on boron-doped silicon are discussed below.

6.2 REVIEW OF RECENT WORK ON THE BROADENING OF THE EXTERNAL ACCEPTOR ABSORPTION PEAKS

The half-widths of the external absorption peaks for boron-doped silicon have been studied by Colbow (1963) and White (1967a and b). With the use of a high resolution spectrometer, these half-widths were measured at various temperatures
(4.20 K, 600 K, 770 K and 900 K) and concentrations (in range 1.0 x 10^14 to 1.2 x 10^16 boron atoms/cm^3). These data were explained in terms of four broadening mechanisms (a) phonon-broadening, (b) concentration broadening, (c) dislocation broadening, and (d) ionized-impurity broadening.

The phonon-broadening theory of Barrie and Nishikawa (1963) was used in the above analysis. In this theory the predominant phonon-broadening mechanism was shown to be a phonon lifetime effect of the excited state. (In essence this lifetime effect resulted from the bound hole being able to change eigenstates through the emission or absorption of a phonon.) For an absorption peak associated with the transition g → μ, where g is the ground state (figure 1.1) and μ, an excited state, Barrie and Nishikawa have shown that the phonon-broadening contribution to the half-width of this peak due to electron-phonon coupling of state μ to a state λ, which lies KT_C energy units below or above state μ, has the following forms

\[ \Delta \omega_\lambda^\mu(T) = h_0^{\mu\lambda} \left[ 1 + 1/(e^{T_C^\lambda/T}/T - 1) \right]^{-1} \lambda \text{ below } \mu \quad (6.1) \]
\[ = h_0^{\mu\lambda} \left[ 1/(e^{T_C^\mu/T}/T - 1) \right]^{-1} \lambda \text{ above } \mu \quad (6.2) \]

T_C^\lambda is called the "characteristic temperature," and h_0^{\mu\lambda} is independent of temperature. (K is Boltzmann's constant.)

As equations 6.1 and 6.2 indicate, \[ \Delta \omega_\lambda^\mu(T) \] is nearly independent of temperature for \( T \ll T_C^\mu \) and linear in \( T \) for \( T \gg T_C^\mu \).

Furthermore, \[ \Delta \omega_\lambda^\mu(0) \] is only non-zero for state λ below state μ. In this thesis λ will be called the "phonon-broadening state" of μ.

White and Colbow attributed the concentration broadening
to the overlap of the hole wavefunctions. In this interpretation the concentration broadening is a measure of the distribution of the density of states across the "impurity bands" (Baltensperger, 1953) of the excited states (the overlap of the ground state wavefunctions for concentrations \( \leq 10^{17} \) boron/cm\(^3\) can be neglected in comparison to that of the excited states). This broadening, furthermore, is expected to be approximately independent of temperature.

The broadening due to dislocations in the sample is a small contribution to the total half-width of the external absorption peaks. White reports a dislocation broadening contribution, \( h_d \), of

\[
h_d \approx 0.02 \text{ meV. (for peak "2" and } 4 \times 10^4 \text{ disl.}/\text{cm}^2) \quad (6.3)
\]

When the phonon, concentration and dislocation broadening contributions were subtracted from the half-widths, Colbow and White found additional broadening above about 60°K. This additional broadening was attributed to ionized-impurity broadening, which is due to the interaction of the bound hole with ionized impurity sites.

6.3 INTERPRETATION OF THE BROADENING OF THE 2p' AND 3p' SPECTRUM

In this section the measurements of the temperature and concentration dependence of the 2p' and 3p' half-widths are discussed (sections 4.2 and 4.3; figures 4.5 and 4.6). These results have been published (Parsons and Bichard, 1967; Parsons, 1968).

One would expect that the broadening mechanisms of the external absorption spectrum, which were discussed in the previous section, to be present as well in the internal
spectrum. Unlike the former spectrum, however, some additional broadening in the internal spectrum may be due to the non-stationary lifetimes of the internal states. These lifetimes have been theoretically estimated to be greater than $10^{-10}$ seconds (see section 2.4). The lifetimes, which are associated with phonon-broadening, however, are typically of the order of $10^{-12}$ seconds (White, 1967a). Thus, these phonon lifetimes are considerably shorter than the above estimate for the non-stationary lifetimes.

In this thesis, therefore, the non-stationary lifetimes of the internal acceptor states will be neglected in comparison to the phonon lifetimes of these states. As a consequence, the internal wavefunctions of equation 2.14 (which neglect the non-stationary lifetimes) will be used to analyze the data. The discussions below will show that the broadening of the $2p'$ and $3p'$ absorption peaks can be explained in terms of these wavefunctions and the broadening mechanisms which were described in the previous section.

The dislocation broadening of the $2p'$ peak, $h^2_{2p'}$, is $\approx 0.05$ meV. (equation 4.1) for the samples used ($5 \times 10^4$ disl./cm$^2$). Since the true $2p'$ half-width is $\approx 0.35$ meV. (figure 4.5b), the dislocation broadening is a small contribution to the total broadening of peak $2p'$.

Since the temperatures of interest are $\approx 60^\circ$K, very few ionized impurities are produced (ionization energy is approximately 44 meV.). Ionized impurity broadening, therefore, need not be considered here. Thus, the important broadening
contributions to be considered in the 2p' and 3p' spectrum are the phonon and concentration broadenings.

There are three assumptions to be made here. (i) The phonon broadening is only temperature (T) dependent, so that the one impurity theory of Barrie and Nishikawa (1963) can be used.† (ii) The concentration broadening is only concentration (N) dependent.† (iii) The true half-width $h_{np'}(N,T)$ [which is $h_{np}$ in figure 4.5] of the $\alpha_{np'}(\nu)$ absorption peak can be decomposed as‡

$$h_{np'}(N,T) = \Delta \omega_{np'}(T) + h_{c}^{np'}(N) + h_{d}^{np'} \quad (n = 2,3) \quad (6.4)$$

where $\Delta \omega_{np'}(T)$, $h_{c}^{np'}(N)$ and $h_{d}^{np'}$ are the contributions to the np' half-width due to phonon, concentration and dislocation broadening, respectively.

For the moment restrict the discussion to the 2p' peak. The 2p' peaks in figure 4.6 were corrected for instrumental broadening in the manner of Appendix B and the true half-widths obtained. In figure 6.1 these half-width results are plotted against $N^{1/3}$ and a smooth curve is drawn through the data points. Since White (1967a) has shown that

† Colbow (1963) and White (1967a and b) made these assumptions in their investigation of the broadening of the external spectra.

‡ The observed $\alpha_{2p'}(\nu)$ and $\alpha_{3p'}(\nu)$ peaks are nearly Lorentzian in shape (section 4.2), and the phonon-broadening profiles are predicted (Barrie and Nishikawa) to be Lorentzian in shape. If the broadening profiles associated with concentration and dislocation effects are also Lorentzian, equation 6.4 is true. Since these last two profiles are not known, equation 6.4 is assumed. The error introduced by this assumption is expected to be less than the experimental error.
Figure 6.1 The Concentration Dependence of $h^2p'(N,T)$ for $T = 6.5 \pm 1.5^\circ K$. $N$ is the Concentration.
the concentration broadening for the external acceptor spectrum is approximately linear in $N^{1/3}$ for $1 \times 10^{14}$ boron/cm$^3 \leq N \leq 2 \times 10^{16}$ boron/cm$^3$, assume that $h_2^{p'}(N)$ is linear in $N^{1/3}$ for $N \leq 1.3 \times 10^{16}$ boron/cm$^3$. In figure 6.1, therefore, a straight line extrapolation (i.e. the dashed line) is used to obtain

$$h_2^{p'}(0,T) = 0.29 \pm 0.05 \text{ meV. } (T=6.5 \pm 1.5^\circ\text{K}) \quad (6.5)$$

With equations 6.5 and 6.4 one can use figure 6.1 to calculate

$$h_c^{2p'}(N) = h_2^{p'}(N,T) - h_2^{p'}(0,T)$$

$$= 0.06 \pm 0.06 \text{ meV. for } N = 2.6 \times 10^{15}/\text{cm}^3$$

and

$$\Delta \omega^{2p'}(T) = h_2^{p'}(N,T) - h_2^{p'} - h_c^{2p'}(N)$$

$$= h_2^{p'}(N,T) - h_d^{2p'} - 0.06 \pm 0.06 \text{ meV.} \quad (6.7)$$

for $N = 2.6 \times 10^{15}/\text{cm}^3$

Since $h_d^{2p'} \approx 0.05 \text{ meV.} \quad (equation 4.1)$ and $h_2^{p'}(N,0) = 0.35 \pm 0.02$ meV. for $N = 2.6 \times 10^{15}/\text{cm}^3 \quad (figure 4.5b)$, equation 6.7 yields

$$\Delta \omega^{2p'}(0) > 0.16 \text{ meV.} \quad (6.8)$$

This result (i.e. a non-zero phonon broadening for the $2p'$ peak) indicates that a state below (in hole energy) state $2p'$ is important in the phonon broadening description of the $2p'$ peak (see section 6.2). The temperature dependence of $h_2^{p'}(N,T)$ seen in figure 4.5b indicates that $\Delta \omega^{2p'}(T)$ is approximately constant for $T \leq 20^\circ\text{K}$ and linear for $T \geq 30^\circ\text{K.} \quad (h_2^{p'}(N)$ and $h_d^{2p'}$ are assumed to be temperature independent)

Therefore, the phonon-broadening states of the $2p'$ state have characteristic temperatures of $T_c \approx 25^\circ\text{K}$ (see section 6.2). This characteristic temperature restricts the possible phonon-
broadening states of state 2p' to those having energy eigenvalues lying within approximately 3 meV. on either side of the 2p' level. Hence, the possible phonon-broadening states of state 2p' are the p3/2 Bloch states, the 3p' state, and unobserved internal states which satisfy the above restriction. Since the phonon-broadening profiles are Lorentzian (see the foot-note on page 56), one can write

$$\Delta \omega_{2p}(T) = \Delta \omega_{v}^{2p}(T) + \Delta \omega_{3p'}^{2p}(T) + \Delta \omega_{s'}^{2p}(T) \quad (6.9)$$

where the subscripts v, 3p', and s' denote the p3/2 Bloch, 3p' and unobserved internal states, respectively.

Consider, first, $\Delta \omega_{v}^{2p}(T)$. In Appendix E, using the theory of Barrie and Nishikawa, $\Delta \omega_{v}^{2p}(T)$ was calculated. As a result of the approximations used to assist in the calculation, the absolute value of the theoretical $\Delta \omega_{v}^{2p}(T)$ was less accurately determined than the relative dependence $\Delta \omega_{v}^{2p}(T)/\Delta \omega_{v}^{2p}(0)$. In figure 6.2 this theoretical ratio is compared to the experimental ratio $\Delta \omega_{v}^{2p}(T)/\Delta \omega_{v}^{2p}(0)$ which is obtained from figure 4.5b and equation 6.7. The choice of

$$h_{c}^{2p}(N) + h_{d}^{2p'} = 0.11 \text{ meV. (N=2.6x10}^{15}/\text{cm}^{3}) \quad (6.10)$$

gave a good fit in figure 6.2.

The good agreement in figure 6.2 indicates that the most important phonon-broadening states of state 2p' are the p3/2 valence band states. (In other words, these results indicate that $\Delta \omega_{v}^{2p}(T)$ is much greater than $\Delta \omega_{3p'}^{2p}(T) + \Delta \omega_{s'}^{2p}(T)$.) The calculation in Appendix E gave $\Delta \omega_{v}^{2p}(0) \approx 0.3$ meV. This theoretical value compares favorably with the
Figure 6.2 A Comparison of the Theoretical $2p'$ Phonon Broadening due to the $p_{3/2}$ Valence Bands and the Total Experimental Phonon Broadening of the $2p'$ Peak.
experimental value of 0.24 meV, which is obtained from figure 4.5b and equations 6.7 and 6.10.

The above discussions have shown that the 2p' phonon broadening data can be explained by $\Delta \omega_{2p'}(T)$ alone. Below a consistency check on this interpretation is made by attempting to explain this 2p' data in terms of $\Delta \omega_{3p'}(T) + \Delta \omega_s(T)$ alone. Assume that there is only one unobserved internal state which contributes to $\Delta \omega_{2p'}(T)$. Since $\Delta \omega_{2p'}(0)$ is greater than zero (equation 6.8) and the 3p' state is above (in hole energy) the 2p' state, this unobserved s' state must lie below the 2p' state. Therefore, in terms of the 3p' and s' broadening states the theoretical 2p' phonon broadening is

$$\Delta \omega_{2p'}(T) = \frac{h_{0_{2p'3p'}}}{e^{T_{3p'/s'}/T} - 1} + h_{0_{3p's'}} (1 + \frac{1}{e^{T_{3p'/s'}/T} - 1}) \quad (6.11)$$

Since $T_{3p'/s'}$ is approximately equal to 250K (see the discussions on page 56) and the above $\Delta \omega_{2p'}(0)$ is equal to $h_{0_{2p'3p'}}$, one can show that the constant $h_{0_{3p's'}}$ cannot be chosen so that equation 6.11 provides a good fit for the 2p' phonon broadening data (i.e. as 'good' as that in figure 6.2).

Now consider the phonon broadening of the 3p' peak. Although the temperature dependence of the 3p' half-width is similar to that of the 2p' half-width in figure 4.5, there are two observations which distinguish these two results. (i) $h_{3p'}(N, 0)$ is less than $h_{2p'}(N, 0)$. (ii) $h_{3p'}(N, T)$ increases
more rapidly with temperature for $T$ greater than $15^\circ K$.

These two observations can be explained in terms of $\Delta \omega_3^{p'}(T)$, the phonon broadening of the $3p'$ peak.

In Appendix E the Bloch states which were important in the calculation of $\Delta \omega_2^{p'}(T)$ were those with energy eigenvalues within 3 meV. of the $2p'$ level. For the $3p'$ peak, a similar calculation of $\Delta \omega_3^{p'}(T)$ indicates that the important Bloch states are those with energy eigenvalues within 3 meV. of the $3p'$ level. From figure 1.1, therefore, one sees that approximately the same number of Bloch states are important in the phonon broadening description of peak $3p'$ as in the description of peak $2p'$. Consequently, the theoretical prediction is

$$\frac{\Delta \omega_3^{p'}(T)}{\Delta \omega_3^{p'}(0)} \approx \frac{\Delta \omega_2^{p'}(T)}{\Delta \omega_2^{p'}(0)} \quad (6.12)$$

By comparing the matrix elements of the electron-phonon interaction between the $3p'$ state and $p_{3/2}$ Bloch states with those matrix elements between the $2p'$ state and $p_{3/2}$ Bloch states, one can show that

$$\frac{\Delta \omega_3^{p'}(0)}{\Delta \omega_2^{p'}(0)} \approx 0.8 \quad (6.13)$$

The observed result (i) is attributed to this ratio of the $3p'$ and $2p'$ phonon broadenings due to the $p_{3/2}$ phonon broadening states. The observed result (ii) is attributed to additional phonon broadening of the $3p'$ peak due to the $4p'$ state. Since
state $4p'$ lies above state $3p'$ and $T_C^{3p',4p'}$ is approximately $12^\circ K$, this contribution to the $3p'$ phonon broadening due to the $4p'$ state would become large only for $T$ greater than $12^\circ K$.

The concentration dependence of the concentration broadening, $h_{2p'}^c(N)$, will now be discussed. $h_{2p'}^c(N)$ was obtained from figure 6.1 and equations 6.6 and 6.5. These results are plotted in figure 6.3. (The smooth curve in figure 6.1 was appropriately redrawn in figure 6.3.) White's (1967a) concentration broadening results are also plotted in figure 6.3. The similarity of the internal and external data in this figure is consistent with the assumption implied in this section that the same phenomenon (i.e. the overlap of the hole wavefunctions in the formation of impurity bands) produces concentration broadening of the internal and external spectra.

6.4 INTERPRETATION OF THE CONCENTRATION-DEPENDENT ASYMMETRY OF THE $2p'$ ABSORPTION PEAK

Below, two possible interpretations of the concentration-dependent asymmetry of the $2p'$ peak are given (figure 4.6). (i) Due to the random array of the impurities, Matsubara and Toyozawa (1961) have theoretically predicted low energy tails for the density of impurity band states. The low energy asymmetry of the $2p'$ peak, therefore, could be attributed to the asymmetrical density of final $2p'$ impurity band states. However, one objection to this interpretation is that no similar asymmetries have been observed (White, 1967a) for the
Figure 6.3  The Concentration Broadening of the 2p* Absorption Peak. Dashed Curves Are the Concentration Broadenings of the External Spectrum (White, 1967a).
external spectrum.

(ii) A second interpretation of the 2p' asymmetry can be obtained by assuming the existence of an internal state (say 2s') which is optically unobserved and nearly degenerate with the 2p' state for low concentrations. With increased concentration states 2p' and 2s' would merge into a single impurity band so that the presence of the 2s' state would become more optically observable. The observed effect of this increased optical activity due to state 2s' with increased concentration would be an asymmetrical 2p' absorption peak.

Since the weaker 3p' absorption peak permitted measurements only for concentrations less than and equal to $1.3 \times 10^{16}$ boron/cm$^3$, no meaningful comparison of the concentration behavior of the 2p' and 3p' peaks is possible. Since the 3p' wavefunctions will have spatial extent greater than that of the 2p' wavefunctions, the former wavefunctions will overlap more than the latter ones. Therefore, the failure to clearly detect the 3p' peak for all the concentrations used (section 4.3) is attributed to a rapid increase in the 3p' concentration broadening for impurity concentrations greater than $1 \times 10^{16}$ boron/cm$^3$. 
CHAPTER 7 - CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK IN THE FIELD OF STUDY

7.1 CONCLUSIONS

The $2p'$ and $3p'$ internal spectrum of boron-doped silicon has been studied with the use of (i) calibrated uniaxial stress ($S \leq 10^9$ dynes/cm$^2$) and polarized light, (ii) variable sample temperature ($5^\circ K \leq T \leq 60^\circ K$), and (iii) different impurity concentrations ($2.6 \times 10^{15}$ boron/cm$^3 \leq N \leq 4.5 \times 10^{17}$ boron/cm$^3$). These studies gave information about the ground state and the $2p'$ and $3p'$ internal states. In addition, it was possible to obtain indirectly information about the stress-induced splitting of the $p_{3/2}$ valence band edge in silicon.

These investigations can be summarized in the form of definite and tentative conclusions.

Definite Conclusions

(i) The ground state is a 4-fold degenerate $\Gamma_{8}$ state.
(ii) The ground state splits into two Kramers' doublets under uniaxial stress. The deformation potential parameters for the ground state which describe this splitting are:

\[ b' = -0.66 \pm 0.04 \text{ eV.} \text{ and } d' = -2.1 \pm 0.2 \text{ eV.} \]

(The ordering of the stress-induced sublevels of the ground state are specified by the signs of these parameters.)

(iii) The $2p'$ and $3p'$ states are each 2-fold degenerate and belong to $\Gamma_{6}$. These results agree with previously reported stress work (Onton et al., 1967; Fisher et al., 1966) but
disagree with reported Zeeman-measurements (Zwerdling et al., 1960a).

(iv) The half-widths of the 2p' and 3p' peaks are very temperature dependent for 0°K ≤ T ≤ 60°K. (figure 4.5)

(v) The temperature dependence of the 2p' and 3p' half-widths is attributed to phonon-broadening which is a lifetime effect. The phonon broadenings of the 2p' and 3p' peaks are primarily due to electron-phonon coupling of the 2p' and 3p' states to the p_{3/2} valence band states, respectively. For the 3p' peak additional phonon broadening above about 15°K can be explained by the electron-phonon coupling of the 3p' state to the 4p' state.

(vi) For the concentration range \(2.6 \times 10^{15} \text{ boron/cm}^3 \leq N \leq 4.5 \times 10^{17} \text{ boron/cm}^3\) the 2p' peak is observed to broaden and become very asymmetrical with increasing concentration.

(vii) The concentration dependence of the concentration broadening of the 2p' peak is similar to that of the external spectrum.

(viii) The present experimental studies can be explained by neglecting the non-stationary lifetimes of the internal states in comparison to the electron-phonon lifetimes of these states.

(ix) The deformation potential parameters b and d for the p_{3/2} valence band edge in silicon were obtained from the parameters b' and d' (see conclusion ii above). The signs of these parameters b and d are in agreement with results which were obtained with the use of cyclotron resonance (Hensel and Feher, 1963; Balslev and Lawaetz, 1965). Since the calculation of b and d from b' and d' is not expected to be very accurate,
the absolute values of b and d from this investigation are not reliable.]

**Tentative Conclusions**

(i) If the stress-induced shift of the 2p' state is negligible compared to the shift of the ground state, the stress results give $|a'| = |a| < 0.59$ eV for the deformation potential (shift) parameters $a'$ and $a$ of the ground state and the $P_{3/2}$ valence band edge in boron-doped silicon, respectively.

(ii) The similar concentration dependence of the concentration broadenings of the 2p' and the external spectra (see the "definite" conclusion vii) indicates that the mechanism which explains the concentration broadening of the external spectrum will also explain the concentration broadening of the internal spectrum. This mechanism is expected to be the overlap of the acceptor wavefunctions in the formation of impurity bands.

(iii) The concentration-dependent asymmetry of the 2p' peak is either due to the asymmetrical density of the 2p' impurity band states or an internal state 2s' which is nearly degenerate with the 2p' state and optically unobserved in the internal spectrum for low impurity concentrations ($N \lesssim 10^{16}$ boron/cm$^3$).

(iv) The change of the stress-perturbed extrinsic background absorption with the direction of the polarization of light is attributed to a change of the stress-perturbed ionization absorption.
7.2 SUGGESTIONS FOR FURTHER WORK

Zeeman-Effect Studies of the Stress-Perturbed 2p' Peak

As section 5.6b suggested, a Zeeman study of the stress-perturbed 2p' absorption peak with the use of polarized light and a high resolution spectrometer would be of interest.

p \rightarrow s' Transitions

Some indications of an s-like state 2s' which is nearly degenerate with the 2p' state was suggested in the stress and concentration studies (sections 5.6b and 6.4). To verify the existence of this 2s' state, however, one would like to observe an absorption peak associated with this state. In addition, the observation of other s-like internal states (especially the "internal ground state" 1s') would be of interest.

A possible experiment in which to observe optical absorption peaks associated with these s-like internal states is to populate the p-like external states and look for p \rightarrow s' transitions. This population of the p-like external states can be accomplished by raising the sample temperature. Unfortunately, however, the phonon broadening associated with these s' states would probably restrict this temperature to less than 35°K.

A preliminary experiment was made by looking for absorption peaks associated with transitions from the external level (1) [see figure 1.1] to s-like states near the 2p' level. The sample temperature was approximately 35°K and the
impurity concentration was \(4.4 \times 10^{16}\) boron/cm\(^3\). The photon energy of approximately 46 meV was produced by a Perkin Elmer monochromator (model 83; this is not the one described in section 3.1). No new peaks (i.e. other than the external spectrum) were observed. However, since the signal-to-noise ratio was approximately 8-to-1, this experiment should be repeated with better instrumentation.

**Si(B,In) Studies**

The energy positions of the 2p\(^f\) internal levels relative to the split-off \(p_{1/2}\) valence band edge are very nearly independent of the acceptor impurity species (Zwerdling et al., 1960a; Onton et al., 1967). If sufficient boron and indium are introduced into silicon, therefore, considerable overlap of the boron and the indium 2p\(^f\) wavefunctions should result and a 2p\(^f\) impurity band would be shared by the indium and boron impurities. Since the ground state for indium is much lower in hole energy than that of boron, negligible impurity banding of the boron and indium ground states is expected for moderate concentrations. If, now, a silicon ingot is heavily doped with indium (\(\approx 10^{17}\) indium/cm\(^3\)) and lightly doped with boron (\(\approx 10^{15}\) boron/cm\(^3\)), excitations from the localized boron ground states to the boron-indium 2p\(^f\) impurity band might be seen.
APPENDIX A - JUSTIFICATION OF THE ASSUMED IONIZATION ABSORPTION MECHANISM

In section 3.3 the ionization absorption mechanism was assumed to be not significantly affected by the presence of the internal acceptor states. The purpose of this Appendix is to show that this assumption is consistent with the conclusions of this thesis.

In general the above assumption is valid only if the probabilities for electric-dipole transitions from the ground state to the $p_{3/2}$ valence band states are independent of any coupling of these $p_{3/2}$ states to the internal acceptor states. The perturbations which can cause this coupling are the acceptor potential $(-e^2/k_0 r)$, which will cause "non-stationary lifetimes" of the $p_{3/2}$ Bloch states, and the electron-phonon interaction $H_{ep}$.

As the conclusions of section 7.1 pointed out, the data of this thesis can be reasonably explained by neglecting the non-stationary lifetimes of the internal acceptor states in comparison to the electron-phonon lifetimes for these states. It is reasonable to assume, therefore, that the corresponding non-stationary lifetimes of the $p_{3/2}$ Bloch states are negligible compared to their electron-phonon lifetimes. With this assumption, consequently, the ionization absorption mechanism can be influenced by the presence of the internal acceptor states only through the electron-phonon coupling of the $p_{3/2}$ Bloch states to these internal states.

Treating $H_{ep}$ as a first order perturbation, the perturbed
Bloch functions are

\[ \psi_{\pi}^{3/2}(r) = \sum_{x'} \frac{\phi_{x'}^{3/2}(r)}{E(x') - E(x')} \]

where \( \phi_{x'}^{3/2}(r) \) is an unperturbed \( p_{3/2} \) Bloch function (the band indices are omitted but a summation over the \( p_{3/2} \) energy bands is implied), \( \psi_{\pi}(r) \) is an internal wavefunction, and \( E(x) \) and \( E_\alpha \) are the eigenvalues of \( \phi_{x}^{3/2}(r) \) and \( \psi_{\pi}(r) \), respectively.

Non-degenerate perturbation theory is used in equation A.1. Strictly speaking, since some of the denominators in the above equation may be very small, degenerate perturbation theory should be used. However, the general arguments and conclusions, which will be deduced from equation A.1, would be unchanged by this latter treatment. The electron-phonon coupling of \( p_{3/2} \) and \( p_{1/2} \) Bloch functions can be included in equation A.1. This inclusion, however, does not change the arguments below.

In equation A.1 the number of Bloch functions \( \phi_{x'}^{3/2}(r) \) in the summation \( \sum_{x'} \) greatly exceeds the number of internal phonon states and phonon energy eigenvalues have not been explicitly written in equation A.1. Since this equation will not be evaluated, however, the following arguments can be understood without explicitly introducing these phonon quantities.

\[ \dagger \] The phonon states and phonon energy eigenvalues have not been explicitly written in equation A.1. Since this equation will not be evaluated, however, the following arguments can be understood without explicitly introducing these phonon quantities.
wavefunctions $\psi^\lambda_\ell(\tau)$ in the summation $\sum_\lambda$. A calculation showed that $| \langle \phi^{3/2}_y(z) | H_{\text{ep}} | \phi^{3/2}_y(z) \rangle |$ is within one or two orders of magnitude of $| \langle \psi^\lambda_\ell(z) | H_{\text{ep}} | \phi^{3/2}_y(z) \rangle |$. Consequently, the former summation ($\sum'_\lambda$) dominates the latter one ($\sum_\lambda$), and the electron-phonon coupling of the $p_{3/2}$ Bloch functions to the internal wavefunctions can be neglected here. The ionization absorption mechanism, therefore, is not significantly influenced by the presence of the internal acceptor levels.

† In this calculation $H_{\text{ep}}$ was treated in the isotropic deformation potential approximation of Bardeen and Shockley (1950). The results of Lax and Burstein (1955) were also used.
APPENDIX B - CORRECTING FOR INSTRUMENTAL BROADENING

The resolving power of the spectrometer is indicated by two vertical lines in figure 3.3. In this figure, one can see that the instrumental broadening is not negligible. Since the true half-widths of the internal absorption spectrum are of interest in this investigation, therefore, some suitable correction for instrumental broadening is necessary.

The well known relationship between the observed intensity distribution \( f(v) \) and the true intensity distribution \( f_T(v) \) is

\[
f(v) = \int_0^\infty f_T(v') f_I(v-v') \, dv' \equiv f_T(v) \ast f_I(v) \tag{B.1}
\]

where \( f_I(v-v') \) is the instrumental profile which is defined as the apparent normalized intensity detected by the spectrometer at frequency \( v \) for a monochromatic source of frequency \( v' \).

As a first step to obtain \( f_I(v-v') \) a 0.6328 micron helium-neon laser beam was detected in the 24, 25, and 26 orders. To be certain that the optical geometry was not changed in this observation, the globar rod (the source) was replaced by a buffed lucite rod which was illuminated by the laser beam. In terms of the grating angle \( \theta \) (i.e. for the littrow mount grating spectrometer used, the grating formula \( m\lambda = d(\sin\theta_i \pm \sin\theta_r) \) reduces to \( m\lambda \approx 2d(\sin\theta) \) since \( \theta_i \approx \theta_r \)) the normalized intensity profile \( I(\theta) \) measured in all three observations was very nearly gaussian

\[ \]

† This technique is original to the author.
\[ I(\theta) = \frac{1}{\sqrt{\pi} \sigma(s)} e^{-\left( \frac{\theta - \theta_{L}}{\sigma(s)} \right)^2} \]

where \( m \lambda_{L} = 2d \sin \theta_{L}, \lambda_{L} = 0.6328 \) microns; and \( \sigma(s) \) depends only on the slit width \( s \). Below an argument is given to relate the \( I(\theta) \) observed in the 24th order to the \( f_{I}(\nu - \nu') \) needed in the 1st order.

Assume that the most important contributions to the instrumental broadening of the littrow mount grating spectrometer are due (i) to wide entrance slits which permit the radiation to be incident on the grating in a non-zero angular spread, and (ii) to wide exit slits which pass diffracted radiation with a non-zero angular spread. With these assumptions and the grating formula, one can show that the same normalized intensity profile \( I(\theta) \) would be obtained by observing laser beams of wavelengths \( \lambda_{L} = 0.6328 \) microns and \( \lambda' = 24 \times 0.6328 = 15.16 \) microns in the 24th order and 1st order, respectively. For frequencies near \( \nu_{L} \) the grating formula yields

\[ \theta - \theta_{L} \approx \frac{\nu - \nu_{L}}{\beta(\nu_{L})} \]

where \( \beta(\nu_{L}) = \nu \left[ (2d\nu_m/c)^2 - 1 \right]^{1/2} \). Using this result and the observed \( I(\theta) \) for the 24th order, one obtains for the 1st order

\[ f_{I}(\nu - \nu') \approx \frac{1}{\sqrt{\pi} \sigma(s, \nu')} e^{-\left( \frac{\nu - \nu'}{\sigma(s, \nu')} \right)^2} \]

where \( \nu' = c/\lambda' \) ( \( c \) is the speed of light) and \( \sigma(s, \nu') \equiv \alpha(s) \beta(\nu') \).
In the wavelength region of interest (14.5 microns ≤ λ ≤ 15 microns) \( \beta(\nu) \) is very slowly varying. Therefore, to consider the instrumental broadening of the 2p\(^f\) and 3p\(^f\) peaks a good approximation is

\[
f_T(\nu - \nu^*) \approx \frac{1}{\sqrt{\pi} \sigma(s, \nu_{np}^*)} e^{-\left(\frac{\nu - \nu^*}{\sigma(s, \nu_{np}^*)}\right)^2},
\]

\((n = 2, 3)\)

where \( \nu_{np}^* \) is the photon energy position of the np\(^f\) peak. Changing notation \( f(\nu) \rightarrow f_\sigma(\nu) \), equation B.1 becomes

\[
f_\sigma(\nu) \equiv f(\nu) = f_T(\nu) * \frac{1}{\sqrt{\pi} \sigma} e^{-\left(\nu/\sigma\right)^2}
\]

Since

\[
f_\sigma(\nu) \times e^{-\left(\nu/\sigma\right)^2} = \frac{1}{\sqrt{\pi} \sigma} e^{-\left(\nu^*/\sigma\right)^2} = f(\nu)
\]

and

\[
f_T(\nu) = \lim_{\sigma \to 0} f_\sigma(\nu)
\]

one can see that \( f_T(\nu) \) can be obtained by extrapolating \( f_\sigma(\nu) \) to \( \sigma = 0 \) given \( f_\sigma(\nu) \) for \( \sigma \geq \sigma(s, \nu_{np}^*) \), where \( s \) is the slit-width used.

Since all data analysis was performed on a digital computer, \( f_{(\sigma^2 + \nu^2)^{1/2}}^{(\nu)} \) in equation B.7 was obtained by numerical integration. The extrapolation (equation B.8) was done on this computer by a least squares fit of a cubic polynomial.

Note that this correction technique is equally applicable to asymmetrical and symmetrical peak profiles.

The \( \sigma(s, \nu_{np}^*) \), which was used in this investigation, is
plotted in figure B.1. In figure B.2 typical observed and corrected absorption coefficients (which were calculated from the observed and corrected transmission intensities, respectively) are compared.

Figure B.1 Parameters Which Were Used for Instrumental Correction
Figure B.2 Correcting the 2p' Absorption Peak for Instrumental Broadening
APPENDIX C - GROUP THEORETICAL CALCULATION
OF RELATIVE TRANSITION PROBABILITIES

Using the general results of Kaplyanskii (1964), Onton et al. (1967) have group theoretically calculated the relative intensities of the stress-induced components of the 2p' and 3p' absorption peaks. The results of their calculation were used in section 5.3. The purpose of this appendix is to describe the main features of this calculation.

First, consider an acceptor energy level \( E_i \) which is \( n_a \)-fold degenerate for zero-stress. Denote the degenerate wavefunctions associated with energy \( E_i \) by \( \psi^{(r)}_i (r) \) \((i = 1, n_a)\). Under uniaxial stress suppose that this energy level splits into \( m_a \) levels. Denote the stress-perturbed energies and wavefunctions associated with these \( m_a \) levels by \( E^{(r)}_a, \kappa \) and \( \psi^{(r)}_a, \kappa (r) \) \((\kappa = 1, \ldots, n_a)\), respectively. Here, \( n_{a, \kappa} \) is the degeneracy of the stress-perturbed \( m_a, \kappa \) level \((a = 1, \ldots, m_a)\). To zero-order in the stress-perturbation, \( \psi^{(r)}_a, \kappa \) can be written as a linear combination of the \( \psi^{(r)}_i \) as

\[
\psi^{(r)}_a, \kappa = \sum_{i=1}^{n_a} \alpha_{a,i}^{\kappa \iota} \psi^{(r)}_i \quad (C.1)
\]

Similarly, the zero-order wavefunctions associated with the stress-induced splitting of the energy level \( E_{\mu'} \) can be written as

\[
\psi^{(r)}_{\mu', \mu} = \sum_{j=1}^{n_{\mu'}} \alpha_{\mu', \mu}^{j \iota} \psi^{(r)}_{\mu'} \quad (C.2)
\]

Now, consider the electric-dipole transition probability, \( T^{(r)}_{\mu', \mu} \), which is associated with a transition between the stress-
perturbed levels $E_{\gamma \gamma'}$ and $E_{\mu \mu'}$. Using the above zero-order wavefunctions, one obtains

$$T_{\gamma \mu'} \propto \sum_{i=1}^{N_{\gamma \gamma'}} \sum_{k=1}^{N_{\mu \mu'}} |\sum_{i=1}^{N_{\gamma \gamma'}} a_{\gamma i}^{\delta i} \langle \gamma \mu' | u \cdot r | \gamma' \mu' \rangle|^2 \tag{C.3}$$

where $u$ is a unit vector in the direction of the light polarization. Therefore, if $I_{\gamma \mu'}$ and $I_{\gamma' \mu''}$ are the intensities of the absorption peaks associated with the transition probabilities $T_{\gamma \mu'}$ and $T_{\gamma' \mu''}$, respectively, the desired relative intensities of the stress-induced components of the $E_{\gamma} \rightarrow E_{\mu}$ absorption peak are given by

$$\frac{I_{\gamma \mu'}}{I_{\gamma' \mu''}} = \frac{T_{\gamma \mu'}}{T_{\gamma' \mu''}} \tag{C.4}$$

For the zero-stress symmetry group $T_d$ and the stress perturbations of interest here, Kaplyanskii (1964) has evaluated the expansion coefficients $a_{\gamma i}^{\delta i}$ associated with the $\Gamma_6$, $\Gamma_7$, or $\Gamma_8$ acceptor energy levels. The electric-dipole matrix elements can be expressed in terms of the group theoretical coupling coefficients $U_{ij \lambda}$ as (Koster et al., 1963)

$$\langle \gamma \mu' | u \cdot r | \gamma' \mu' \rangle = \sum_{\lambda} c_{\mu \lambda}^{\gamma} U_{ij \lambda}^{\alpha} \tag{C.5}$$

where $c_{\mu \lambda}^{\gamma}$ is an undetermined parameter (i.e. cannot be evaluated from symmetry arguments alone). Since the components of the $\Gamma_8 \rightarrow \Gamma_6$ and $\Gamma_8 \rightarrow \Gamma_7$ transitions involve only one parameter which will cancel out in equation C.4, the relative intensities of these components can be calculated from symmetry considerations alone (Onton et al., 1967; Dickey and Dimmock, 1967). However, the stress-perturbed $\Gamma_8 \rightarrow \Gamma_8$ transition involves
two parameters which are complex in general and do not cancel out in equation C.4. Onton et al. (1967) have plotted the relative intensities of the components of the $\Gamma_g \rightarrow \Gamma_g$ transition as a function of the ratio of these parameters for all possible values of this ratio.
APPENDIX D - DEFORMATION POTENTIAL PARAMETERS

The effect of strain can be conveniently treated with the use of the so-called "deformation potential parameters." The purpose of this appendix is to introduce two sets of deformation potential parameters (i) \( a, b \) and \( d \) for the \( p_{3/2} \) valence band edge in silicon, and (ii) \( a', b' \) and \( d' \) for the acceptor ground state in boron-doped silicon. In addition, this appendix gives formulae which are used in section 5.4 to calculate \( a', b' \) and \( d' \).

There are three main points about the deformation potential theory. (a) The effect of strain is assumed to be a first order perturbation so that a matrix form for the strain Hamiltonian \( H_e \) can be written in the representation of the unperturbed wavefunctions \( \psi_i / \xi \) as

\[
(H_e)_{ii'} \equiv \langle \psi_i | H_e | \psi_{i'} \rangle = \sum_{\mu, \nu, x, y, z} M_{ii', \mu} \epsilon_{\mu, \nu}
\]  

where \( \epsilon_{\mu, \nu} \) is the strain tensor. (b) Symmetry arguments are used to reduce the form of the tensor \( M_{ii', \mu, \nu} \) to the minimum number of undetermined parameters (i.e. which cannot be evaluated from symmetry arguments alone). (c) These parameters, which are called the "deformation potential parameters", are evaluated by experiment.

\footnote{The linear stress-dependence of the stress-induced splittings of the \( 2p^* \) and \( 3p^* \) peaks of figure 4.4 justifies this assumption here.}

\footnote{The strain tensor will be defined as \( \epsilon_{\mu, \nu} = \gamma_{\mu, \nu} (\partial \beta / \partial \alpha_{\mu} + \partial \beta / \partial \alpha_{\nu}) \) where \( \mu, \nu = x, y, z \) and \( \beta = (\beta_x, \beta_y, \beta_z) \) is the strain. The strain tensor is related to the stress tensor (which is known here) through the elastic compliances \( \gamma_{ij} \), \( \gamma_{12} \) and \( \gamma_{11} \) (Huntington, 1958).}
(i) With the use of cyclotron resonance Hensel and Feher (1963) studied the stress-induced splitting of the 4-fold degenerate $p_{3/2}$ valence band maxima in silicon. From an observed shift of the cyclotron resonance line due to a stress-induced interaction between one of the $p_{3/2}$ substates and the $p_{1/2}$ valence band states, furthermore, they were able to order the stress-induced $p_{3/2}$ sublevels. Their results are schematically shown in figure D.1a.

Restrict the attention to the Bloch functions $\phi^{3/2}_m(\epsilon)$ ($m = -\frac{3}{2}, \cdots, \frac{1}{2}$) and $\phi^{1/2}_{m'}(\epsilon)$ ($m' = -\frac{1}{2}, \frac{1}{2}$) at the $p_{3/2}$ and $p_{1/2}$ band maxima, respectively [notation introduced in section 2.3]. In the manner of equation D.1 the effect of strain on these Bloch functions can be described by the $6 \times 6$ matrix (Hasegawa, 1963)

$$H'_{\epsilon} = \begin{bmatrix} H^{3/4, 3/2}_{\epsilon} & H^{3/4, 1/2}_{\epsilon} \\ H^{1/2, 3/2}_{\epsilon} & H^{1/2, 1/2}_{\epsilon} \end{bmatrix} \quad (D.2)$$

where $H^{3/4, 3/2}_{\epsilon}$ is a $4 \times 4$ matrix which describes the strain-induced effects within the $p_{3/2}$ multiplet, $H^{1/2, 1/2}_{\epsilon}$ is a $2 \times 2$ matrix which describes the strain-induced effects within the $p_{1/2}$ multiplet, and $H^{1/2, 3/2}_{\epsilon}$ and $H^{1/2, 1/2}_{\epsilon}$ are $3 \times 2$ and $2 \times 3$ matrices, respectively, which describe the strain-induced coupling of the $p_{3/2}$ and $p_{1/2}$ Bloch states.

---

† Hensel and Feher did not label the valence band maxima by irreducible representations. Instead they used the "$M_j$" notation.
(a) $p_{3/2}$ and $p_{1/2}$ Valence Bands in Silicon

(b) Acceptor Ground State in Boron-Doped Silicon

Figure D.1. The Effects of Uniaxial Compression on (a) the $p_{3/2}$ and the $p_{1/2}$ Valence Bands in Silicon, and (b) the Acceptor Ground State in Boron-Doped Silicon. (Schematic) For Tension the Orderings of the $p_{3/2}$ and Ground State Stress-Induced Sublevels Are Reversed. The Symmetry Groups Are Shown Beneath the Energy Bands or the Energy Levels.
Since the unperturbed $p_{3/2}$ band maxima belongs to $\Pi^+_8$ (see figure D.1a), the matrix form of $H_\epsilon^{3/2}$ in the representation of the $\phi^m_{3/2}$ ($m = -3/2, \cdots, 3/2$) can be conveniently written as (Kleiner and Roth, 1959)\footnote{\textit{a}, \textit{b} and \textit{d}, which refer to hole energies, were used by Pikus and Bir (1959). The Equivalent Parameters $D_\nu^* = -\alpha$, $D_u = -3/2 \textit{b}$ and $D_\nu^* = -\sqrt{3}/2 \textit{d}$, which refer to electron energies, were used by Kleiner and Roth (1959).}

\[
H_\epsilon^{3/2} = a (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) + b \{ (J_x^2 - \frac{5}{4} J) \epsilon_{xx} + (J_y^2 - \frac{5}{4} J) \epsilon_{yy} + (J_z^2 - \frac{5}{4} J) \epsilon_{zz} \} + 2d J_z \{ [J_x J_y]_+ \epsilon_{xx} + [J_y J_z]_+ \epsilon_{yy} + [J_z J_x]_+ \epsilon_{zz} \}
\]

where $J_d$ ($d = x, y, z$) are the angular momentum matrices for $j = 3/2$ in the representation $[J_d J_d]_+ = \frac{1}{4} (J_d^2 + J_d^2)$ and $I$ is the unit matrix. The three constants $a$, $b$ and $d$ are called the "deformation potential parameters for the $p_{3/2}$ valence band edge."\footnote{\textit{a}, \textit{b} and \textit{d}, which refer to hole energies, were used by Pikus and Bir (1959). The Equivalent Parameters $D_\nu^* = -\alpha$, $D_u = -3/2 \textit{b}$ and $D_\nu^* = -\sqrt{3}/2 \textit{d}$, which refer to electron energies, were used by Kleiner and Roth (1959).} $a$ describes the stress-induced shift of the center of gravity of the entire $p_{3/2}$ valence band edge and does not contribute to the splitting. $b$ and $d$ define this splitting of the $p_{3/2}$ maxima for stress along the $\langle 001 \rangle$ and $\langle 111 \rangle$ directions, respectively.

Neglecting the interband matrices $H_\epsilon^{3/2}$ and $H_\epsilon^{3/2}$, the energy eigenvalues of the stress-perturbed Bloch states at the $p_{3/2}$ band maxima, shown in figure D.1a, are given by equation D.3 (Hensel and Feher, 1963)

\[
\begin{align*}
E (\Gamma^+_7) &= \epsilon_0 + a S (s_{z_{12}} + s_{z_{11}}) + b S (s_{z_{12}} - s_{z_{11}}) \quad \text{Stress in} \langle 001 \rangle \\
E (\Gamma^+_6) &= \epsilon_0 + a S (s_{z_{12}} + s_{z_{11}}) - b S (s_{z_{12}} - s_{z_{11}}) \quad \text{Direction} \langle 111 \rangle
\end{align*}
\]

and

\[
-\text{-----------------------------}
\]

\[
\begin{align*}
E (\Gamma^+_7) &= \epsilon_0 + a S (s_{z_{12}} + s_{z_{11}}) + b S (s_{z_{12}} - s_{z_{11}}) \quad \text{Stress in} \langle 001 \rangle \\
E (\Gamma^+_6) &= \epsilon_0 + a S (s_{z_{12}} + s_{z_{11}}) - b S (s_{z_{12}} - s_{z_{11}}) \quad \text{Direction} \langle 111 \rangle
\end{align*}
\]

\[
-\text{-----------------------------}
\]
\[ E(\Gamma_7^+) = E_o + a S (2s_{12} + s_{11}) + \frac{d}{4} S s_{7+} \]
\[ E(\Gamma_7^+ + \Gamma_1^+) = E_o + a S (2s_{12} + s_{11}) - \frac{d}{4} S s_{7+} \]  
\{ \text{Stress in } <111> \text{ Direction} \}

where \( S \) is the stress, which is negative for compression, and \( E_o \) is the zero-stress energy position of the \( p_{3/2} \) valence band maxima. Including the interband matrices produces a further shift of the \( E(\Gamma_7^+) \) and \( E(\Gamma_1^+) \) levels as (Hasegawa, 1963)

\[ E(\Gamma_7^+) \rightarrow E(\Gamma_7^+) + \frac{2d^2S^2}{\Lambda} (s_{7+} - s_{7-})^2 \]  
\{ \text{Stress in } <001> \text{ Direction} \}

\[ E(\Gamma_7^+ + \Gamma_1^+) \rightarrow E(\Gamma_7^+ + \Gamma_1^+) + \frac{2d^2S^2}{\Lambda} S_{7+} \]  
\{ \text{Stress in } <111> \text{ Direction} \}

where \( \Lambda \) is the spin-orbit splitting of the valence bands in silicon (\( \Lambda \approx 44 \text{ meV.} \), Zwerdling et al., 1960a). Since \( S^2 \) appears in equations D.6 and D.7, the interband coupling is a second-order strain (or stress) effect and can be neglected for strains less than \( 10^{-4} \) (Hasegawa, 1963). As the above discussions mentioned, however, a careful study of these second order effects permits one to order the stress-induced sublevels of the \( p_{3/2} \) maxima (Hensel and Feher, 1963).

(ii) Consider, now, the acceptor ground state in boron-doped silicon. In section 5.2 the wavefunctions for the unperturbed ground state were shown to transform as \( \Gamma_8^0 \) under \( \overline{T_d} \). Denote the four degenerate wavefunctions which are associated with this unperturbed ground state by \( \psi_m^m(\zeta) \) (\( m = -\frac{3}{4}, \cdots, \frac{3}{4} \)). In the manner of equation D.1 a \( 4 \times 4 \) strain matrix \( (H_\zeta')_{m,m} \), in the representation of these wavefunctions \( \psi_m^m(\zeta) \) can be constructed. Although the \( \psi_m^m(\zeta) \) transform as \( \Gamma_8^0 \) under \( \overline{T_d} \) while the \( \psi_m^{3/4}(\zeta) \) transform as \( \Gamma_8^{1+} \) under \( \overline{C}_h = \overline{T_d} \times C_2 \) (see section 5.1), the form of \( H_\zeta' \) is identical to \( H_\zeta^{3/4} \) (Bir et al., 1963). However,
α, β, δ are replaced by α', β' and δ', which are the deformation potential parameters for the acceptor ground state in boron-doped silicon. In section 5.3 the wavefunctions of the unperturbed 2p' and 3p' internal states were shown to transform as $\Gamma_6$ under $\overrightarrow{U}$. As the selection rule arguments in that section indicate, the ordering of the stress-induced sublevels of the ground state is that ordering shown in figure 5.2. For clarity, these stress-induced sublevels are again shown in figure D.1b. Corresponding to equations D.4 and D.5, the eigenvalues of these ground state sublevels are

\[
E(\Gamma_7) = E_2 + \alpha'(z_s + s_w)S + b' s(s_s - s_d) \quad \text{Stress in } \langle 001 \rangle
\]

\[
E(\Gamma_6) = E_2 + \alpha'(z_s + s_w)S - b' s(s_s - s_d) \quad \text{Direction}
\]

and

\[
E(\Gamma_7') = E_2 + \alpha'(z_s + s_w)S + \frac{\beta'}{\gamma} s \quad \text{Stress in } \langle 111 \rangle
\]

\[
E(\Gamma_5 + \Gamma_7) = E_2 + \alpha'(z_s + s_w)S - \frac{\beta'}{\gamma} s \quad \text{Direction}
\]

---

† Bir et al. (1963) refer to α', β' and δ' as the "deformation potential constants of the impurity center."
APPENDIX E - CALCULATION OF $\Delta \omega^{2p'}_V(T)$

A calculation of the phonon broadening $\Delta \omega^{2p'}_V(T)$ of the 2p' absorption peak due to electron-phonon coupling of the 2p' internal state to the $p_{3/2}$ Bloch states was made. The purpose of this appendix is to outline this calculation.

In section 5.3 the wavefunctions $\psi^{2p'}_V(r)$ of the 2p' state were shown to have a $\Gamma_6$ symmetry. Since $\Gamma_6$ is a 2-dimensional irreducible representation, the 2p' state is only spin degenerate. To calculate $\Delta \omega^{2p'}_V(T)$, therefore, the "non-degenerate" (i.e. neglecting spin which is not important here) phonon broadening theory of Barrie and Nishikawa (1963) can be used.

The appropriate formula for $\Delta \omega^{2p'}_V(T)$ is (Barrie and Nishikawa)

$$\Delta \omega^{2p'}_V(T) = 2\pi \sum \sum |V_{2p',nG,2p,nG}|^2 \left[ (1 + \nu_{2p'}^k) \delta(E_{2p'} - E_n(r) - \hbar \omega_2) 
+ \nu_{p'}^k \delta(E_{2p'} - E_n(r) + \hbar \omega_2) \right]$$  \hspace{1cm} (E.1)

where the summations are over the band indices $n$ and the wavevectors $k$ of the $p_{3/2}$ Bloch functions $\phi^{3/2}_{nG}(r) = \sqrt{\lambda/\pi} \epsilon^{3/2}_{nG} r e^{i\xi \cdot r}$. The matrix elements $V_{2p',nG,2p,nG}$ of the electron-phonon interaction are treated in the isotropic deformation potential approximation of Bardeen and Shockley (1950). In this approximation

$V_{2p',nG,2p,nG}$ can be written as (Lax and Burstein, 1955)

$$V_{2p',nG,2p,nG} = i \left( \frac{\hbar}{2N\lambda} \right)^{\frac{1}{2}} \Theta_{2p',nG}^{3/2}(\xi)$$  \hspace{1cm} (E.2)

where $\xi$ is the deformation potential constant, $N$ is the number of unit cells, $\lambda$ is the mass per unit cell and

$$\Theta_{2p',nG}(\xi) = \int d\xi \varphi^{2p'}_{nG}(\xi) \phi^{3/2}_{nG}(\xi) e^{i \xi \cdot r}$$  \hspace{1cm} (E.3)

The temperature $T$ is present in the $\Delta \omega^{2p'}_V(T)$ of equation E.1 through

$$\nu_{2p'}(\xi) = \frac{1}{e^{\hbar \omega_2/\hbar T} - 1}$$  \hspace{1cm} (E.4)
The phonons of interest are the longitudinal long-wavelength acoustic phonons (Barrie and Nishikawa). The energy spectrum of these phonons is given by

$$\omega_k = v q, \quad q = |q|$$

(E.5)

where $q$ is the wavevector of the phonons and $v$ is the velocity of sound which is assumed to be independent of the direction of the wave propagation.

An effective mass wavefunction is used to evaluate equation E.3. The envelope functions $F_{k_{m',m}}^{2p',(r)}$ for the effective mass wavefunctions $\psi_{2p',(r)}^{m'}$ (equation 2.14) are modified hydrogenic 2p-wavefunctions. Since these functions $F_{k_{m',m}}^{2p',(r)}$ are not spherically symmetrical, it is difficult to evaluate equation E.3. However, the calculation can be simplified in the following manner. In the effective mass theory for the simple valence band (see sections 2.2 and 2.4) the 2s' state is degenerate with the 2p' state. Since in reality the distinction between "s-like" and "p-like" states is not that good (i.e. due to the periodic function $\phi_{n'p'}^{(m',r)}$ in equation 2.14), a reasonable approximation is

$$\Theta_{2p',n'q}^{(m',r)}(\xi) \approx \Theta_{2s',n'q}^{(m',r)}(\xi)$$

(E.6)

Since the envelope functions $F_{k_{m',m}}^{2s',(r)}$ for the 2s' state are spherically symmetrical $\Theta_{2s',n'q}^{(m',r)}(\xi)$ can be evaluated more easily. Corresponding to equation E.3, one obtains

$$\Theta_{2s',n'q}^{(m',r)}(\xi) = \int d_r \psi_{2s',(r)}^{2s',(r)} \phi_{n'p'}^{(m',r)}(r)$$

$$= \frac{1}{V} \sum_{m''}^{3s_h} \int d_r F_{k_{m',m}}^{2s',(r)}(r) \phi_{n''p'}^{(m',r)}(r) e^{i(\xi + q) \cdot r}$$

(E.7)

The summation $\sum_{m''}$ in the above equation is over spin states.
Since spin is not important in the phonon-broadening theory, this summation and the subscript \( m' \) will be ignored. Expressing the above envelope functions in a Fourier series (see equation 2.6), equation \( E.7 \) becomes
\[
\Theta_{\alpha', \alpha''} (\xi) = \frac{1}{V} \sum_{\xi} A_{\chi}^{\alpha', \alpha''} (\xi) \sum_{\tau} u_{\alpha'}^{\chi} (\tau) \cdot u_{\alpha''}^{\chi} (\tau) e^{i(\xi + \eta - \eta')} \xi
\] (E.8)

Since the product \( u_{\alpha'}^{\chi} (\tau) \cdot u_{\alpha''}^{\chi} (\tau) \) has the periodicity of the lattice, one can write
\[
\sum_{\xi} u_{\alpha'}^{\chi} (\tau) \cdot u_{\alpha''}^{\chi} (\tau) = \sum_{K_{n}} G_{n_{\xi}} (K_{n}) \sum_{K_{n}} e^{i K_{n} \cdot \xi}
\] (E.9)

where the \( K_{n} \)'s are the reciprocal lattice vectors. Combining the above two equations, one obtains
\[
\Theta_{\alpha', \alpha''} (\xi) = \sum_{K_{n}} \sum_{\lambda} G_{n_{\xi}} (K_{n}) A^{2s', \chi}_{\xi} (\xi') \sum_{K_{n} + \eta} S_{\lambda'}^{\chi} K_{n} + \eta + \xi
\] (E.10)

The smallest non-zero \( K_{n} \) has magnitude
\[
| K_{n} | \approx \frac{1}{(\pi a_{*}/2)^{1/2}} \frac{2\pi}{\Delta_{\xi}} \approx 10^{8} \text{cm}^{-1}
\] (E.11)

where \( \Delta \) is the volume of the unit cell. \( | A^{2s', \chi}_{\xi} (\xi') | \) has large amplitude only for (Kohn, 1957)
\[
| s' | \ll 1/\alpha_{*} \approx 10^{6} \text{cm}^{-1}
\] (E.12)

where \( \alpha_{*} \) is the effective-mass Bohr radius for the \( p_{1/2} \) valence band (\( m_{*} = 0.25m \)). The \( p_{3/2} \) Bloch functions \( \varphi_{n_{\eta}}^{\nu/2} (\tau) \) of interest are those ones with eigenvalues \( E_{n}(\xi) \) near the \( 2p' \) level. One sees in figure 1.1, therefore, that these functions have
\[
| s' | \ll 5 \times 10^{6} \text{cm}^{-1}
\] (E.13)

Since the phonons of interest have large wavelengths, their wavevectors \( \xi \) are expected to lie within the first Brillouin zone. Since equations E.11, E.12 and E.13 show that \( \xi \) and \( \xi' \) are
also in the first Brillouin zone, one obtains
\[ \delta_{\eta',\eta,\frac{1}{2}+\tau} \sim \delta_{\eta',\frac{1}{2}+\tau} \delta_{\Delta v',0} \] (E.14)
and equation E.10 becomes
\[ \Theta_{2\alpha',\eta}(\xi) \sim \sum_{\eta} \frac{C_{n,0}^{*}(\xi)}{2 \pi} A_{1}(\xi) \delta_{\eta',\frac{1}{2}+\tau} \]
\[ = \left( \frac{1}{V} \right)^{2} \left( u_{0}^{\alpha_{2}} \right) \left( u_{n}^{2^{\alpha_{2}}} \right) \left( \frac{d}{d\xi} F_{\phi}(\xi) \right) e^{i(\xi+\tau)^{2}} \] (E.15)
Assume that
\[ \frac{1}{V} \left| \left( u_{0}^{\alpha_{2}}(\xi) \right) \left( u_{n}^{2^{\alpha_{2}}}(\xi) \right) \right| \sim 1 \] (E.16)
As a result of this approximation, the calculation of the absolute value of \( \Delta \omega_{2}(\tau) \) is not expected to be very accurate. However, the predicted temperature dependence of \( \Delta \omega_{2}(\tau) \) is expected to be quite accurate since the error introduced by assuming equation E.16 should approximately cancel out in the ratio \( \Delta \omega_{2}(\tau) / \Delta \omega_{0}(0) \).

Evaluating equation E.15, one sees that the \( \phi_{n_{2}}^{2}(\xi) \)'s of importance are those Bloch functions with eigenvalues \( E_{n}(\xi) \) satisfying
\[ \left| E_{n}(\xi) - E_{2}(\tau) \right| \lesssim 3 \text{ meV} \] (E.17)
Consequently, the exact curvature of the \( p_{3/2} \) valence bands is not of great importance and a good approximation is to replace them by two parabolic bands (effective masses \( 0.2m \) and \( 0.5m \) were used; see figure 1.1).

The summations in equation E.1 were replaced by
\[ \frac{\Sigma}{\xi} \rightarrow \frac{\Sigma}{2^{3/2}} \int d^{3} \xi \quad ; \quad \frac{\Sigma}{\xi} \rightarrow \frac{\Sigma}{2^{3/2}} \int d^{3} \xi \] (E.18)
One integration was performed numerically on a digital computer. The following numerical values for the parameters were
used

\[ N \frac{M}{V} = 2.3 \text{ g/cm}^3 \]
\[ v = 8.3 \times 10^5 \text{ cm/sec.} \]
\[ \Xi = 15 \text{ eV.} \]

The final results are quoted in section 6.3.
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