1969

Energy Band Structure of Gallium Antimonide.

Hwe Ik Zhang

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_disstheses/1630

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
This dissertation has been microfilmed exactly as received 70-277

ZHANG, Hwe Ik, 1938-
ENERGY BAND STRUCTURE OF GALLIUM ANTIMONIDE.

The Louisiana State University and Agricultural and Mechanical College, Ph.D., 1969
Physics, solid state

University Microfilms, Inc., Ann Arbor, Michigan
ENERGY BAND STRUCTURE OF GALLIUM ANTIMONIDE

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Physics and Astronomy

by

Hwe Ik Zhang
B.S., Seoul National University, 1961
May 1969
ACKNOWLEDGEMENT

The author is greatly indebted to Professor Joseph Callaway for his guidance during the whole course of this investigation. He wishes to express his appreciation to Professor John Fry and Dr. Makoto Okazaki for their valuable advice.

The support for this research from the Air Force Office of Scientific Research is greatly appreciated. A financial assistance pertinent to the publication of this dissertation from the "Dr. Charles E. Coates Memorial Fund of the LSU Foundation donated by George H. Coates" is gratefully acknowledged.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vi</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THEORY OF THE PSEUDO-HAMILTONIAN</td>
<td>6</td>
</tr>
<tr>
<td>III. PARAMETERIZATION OF PSEUDO-HAMILTONIAN</td>
<td>13</td>
</tr>
<tr>
<td>A. Local Pseudopotential</td>
<td>14</td>
</tr>
<tr>
<td>B. Nonlocal Pseudopotential</td>
<td>15</td>
</tr>
<tr>
<td>C. Pseudo-spin-orbit interaction</td>
<td>17</td>
</tr>
<tr>
<td>IV. DETERMINATION OF PARAMETERS AND BAND CALCULATION</td>
<td>20</td>
</tr>
<tr>
<td>V. CARRIER CONCENTRATION DEPENDENCE OF EFFECTIVE MASSES</td>
<td>29</td>
</tr>
<tr>
<td>VI. OPTICAL PROPERTIES</td>
<td>42</td>
</tr>
<tr>
<td>VII. PRESSURE DEPENDENCE OF THE BAND STRUCTURE</td>
<td>48</td>
</tr>
<tr>
<td>VIII. CONCLUSION</td>
<td>56</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>58</td>
</tr>
<tr>
<td>TABLES AND FIGURES</td>
<td>61</td>
</tr>
<tr>
<td>APPENDICES</td>
<td></td>
</tr>
<tr>
<td>A. Structure Factors in Zinc-blende Structure</td>
<td>87</td>
</tr>
<tr>
<td>B. Some Properties of Projection Operator</td>
<td>90</td>
</tr>
<tr>
<td>C. Cancellation Property of Pseudo-spin-orbit Interaction</td>
<td>94</td>
</tr>
<tr>
<td>D. A General Form of Hermitian Pseudo-Hamiltonian</td>
<td>97</td>
</tr>
<tr>
<td>VITA</td>
<td>100</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>I Pseudo-Hamiltonian parameters.</td>
<td>61</td>
</tr>
<tr>
<td>II Some important energy level separations and effective mass in GaSb.</td>
<td>62</td>
</tr>
<tr>
<td>III Energy values of the conduction band near ( k = 0 ).</td>
<td>63</td>
</tr>
<tr>
<td>IV Coefficients of the energy expansion.</td>
<td>64</td>
</tr>
<tr>
<td>V Comparison of calculated effective masses with experimentally measured values for conduction band.</td>
<td>65</td>
</tr>
<tr>
<td>VI Anisotropy of conduction band effective mass.</td>
<td>66</td>
</tr>
<tr>
<td>VII Comparison of calculated heavy hole masses with experimental values.</td>
<td>67</td>
</tr>
<tr>
<td>VIII Pseudo-Hamiltonian parameters used in Chapters VI and VII.</td>
<td>68</td>
</tr>
<tr>
<td>IX Parameters of the model local pseudopotentials for Ga and Sb atoms.</td>
<td>69</td>
</tr>
<tr>
<td>X Band structure calculated by model pseudopotential and by actual pseudopotential.</td>
<td>70</td>
</tr>
<tr>
<td>XI Pressure coefficients of some important level separations.</td>
<td>71</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Procedure of determining pseudo-Hamiltonian parameters and calculating band structure.</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>Calculated energy bands of GaSb along important symmetry axes.</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>Effective mass versus Fermi energy for conduction band.</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>Effective mass versus Fermi energy for light hole band.</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>Effective mass versus Fermi energy for heavy hole band.</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>Effective mass versus Fermi energy for split-off band.</td>
<td>79</td>
</tr>
<tr>
<td>7</td>
<td>Effective mass versus carrier concentration for conduction band.</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>Effective mass versus carrier concentration for light hole band.</td>
<td>81</td>
</tr>
<tr>
<td>9</td>
<td>Effective mass versus carrier concentration for heavy hole band.</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>Effective mass defined by (5.17) versus carrier concentration for conduction band.</td>
<td>83</td>
</tr>
<tr>
<td>11</td>
<td>Imaginary part of the dielectric constant of GaSb.</td>
<td>84</td>
</tr>
<tr>
<td>12</td>
<td>Real part of the dielectric constant of GaSb.</td>
<td>85</td>
</tr>
<tr>
<td>13</td>
<td>Reflectivity of GaSb as a function of photon energy.</td>
<td>86</td>
</tr>
</tbody>
</table>
ABSTRACT

A pseudo-Hamiltonian including local and nonlocal pseudo-potentials and a pseudo-spin-orbit interaction has been determined for GaSb. The 14 parameters of this pseudo-Hamiltonian are selected empirically. The lowest 8 energy levels and wave functions are calculated at 1505 points in the 1/48 of the Brillouin zone. This calculation has reasonably reproduced most of the basic features of the energy band structure, including the spin-orbit splittings of the valence bands, which are well established for GaSb.

A detailed analysis of the energy band shape near \( k = 0 \) is performed. The anisotropy and dependence on carrier concentration of the effective masses near \( k = 0 \) are calculated for the conduction band, light hole band, heavy hole band, and split-off valence band. A calculation of the imaginary part of the dielectric constant is performed in the energy range from 0 to 6 eV and the real part of the dielectric constant and the reflectivity are obtained using the Kramers-Kronig relation. The calculated reflectivity is in good agreement with experiment. The pressure dependence of the band structure is discussed and the pressure coefficients of certain energy levels are calculated, the results also being in satisfactory agreement with experiment.
CHAPTER I
INTRODUCTION

Electronic energy band theory, which is based upon single particle approximation and Bloch's theorem, has been very successful in explaining much of the important electronic behavior in the solid state. However, many of the attempts to calculate the energy band structure for actual materials strictly from first-principles have not been successful in producing results with an accuracy comparable to that of available experimental data. This failure can be ascribed mainly to our inaccurate knowledge of the crystalline potentials and the lack of a practical method of solution, rather than to the inadequacy of the energy band theory itself.

In these circumstances, we can proceed by using a semi-empirical approach in energy band calculations, incorporating some well established experimental information at certain stages. In this approach, we actually replace some processes which require a great amount of computational effort by some parameters which can be conveniently obtained from experimental information. By doing this, we can also avoid the difficulty of finding the actual crystalline potential.

In practice, there are certain important criteria for determining the validity of these semi-empirical energy band calculations. In the first place, the theoretical framework in which the parametrized quantities appear should be reasonably justified. This framework
should be capable of producing the same results in a certain range as the more fundamental formalism would be expected to do; and it should be simple enough so that it can be useful in practical computation. The range of the validity of the calculated results depends mainly on the validity of the theoretical framework. In the second place, the experimental situation should be transparent enough to provide some of the vital experimental information unambiguously and without much experimental uncertainty. Since the experimental information holds a key role in this approach, numerical accuracy of the calculated values is directly related to that of the employed experimental data.

One of the most successful and widely used schemes of this semi-empirical approach is the empirical pseudopotential method. This particular procedure is both well established theoretically, and simple to apply in a calculation.

The empirical pseudopotential scheme has been adopted in the present work, which has been undertaken in order to perform a theoretical investigation on a semiconducting compound gallium antimonide (GaSb). The pseudo-Hamiltonian used is nonlocal, and includes spin-orbit interaction. This investigation also provides a verification of the ability of the empirical pseudopotential approach to give a reasonably precise fit to the band structure which has been carefully investigated experimentally.

A considerable amount of information concerning the energy band structure of GaSb has been obtained from various experimental investigations. A comprehensive description of the available
experimental information has been given by Kosicki (1967). Among the characteristic features of the band structure of this material, the small energy level separations between the lowest conduction band minimum at [000] and the subsidiary minima in [111] and [100] directions of the conduction band are of interest, especially in the interpretation of the properties of the doped samples under high pressure (Kosicki et al., 1966a, Kosicki et al., 1966b). The most valuable experimental information for the present calculations is obtained mainly from optical measurements, such as absorption spectra and reflectivity spectra.

We will review briefly some of the previous band calculations for GaSb. The band structure of GaSb was first calculated by Cohen and Bergstresser (1966) using a local pseudopotential. However, their work is not completely satisfactory in that some important characteristics of the band structure are not accurately reproduced. In particular, the calculated energy level separations between the three conduction band minima are too large compared with the experimentally measured values. In a preliminary calculation, we introduced a nonlocal pseudopotential and obtained substantial improvement with regard to the lowest conduction band (Zhang and Callaway, 1968). In both the above calculations, the spin-orbit interaction was not included.

Recently, Herman et al. (1968) calculated energy band structure for a large number of semiconductors using the empirically adjusted OPW method. In order to improve the results of an ordinary OPW band calculation starting with some physically realistic trial crystal
potential, they employed three empirically adjustable parameters. One parameter corresponds to one of the local pseudopotential parameters and the other two are related to the core energy levels of the anion and cation for III-V compounds. Values of the three parameters are chosen to make some of the calculated level separations agree with experiment. For GaSb, they obtained the proper shape for the lowest conduction band, which provided the main criteria for their selection of the parameters. Another band structure calculation for GaSb has been performed by Higginbotham et al. (1968). In their calculation the potential matrix elements at \( k=0 \) were selected empirically and then the \( k \cdot p \) method was employed to calculate the energy bands throughout the whole Brillouin zone.

The results of the present calculation agree substantially with the above two calculations in the region between the lowest conduction band and the valence bands. However, there are some quantitative disagreements in regard to the highest valence band and the second lowest conduction band. A more detailed comparison of results will be found in Chapter IV.

In Chapter II, the theory of pseudopotential is reviewed. A pseudo-Hamiltonian, which includes nonlocal pseudopotential and spin-orbit interaction is derived for the purpose of making empirical energy band calculations.

In Chapter III, this pseudo-Hamiltonian is reduced to a parameterized form. On the basis of plane wave states, the typical matrix elements for the local pseudopotential, the nonlocal
pseudopotential and the pseudo-spin-orbit interaction are given explicitly.

In Chapter IV, we describe the procedure of determining the pseudo-Hamiltonian parameters using the available experimental information concerning the energy bands of GaSb. The main features of calculated energy band structure are given and compared with experiment. A comparison with other calculations is also made.

In Chapter V, a detailed analysis of the energy band shape near \( \mathbf{k} = 0 \) is performed. The carrier concentration dependency and the anisotropy of the effective masses near \( \mathbf{k} = 0 \) are calculated for the conduction band, light hole band, heavy hole band, and split-off band.

In Chapter VI, the imaginary part of the dielectric constant is calculated and the real part of the dielectric constant is obtained by Kramers-Kronig relations. Using this dielectric constant, the reflectivity is calculated.

In Chapter VII, the pressure dependence of the band structure is discussed and the pressure coefficients of certain energy bands are calculated.

In the last Chapter, a brief discussion of the results and conclusions is made for the present investigation.
CHAPTER II

THEORY OF THE PSEUDO-HAMILTONIAN

The pseudopotential method was first introduced by Phillips and Kleinman (1959). This method was based upon the orthogonalized-plane-wave (OPW) method of Herring (1940). Phillips and Kleinman noted that the orthogonalization procedure of the OPW method produced the same effect as a repulsive potential added to the true crystal potential. Cohen and Heine (1961) subsequently made a detailed analysis of this repulsive character and demonstrated that a substantial part of the true potential is cancelled within the core region. More recently, the spin-orbit interaction has been incorporated into the pseudopotential scheme by Weisz (1966) and a general form of the pseudo-Hamiltonian including nonlocal terms and spin-orbit interaction has been used by Stark and Falicov (1967) for the calculation of the band structure of Zn and Cd.

In this Chapter, we will derive a form of the pseudo-Hamiltonian including spin-orbit interaction, which will be convenient for the empirical energy band calculation.

The electronic states in the crystal including spin variables are determined by the Schrödinger equation

\[ [H^0 + H^S] \psi_n = E_n \psi_n \]  \hspace{1cm} (2.1)

with

\[ H^0 = \frac{p^2}{2m} + V(r) \]

\[ H^S = \frac{\hbar}{4mc^2} \left[ \nabla V(r) \times \frac{p}{m} \cdot \sigma \right] \]
Here \( p \) is the momentum operator, \( V(r) \) is the crystal potential and \( \sigma \) is the Pauli spin operator. In the solid state, we are not interested in the solutions corresponding to the atomic core states. However, let us consider a set of core eigenstates of (2.1), \( \{ |\Psi^c_t >, t=1, 2, ..., M \} \), which satisfy

\[
[H^o + H^s] |\Psi^c_x > = E^c_x |\Psi^c_x >
\]

where \( M \) is the number of core states in the given crystal. Let us define operators \( P_t \) and \( Q \) as

\[
P_t = |\Psi^c_x > < \Psi^c_x |,
\]

\[
Q = \sum_{k=1}^{M} g^c_k |\Psi^c_x > < \Psi^c_x | = \sum_{k=1}^{M} g^c_k P_k
\]

where \( g^c_k \) is a constant associated with state \( |\Psi^c_t \rangle \), and consider the solutions of the equation

\[
[H^o + H^s + Q] |\Phi > = E |\Phi >
\]

We can represent the eigenfunction \( |\Phi > \) as

\[
|\Phi > = \sum_{k=1}^{M} \alpha^c_k |\Psi^c_x > + \sum_{\eta=1}^{\infty} \beta_\eta |\Psi_\eta >
\]

where the states \( |\Psi_\eta > \) are the solutions of (2.1) which do not correspond to core states. We substitute \( |\Phi > \) in (2.5) by (2.6) and obtain
From (2.8) and (2.9) we observe the following results:

1. If for a particular \( n \), \( \beta_n \neq 0 \), then \( E = E_n \) and \( \beta_n' = 0 \)
   where \( n' \) is different from \( n \).

2. If \( \alpha_t \neq 0 \) for a particular \( t \), \( g_t = E_t - E_t^c \)

Therefore, if we solve (2.5) with

\[
Q = \sum_{k=1}^{M} \left( E - E_k^c \right) \left| \psi_k^c \right> \left< \psi_k^c \right|
\]

we obtain the same set of eigenvalues as we would obtain from (2.1). It is convenient to separate the operator \( Q \) into two parts in the following fashion.

\[
Q = \sum_{k=1}^{M} \left[ E P_k - \frac{1}{2} E_k^c P_k - \frac{1}{2} P_k E_k^c \right]
\]

and we can rewrite (2.5) as
\[
\left[ \frac{p^2}{2m} + V_P + H_P^S \right] \Phi = E \Phi
\]

with

\[
V_P = V(r) + \sum_{k=1}^{M} \left[ E P_k - \frac{1}{2} (H^0 P_k + P_k H^0) \right]
\]

\[
H_P^S = H^S - \frac{1}{2} \sum_{k=1}^{M} (H^S P_k + P_k H^S)
\]

We note that (2.12) has the form of a wave equation containing a changed potential (nonlocal) and changed spin-orbit interaction but still yields the same set of eigenvalues as the original wave equation (2.1). We will call \( V_P \) and \( H_P^S \) the pseudopotential and pseudo-spin-orbit interaction, respectively. The main advantage in solving (2.12) rather than (2.1) lies in the fact that the substantial parts of \( V(r) \) and \( H^S \) in the core region are cancelled out by the terms containing \( P_k \), and therefore the equation can reasonably be represented on the basis of a practically manageable number of plane wave states. The cancellation property of \( V_P \) can be demonstrated in a manner similar to the discussion by Cohen and Heine (1961). A discussion of the cancellation in \( H_P^S \) is made in Appendix B.

Up to this point, we did not make any approximation. If we attempt to solve (2.12) accurately, we need a set of accurate core
solutions just as we need them in OPW method and we also need an estimated eigenvalue $E$, which in principle should be determined self consistently. Instead of doing this, we can parametrize $V_p$ and $H_p$ in the forms which would most likely appear if we went through all the procedures to evaluate $V_p$ and $H_p$ accurately. The parameters included in $V_p$ and $H_p$ then can be determined using experimental informations. Following this alternative, we can avoid much of the computational difficulties encountered in the direct calculations. In Appendix D, we attempted to make a more general argument for the pseudo-Hamiltonian which would be useful in the empirical energy band calculation.

It is usually convenient to work with states of definite spin eigenvalue $S_z$. Therefore let us consider a set of orthonormal states $\{|\psi_j\rangle, j=1,...,\infty\}$ which satisfy

$$
H^s |\psi_j\rangle = E^s_j |\psi_j\rangle \\
\frac{1}{2} s_z |\psi_j\rangle = S^s_z |\psi_j\rangle
$$

The states defined this way correspond to the solutions obtained without including spin-orbit interaction. If we expand core states into this set of states as

$$
|\psi^c_t\rangle = \sum_{j=1}^{\infty} c^c_{tj} |\psi_j\rangle
$$

it is expected that $c^c_{tj} \approx \delta_{tj}$ for the case in which the spin-orbit interaction is not very strong. And also

$$
P_t = \sum_{j=1}^{\infty} \sum_{j'=1}^{\infty} c^*_{tj} \cdot c_{tj'} |\psi_j\rangle \langle \psi_{j'}|
$$
would not be much different from \(|\psi_t > < \psi_t|\). In the following argument, we will replace \(P_t\) by \(|\psi_t > < \psi_t|\). Assuming that the qualitative properties of \(P_t\) would not be changed much by this replacement.

We now estimate the nonlocal character of \(V_P\) associated with the operator \(|\psi_t > < \psi_t|\). The core state \(|\psi_t >\) can, in a good approximation, be expressed as a linear combinations of atomic orbitals (LCAO):

\[
|\psi_t > = \frac{\Omega^{\frac{1}{2}}}{(2\pi)^{3/2}} \sum_{K} e^{-iK \cdot \mathbf{R}} U_K (r-R_{\mu}) \quad (2.15)
\]

where \(\Omega\) is the volume of the unit cell and \(U_K (r-R_{\mu})\) is the atomic state centered at the atomic site \(R_{\mu}\). A typical matrix element based upon the plane wave states will be

\[
< \mathbf{k} + \mathbf{K} | |\psi_t > < \psi_t | \mathbf{k} + \mathbf{K} >
\]

where \(\mathbf{K}_i\) and \(\mathbf{K}_j\) are the reciprocal lattice vectors and

\[
< \mathbf{k} + \mathbf{K} | |\psi_t > = \frac{\Omega^{\frac{1}{2}}}{(2\pi)^{3/2}} \sum_{K} e^{-iK \cdot \mathbf{R}} U_K (r-R_{\mu}) d^3r \quad (2.16)
\]

The \(k^3\)-dependence of the pseudopotential arises from the factor \(e^{-iK \cdot (r-R_{\mu})} U_K (r-R_{\mu})\). The nonlocal character is more appreciable for atomic states which are more spread out. We therefore divide the pseudopotential into two parts, one local and another nonlocal:

\[
V_P = V_P^l + V_P^n
\]
where

\[ V_p^n = \sum \Gamma \left| \psi_t \right\rangle \left\langle \psi_t \right| \]

\[ V_p^o = V_p - V_p^n \]

The summation in \( V_p^n \) runs only over the states \( |\psi_t \rangle \) which correspond to the last occupied core shells. In this form of \( V_p \), we assume that the nonlocal character of the pseudopotential is adequately represented by \( V_p^n \) treating the constants \( G_t \) as adjustable parameters. The remaining part of \( V_p \), which is denoted by \( V_p^o \), will be regarded as a local operator and called as local pseudopotential.
The pseudo-Hamiltonian we have introduced in Chapter II can be written as

$$H_p = \frac{p^2}{2m} + V_p^o + V_p^n + H_P^s$$  \hspace{1cm} (3.1)

where

$$V_p^o = \sum_{\mathbf{k}} \frac{M}{k} \left( E - E_k^o \right) \left| \psi_{\mathbf{k}}^+ \right\left< \psi_{\mathbf{k}}^- \right| - \sum_{\mathbf{k}} G_{\mathbf{k}} \left| \psi_{\mathbf{k}}^+ \right\left< \psi_{\mathbf{k}}^- \right|$$  \hspace{1cm} (3.2)

$$V_p^n = \sum_{\mathbf{k}} G_{\mathbf{k}} \left| \psi_{\mathbf{k}}^+ \right\left< \psi_{\mathbf{k}}^- \right|$$  \hspace{1cm} (3.3)

$$H_P^s = H^s - \frac{1}{2} \sum_{\mathbf{k}} \left\{ \begin{array}{c} H^s \left| \psi_{\mathbf{k}}^+ \right\left< \psi_{\mathbf{k}}^- \right| + \left| \psi_{\mathbf{k}}^- \right\left< \psi_{\mathbf{k}}^+ \right| H^s \end{array} \right\}$$  \hspace{1cm} (3.4)

We have assumed that $V_p^o$ given in (3.2) can be approximated by a local operator. The operators $V_p^n$ and $H_P^s$ are nonlocal.

In this Chapter, the typical matrix elements of the pseudo-Hamiltonian will be given on the basis of plane wave states and all the possible form factors will be parameterized into a most convenient form for the purpose of calculating band structure. The expression of the kinetic energy term is trivial in the plane
wave representation. The remaining three terms in (3.1) will be considered in the following sections.

A. Local Pseudopotential

The local pseudopotential given in (3.2) can be expanded in the Fourier series

\[ V_p^0 = \sum_j \left[ S^S(K_j) V^S(K_j) + i S^A(K_j) V^A(K_j) \right] e^{-i K_j \cdot \vec{\tau}} \]  

(3.5)

Here we take the origin of the coordinates to be halfway between two different atoms, and the symmetric and antisymmetric part of the structure factor \( S^S(K_j) \) and \( S^A(K_j) \) are

\[ S^S(K_j) = \cos K_j \cdot \vec{\tau}, \quad S^A(K_j) = \sin K_j \cdot \vec{\tau} \]

with

\[ \vec{\tau} = a \left( \frac{1}{8}, \frac{1}{8}, \frac{1}{8} \right) \]

being the lattice parameter. A general argument on the structure factors of zinc-blende structure is given in Appendix A. The matrix element of \( V_p^0 \) at a point \( K \) in the Brillouin zone is written as

\[ \langle \vec{\omega} + K_i | V_p^0 | \vec{\omega} + K_j \rangle = S^S(\vec{\omega}) V^S(\vec{\omega}) + i S^A(\vec{\omega}) V^A(\vec{\omega}) \]  

(3.6)

with

\[ \vec{\omega} = K_j - K_i \]

Being local, this matrix element is independent of \( K \).
We set $V^S(K) = 0$ and $V^A(K) = 0$ for all $K$ except those five of the smallest magnitude, $[000]$, $[111]$, $[200]$, $[220]$, $[311]$.

For convenience, we represent each of $S^S(K)$, $S^A(K)$, $V^S(K)$, and $V^A(K)$ with the value of $K^2$ in the unit of $(2\pi/a)^2$ at the lower suffix, for example, $V^S_3$ represents $V^S(K)$ for $K$ of $[111]$ type. Since $S^A_0$, $S^S_4$, and $S^A_8$ vanish, we do not need to have $V^A_0$, $V^S_4$, and $V^A_8$. Also we arbitrarily put $V^S_0 = 0$ which would only shift the reference point of the energy levels. We have then six local pseudopotential parameters to determine, namely, $V^S_3$, $V^A_3$, $V^A_4$, $V^S_8$, $V^S_{11}$, $V^A_{11}$.

This local pseudopotential is identical in form with the pseudopotential used by Cohen and Bergstresses (1966). However, since we consider explicitly the nonlocal part of the pseudopotential apart from this, there is some difference in its physical meaning. The six local (pseudopotential) parameters are regarded as adjustable and will be determined empirically.

B. Nonlocal Pseudopotential

The nonlocal pseudopotential given by (3.3) is expressed in terms of the crystal core states $|\psi_t>$ which correspond to the last occupied core shells. We make the tight binding approximation for the crystal core states and express them as the linear combinations of atomic orbitals given by (2.15). In Appendix B, it is shown that the nonlocal pseudopotential obtained this way amounts to the summation of the atomic nonlocal pseudopotential. The atomic states of Ga and Sb in the last occupied shells correspond to the
configurations

\[ 3s^2, 3p^6, 3d^{10}, \text{ for Ga}, \]
\[ 4s^2, 4p^6, 4d^{10}, \text{ for Sb}. \]

We will represent any quantity associated with Ga by a superscript
III and any one associated with Sb by V. A typical matrix element
of the nonlocal pseudopotential on the plane wave basis will be

\[ \langle \mathbf{k} + \mathbf{K}_1 | V^\text{p III} | \mathbf{k} + \mathbf{K}_j > = \sum_{\ell=0}^{2} \left[ G^\text{III}_\ell S^\text{III}_\ell (\mathbf{K}_j - \mathbf{K}_1) \langle \mathbf{k} + \mathbf{K}_1 | U^\text{III}_\ell \rangle \right] \]
\[ \times \langle \mathbf{k} + \mathbf{K}_1 | V^\text{V} | \mathbf{k} + \mathbf{K}_j > + G^\text{V}_\ell S^\text{V} (\mathbf{K}_j - \mathbf{K}_1) \langle \mathbf{k} + \mathbf{K}_1 | U^\text{V}_\ell \rangle \langle \mathbf{k} + \mathbf{K}_1 | V^\text{V} | \mathbf{k} + \mathbf{K}_j > \]
where θ' is the angle between \( k + K_i \) and \( k + K_j \), \( P_{l}(\cos \theta') \) is the Legendre polynomial, and

\[
W^m_l = \frac{4\pi (2l+1)}{\Omega} G^m_l
\]

\[
B^m_l (k + K_j) = \int_0^\infty r j_l (|k+K_j| r) P^{m}_l (r) \, dr
\]

and \( W^l_k \) and \( B^l_k (k + K_j) \) are similarly related. The six parameters \( W^I_{111}, W^I_{111}, W^V_2, W^V_1, W^V_2 \) will be called as nonlocal (pseudopotential) parameters and will be determined empirically.

C. Pseudo-spin-orbit Interaction

The pseudo-spin-orbit interaction \( H^S_p \) is defined in (2.14) and approximated in (3.4). The crystal spin-orbit interaction \( H^S \) which is given by

\[
H^S = \frac{\hbar}{4m^2c^2} \left[ \nabla V(r) \times \mu \right]
\]

can be expressed as a summation of atomic components:

\[
H^S = \mu \cdot \sum_{\mu} h^S_{\mu}
\]

with

\[
h^S_{\mu} = \frac{\hbar}{4m^2c^2} \left[ \nabla V_A (r - \mu) \times \mu \right]
\]

where \( V_A (r - \mu) \) is the contribution to the crystal potential \( V(r) \) from the atom located at the site \( \mu \).

As we have done for the nonlocal pseudopotential, we approximate
the crystal core states $|\Psi_t\rangle$ in (3.4) by the linear combination of atomic orbitals given by (2.15). Then, because of the singularity of $W_A(r - r_\mu)$ near $r = r_\mu$, we obtain in a good approximation

$$H^s |\Psi_t\rangle = \zeta \cdot \sum_\mu \frac{\hbar}{\mu} |U_t (R_\mu)\rangle$$  \hspace{1cm} (3.9)

where $|U_t (R_\mu)\rangle$ is the atomic state of the atom located at $R_\mu$.

Following the argument of Appendix A, the matrix element of pseudo-spin-orbit interaction can be expressed in terms of atomic components of the type

$$\langle t \pm K_i | \frac{\hbar}{\mu} - \frac{1}{2} \sum_k \left\{ \frac{\hbar}{\mu} |U_k\rangle \langle U_k| + |U_k\rangle \langle U_k| \frac{\hbar}{\mu} \right\} |K_i + K_j\rangle$$

Weisz (1966) has shown that, in a reasonable approximation, this expression can be reduced to the form

$$-i \langle t \pm K_i | (\frac{\hbar}{\mu} - \frac{1}{2} \sum_k \{ \frac{\hbar}{\mu} |U_k\rangle \langle U_k| + \frac{\hbar}{\mu} \}) | K_i + K_j \rangle$$

where $\lambda_p$ and $\lambda_d$ are constants associated with p and d atomic states, respectively. Therefore, a typical matrix element of the pseudo-spin-orbit interaction $H^s_p$ can be written as

$$\langle t \pm K_i, s' | H^s_p | K_i + K_j, s' \rangle = -i \zeta ss' \cdot (K_i + K_j) \langle t \pm K_i | (K_i, K_j) \rangle$$

$$+ \left[ S^\pi (K_j - K_i) \{ \lambda^{\pi}_2 + (K_i + K_j) \cdot (K_i + K_j) \lambda^{\pi}_2 \} + S^\tau (K_j - K_i) \{ \lambda^{\tau}_2 + (K_i + K_j) \cdot (K_i + K_j) \lambda^{\tau}_2 \} \right]$$  \hspace{1cm} (3.10)
where \( s \) and \( s' \) denote the spin eigenstates of \( \sigma_z \), and \( \lambda_{1V} \), \( \lambda_{2V} \); \( \lambda_1^V \), \( \lambda_2^V \) are adjustable constants representing the contributions from \( p \) and \( d \) states for the atom \( III \) (Ga) and atom \( V \) (Sb). In this form of the pseudo-spin-orbit interaction, the contribution from the original spin-orbit interaction is contained in the constants \( \lambda_{1}^{III} \) and \( \lambda_{1}^{V} \), the atomic potential being approximated as \( \delta \)-functions. For GaSb, the energy levels subject to the spin-orbit coupling are expected to be \( p \)-like and therefore we set \( \lambda_{2}^{III} = \lambda_{2}^{V} = 0 \). We define the symmetric and antisymmetric parameters by

\[
\lambda^S = \lambda_1^{III} + \lambda_1^{V}, \quad \lambda^A = \lambda_1^{III} - \lambda_1^{V}
\]

and obtain the final form

\[
\langle k + K_i, s | H^p | k + K_j, s' \rangle = -i \delta_{ss'} \left( (k + K_i) \times (k + K_j) \right) \left[ S^S(k_j - k_i) \lambda^S + i S^A(k_j - k_i) \lambda^A \right]
\]

The spin-orbit parameters \( \lambda^S \) and \( \lambda^A \) are determined in the next Chapter.
CHAPTER IV
DETERMINATION OF PARAMETERS AND BAND CALCULATION

To determine the parameters of the pseudo-Hamiltonian, we need experimental data concerning the band structure of the material. The experimental information we have used as reference values were selected according to the following criteria.

(1) It should be representative of the most important features of the band structure.
(2) There should not be much ambiguity in the interpretation of its data, and the data themselves should not have much experimental uncertainty.
(3) The calculation of corresponding theoretical quantities should not be too much involved.

The most important region of the band structure is that containing the upper valence bands and the lower conduction bands. The level separations between the highest valence band and the lowest and second lowest conduction bands together with the relative conduction band levels at the three points \( \Gamma \), \( L \), and \( X \) in the Brillouin zone are taken for the reference values. Also taken as reference values are the conduction band effective mass and the spin-orbit splitting of the valence band at the center of the Brillouin zone.

The transitions from the two valence bands, split by spin-orbit coupling, to the lowest conduction band along the \([111]\) axis reveal
two strong peaks in the optical spectrum and these also are valuable for the band structure. In selecting the experimental values for our use as the reference values, we have tried to take values obtained at low temperature if such are available, but we did not attempt to make actual temperature corrections.

The value of the fundamental optical gap $E(\Gamma_6) - E(\Gamma_8)$ at low temperature is well established from the oscillatory magnetoabsorption spectra and infrared absorption edge. Zwerdling et al. (1959) obtained a value $0.813 \pm 0.001$ eV analyzing the oscillatory magneto-absorption spectra at 4.2 K. Johnson and Fan (1965) confirmed this value obtaining a value $0.8128$ eV from the observation of an exciton peak at 1.7 K. For the values of most of the other energy level separations at $\Gamma$, L, X points and along the [111] axis, we take the low temperature reflectivity spectrum of Greenaway (1962) together with the interpretation by Phillips (1963) and by Cardona (1964). Greenaway (1962) obtained reflectivity peaks at $0.37$ eV, $1.4$ eV, $1.9$ eV, $2.08$ eV, $2.55$ eV, $3.74$ eV, $4.33$ eV, $4.70$ eV, and $5.7$ eV at 80 K. We listed these values in Table 1 according to the usual interpretation for them. Sagar obtained $0.08$ eV for the value of $E(L_6^{(1)}) - E(\Gamma_6)$, the level separation between the conduction band minima located at L and $\Gamma$ points, from the effect of pressure on the resistivity and Hall coefficient. This value agrees with the more recent measurement of Harland and Woolley (1966), $0.084$ eV. For the values of $E(X_6) - E(\Gamma_6)$, $0.3$ eV is a generally accepted value [Ehrenreich (1961), Haga and Kimura (1964)]. From the measurement of optical
absorption at high pressure, Kosicki (1967) obtained a value between 0.75 eV and 0.81 eV for $E(\Gamma_{8v}) - E(\Gamma_{7v})$, the spin-orbit splitting of the valence bands at $\Gamma$ point.

A number of values have been obtained from various experiments for the effective mass at the conduction band minimum. Zwerdling et al. (1959) determined the cyclotron resonance electron effective mass from oscillatory magnetoabsorption data and obtained 0.047 $m_0$; Piller (1963) obtained a value 0.049 $m_0$ from Faraday rotation measurements; Becker et al. (1961) obtained 0.052 $m_0$ from the shift of fundamental absorption edge. Yep and Becker (1966) measured the effective mass for a number of low-carrier concentration samples using Subnikov-de Haas effect and obtained smaller values (0.042 $m_0$, 0.039 $m_0$, 0.039 $m_0$, 0.044 $m_0$ for the four samples with varying degrees of concentration). Allowing for the dependence of the effective mass on the carrier concentration, they estimated a value 0.040 $m_0$ at zero concentration.

The process of determining the pseudo-Hamiltonian parameters was divided into two steps:

1. Determination of the local and nonlocal pseudopotential parameters neglecting the spin-orbit interaction.

2. Determination of the pseudo-spin-orbit interaction parameters.

In the first step, we constructed a Hamiltonian matrix at each $k$-point using the local and nonlocal pseudopotentials presented in (3.6) and (3.8) (with tentatively assumed parameters). The wave functions of the atomic states, used in the calculation of the nonlocal
pseudopotential matrix elements, have been obtained from Herman and Skillman's Table (Herman and Skillman, 1965). The Hamiltonian matrix is based on 59 plane wave states of the six different types of reciprocal lattice vectors, namely [000], [111], [200], [220], [311], and [222]. This matrix was reduced to the dimension of \(~15 \times 15\) employing Löwdin's perturbation method. In the application of Löwdin's perturbation method to reduce the dimension of the matrix, we write the perturbed Hamilton matrix elements in the form

\[ H'_{mn} = H_{mn} + \sum_{l=N_0+1}^{N} \frac{H_{ml} H_{ln}}{E - H_{ll}} \]  

(4.1)

with the substitution for \(E\)

\[ E = H_{mm} \quad \text{for} \quad m = n \]  

\[ = E_0 \quad \text{for} \quad m \neq n \]  

(4.2)

where \(E_0\) is the estimated value of the energy at the lowest conduction band minimum. These substitutions for the value \(E\) are very similar to the method introduced by Brust (1964). We then diagonalized this reduced matrix and obtained the eigenvalues and eigenfunctions for the \(~15\) energy levels. We have repeated the above process of band calculation, comparing the result with the reference values we have taken from experiment and varying the assumed parameters, until we determined the optimum set of values for the six local pseudopotential parameters and six nonlocal pseudopotential parameters.
listed in Table I. With these parameters, the lowest conduction band is determined almost completely because this band is not split by the spin-orbit interaction. A calculated band structure with this pseudopotential (with slightly different set of parameters) without including the spin-orbit interaction was previously published (Zhang and Callaway, 1968).

To introduce the spin-orbit interaction, it is necessary to double the dimensions of all the matrices involved in band calculation because every basis state becomes a two component spinor. It is not practical, however, to introduce the spin-orbit interaction into the original Hamiltonian which would make it into a complex matrix of dimension 118 x 118. We therefore represent the pseudo-spin-orbit interaction given in (3.11) on the basis of the reduced set of ~15 plane wave spinors, which gives a ~30 x 30 matrix. The previous Hamiltonian matrix of dimension ~15 x 15 becomes another ~30 x 30 matrix. A new total Hamiltonian matrix of dimension ~30 x 30 is obtained by adding these two matrices and this represents the complete pseudo-Hamiltonian we are going to solve. We obtain the band structure including the spin-orbit coupling effects by diagonalizing this matrix. The two spin-orbit interaction parameters $\lambda^S$ and $\lambda^A$ were determined in such a way that the spin-orbit splitting of the valence band agreed with experiment at $\Gamma$ point and along the $[111]$ axis.

The usual $k\cdot p$ perturbation calculation of effective masses should be modified to take account of the nonlocal pseudopotential and the spin-orbit interaction. Golin (1968) derived the necessary matrix
elements for these modifications. If the wave function corresponding to the energy level $n'$ at $k=0$ is expressed in the plane wave spinors by

$$u_{n'0} = \sum_{j,s} b_{n'js} |\psi_j, s>$$  \hspace{1cm} (4.3)

the effective mass $m^*$ in the lowest conduction band at $k=0$ is obtained by

$$\frac{m_o}{m^*} = 1 + \sum_{n' \neq n} \frac{Z}{m_o} \left| \frac{P_{nn'}^x + Q_{nn'}^x + S_{nn'}^x}{E_n(0) - E_{n'}(0)} \right|^2$$  \hspace{1cm} (4.4)

with

$$P_{nn'} = \hbar \sum_{j,s} K_j b_{njjs}^* b_{n'js}$$  \hspace{1cm} (4.5)

$$Q_{nn'} = \frac{m_o}{\hbar} \sum_{j,s} b_{njjs}^* b_{n'js} \left[ \nabla_{k} V_{tk}(K_j, K_j') \right]_{k=0}$$  \hspace{1cm} (4.6)

$$S_{nn'} = \frac{\hbar}{2} \sum_{s,s'} \sigma_{ss'} \times \sum_{j,j'} (K_{j'} - K_j) b_{njjs}^* b_{n'js'}$$  \hspace{1cm} (4.7)

$$\times \left[ S^S (K_{j'} - K_j) \chi^S + \epsilon^S (K_{j'} - K_j) \chi^A \right]$$
Here the suffix \( n \) denotes the lowest conduction band, and \( V_k (K_j, K_{j'}) \) is the matrix elements of the nonlocal pseudopotential, namely

\[
V_k (K_j, K_{j'}) = \langle K_j + K_{j'} | V_p^n | K_j + K_{j'} \rangle
\]

It is found that the contribution of the nonlocal pseudopotential terms \( \Sigma_{nn'} \) to the effective mass is as much as 30%, while the spin-orbit interaction terms \( S_{nn'} \) contribute about 2% to the effective mass.

In Fig. 1, the procedure of determining the pseudo-Hamiltonian parameters and the band calculation is presented schematically. In practice, it is not possible to explore systematically the effect of all possible parameter variations in a reasonable amount of computer time. We were able, however, to obtain a set of parameters which yielded a satisfactory band structure. The determined values of the pseudo-Hamiltonian parameters are given in Table I. The experimental values for some important energy level separations and the effective mass, which have been used as the reference values, are listed in Table II, together with the calculated values using the parameters we determined. The calculated energy bands along the major symmetry axes are shown in Fig. 2. The splitting of the Kramers' degeneracy of the energy levels along the \( \Sigma \) axis has not been indicated in Fig. 2. The magnitude of the largest splitting of Kramers' degeneracy is order of 0.1 eV at the general point in the Brillouin zone. The two fold degeneracy of the level along the \( [111] \) axis is not lifted. The value of the lattice parameter we have used in our calculation is \( a = 6.096 \text{ Å} \),
which was measured by Miller et al. (1960).

A comparison of our calculated energy bands, which did not include the spin-orbit coupling effects, has been compared with those of Cohen and Bergstresser (1966) in a previous publication (Zhang and Callaway, 1968). Here we briefly compare our results with the calculated energy bands of Herman et al. (1968) and of Higginbotham et al. (1968). The shapes of the lowest conduction band obtained by these three calculations generally agree, although the value of the energy separation \( E(X_{6c}) - E(G_{6c}) \) calculated by Higginbotham et al. is much larger than those values obtained by the other two calculations. The most significant disagreement between our results and others is observed at the values of \( E(E_{7c}) - E(E_{8c}) \), the level separation between the highest valence band and the second lowest conduction band at \( k=0 \). These values are 3.82 eV (present work), 3.35 eV (Herman et al. without including spin-orbit coupling) and 3.1 eV (Higginbotham et al.). There is some controversy in the experimental interpretation for this level separation (Herman et al., 1968). Another disagreement arises for the value of spin-orbit splitting \( E(X_{7v}) - E(X_{6v}) \) near the Brillouin zone boundary in [100] direction. Herman et al. obtained 0.37 eV, and Higginbotham et al. obtained 0.3 eV for this value, while we obtained a very small value 0.04 eV. Experimentally, there has been no reported observation for this splitting (Kosicki, 1967). A rather interesting agreement between all these three calculations is observed at the values of level separations \( E(L_{6c}) - E(L_{4v}, L_{5v}) \), and \( E(L_{6c}) - E(L_{6v}) \). All the three calculations agree at values around 1.9 eV and 2.4 eV.
for this doublet, while the faint peaks observed at 1.4 eV and 1.9 eV in the reflectivity spectra have usually been attributed to these two level separations [Phillips (1964), Cardona (1964), Kosicki (1967)].
CHAPTER V

CARRIER CONCENTRATION DEPENDENCE OF EFFECTIVE MASSES

The dependence of the conduction band effective mass upon the carrier concentration has recently been investigated for many III-V semiconducting compounds. Palik and Wright (1967) provided a summary of a large number of experimental results which show that the carrier concentration dependence of the effective mass in those materials is quite significant. In InSb, for example, the value of the effective mass measured for the sample with carrier concentration $\sim 10^{18}$ cm$^{-3}$ is about three times as large as the corresponding value for the sample with carrier concentration $\sim 10^{15}$ cm$^{-3}$. On the theoretical side of the investigation, this dependency has been explained by $k\cdot p$ perturbation theory of Kane (1956, 1966). Kolodziejczak et al. (1966a, 1966b), in particular, calculated the carrier concentration dependence of the effective masses for a large number of III-V compounds using the $k\cdot p$ theory and experimentally obtained band parameters. According to the $k\cdot p$ theory, the effective mass not only depends upon the carrier concentration but also has a significant anisotropy. The heavy hole mass possesses a strong anisotropy and the masses of conduction band, light hole band and split-off band also reveal some degree of anisotropy.

For GaSb, Yep and Becker (1966) obtained the conduction band effective masses for a set of samples with different degrees of carrier concentration by analyzing the measured Shubnikov-de Haas
oscillations. In addition to reporting their own results, they provide a summary of those values obtained by other investigators with different methods and samples. Stradling (1966) measured the cyclotron resonance effective masses for heavy hole band and light hole band in three different directions and observed a strong anisotropy in heavy hole mass. More recently, Seiler and Becker (1969) measured the anisotropy in the conduction band effective mass using the Shubnikov-de Haas effect.

In the present Chapter, we will investigate the carrier concentration dependence and anisotropy of the effective masses for four different bands, namely, the conduction, light hole, heavy hole and split-off bands. For the conduction band and light hole band, we will also consider the inversion asymmetry splitting explicitly. The present investigation differs from most of the previous theoretical investigations in that the present results are obtained directly from the calculated energy bands while most of the previous calculations on this subject were performed in \( k \cdot p \) theory using experimentally obtained band parameters and therefore not related to any particular energy band calculation.

In order to determine the effective mass as a function of the Fermi energy in a number of different directions, it is necessary to obtain an analytical representation of the energy band \( E(k) \) in the space of the wave vector \( k \). An energy band is a scalar in \( k \) space and therefore it possesses \( \Gamma_1 \) symmetry in cubic crystals. If we neglect the spin-orbit coupling effect, a nondegenerate band, the conduction band for example, can be expanded in Kubic harmonics as
\[ E(k_z) = E_0 + E_2 k_z^2 + (E_4^{(0)} + E_4^{(2)} K_{4.1}) k_z^4 + \ldots \]

\[ (5-1) \]

where the cubic harmonics \( K_{4.1} \) and \( K_{6.1} \) are given by (Von der Lage and Berthe, 1947)

\[ K_{4.1} = \frac{5}{4} \sqrt{21} \left[ \frac{k_x^4 + k_y^4 + k_z^4}{k_z^4} - \frac{3}{5} \right] \]

\[ (5-2) \]

\[ K_{6.1} = \sqrt{\frac{693}{32}} \left[ \frac{k_x^2 k_y^2 k_z^2}{k_z^6} + \frac{1}{22} \left( \frac{k_x^4 + k_y^4 + k_z^4}{k_z^4} - \frac{3}{5} \right) - \frac{1}{105} \right] \]

Callaway (1961) has used this expansion for analysis of the lithium band structure.

The valence bands, which are degenerate at \( k=0 \), may not adequately be approximated by the above expansion due to the nonanalyticity at the point of degeneracy. Without spin-orbit coupling, the valence bands near \( k=0 \) are determined by \( k \cdot p \) perturbation theory as solutions of the secular equation (Dresselhaus et al., 1955):

\[
\begin{vmatrix}
L k_x^2 + M (k_y^2 + k_z^2) - E & N k_x k_y & N k_x k_z \\
N k_x k_y & L k_y^2 + M (k_x^2 + k_z^2) - E & N k_y k_z \\
N k_x k_z & N k_y k_z & L k_z^2 + M (k_y^2 + k_x^2) - E
\end{vmatrix} = 0
\]

\[ (5-4) \]

The quantities \( L, M, \) and \( N \) are sums of certain matrix elements. It is obvious that the solution of (5-4), in general, may give rise to
second order anisotropic terms in $k$ space.

If we include the spin-orbit coupling effect, even the conduction band may not adequately be approximated by (5-1) because it becomes doubly degenerate at $k=0$ and along some symmetry axes. On the other hand, the shape of the energy band around $k=0$ can be analyzed by $k \cdot p$ perturbation theory. For small $k$, the band including spin-orbit coupling effect has been given by the three band approximation of Kane (1966) in the form

$$E^\pm = E_0 + \left( E_2^{(1)} + E_2^{(2)} T_2 \right) k^2 \pm E_3 T_3 |k|^3$$

(5-5)

where

$$T_2 = \frac{1}{k^4} \left( k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2 \right)$$

(5-6)

and

$$T_3 = \frac{1}{k^3} \left[ k^2 \left( k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2 \right) - 9 k_x^2 k_y^2 k_z^2 \right] \frac{1}{k}$$

(5-7)

The constant $E_3$ vanishes for the heavy hole band. We here observe that the energy expansion in (5-5) does not include any higher order terms other than $k^3$ and therefore fails to represent the energy bands at the region where the bands are no longer quadratic in $k$ space. It is expected, however, that the expression in (5-1) would
give reasonable representation for the higher order terms in the energy expansion. We therefore represent the energy bands in the following way:

\[ E(k) = E_0 + (E_1^{(1)} + E_1^{(2)} k_2) k_2^2 + E_3 T_3 |k|^3 \]

\[ \times \left( E_4^{(1)} + E_4^{(2)} k_{4,1} \right) k_4^4 \]

\[ + \left( E_6^{(1)} + E_6^{(2)} k_{6,1} + E_6^{(3)} k_{6,1} \right) k_6^6 + \cdots \]  

(5-8)

for the purpose of analyzing the effective masses associated with \( \Gamma \) point. The term \( E_3 T_3 |k|^3 \) represents the inversion asymmetry splitting and we have two split bands for every band which would otherwise be doubly degenerate. These two split bands are represented by roughly the same set of coefficients in (5-8) except that the signs of \( E_3 \) are opposite to each other. This is obvious from the expression in (5-5). The band represented by positive \( E_3 \) and the one represented by negative \( E_3 \) will be called as upper band and lower band, respectively. (For the sake of convenience, we represented the values of both conduction and valence band energy as positive. In every case we set \( E_0 = 0 \).) For the heavy hole band, the splitting is very small and we put \( E_3 = 0 \) from the beginning.

The coefficients \( E_2^{(1)}, E_2^{(2)}, E_3, E_4^{(1)}, E_4^{(2)}, E_6^{(1)}, E_6^{(2)}, E_6^{(3)} \) have been determined by a weighted least-square procedure using the energy values at 21 different \( k \) points in the neighborhood of \( \Gamma \) point. The energy values used in this procedure were obtained by the band calculation described in Chapter IV using the pseudo-Hamiltonian parameters given in Table I. The weights in this least square
procedure were provided in such a way that the values

$$\sum_{j=1}^{21} \left[ \frac{E_0(k_j) - E(k_j)}{E_0(k_j)} \right]^2$$

should be minimized. Here $E_0(k_j)$ and $E(k_j)$ are the energy values obtained by the band calculation and by the expansion (5-8), respectively.

In Table III, the energy values $E_0(k_j)$ and $E(k_j)$ for 21 $k$-points are listed for conduction band. We obtained similar results for valence bands. The unit of $k$ used in the expansion (5-8) is $10^3 (a/2\pi)$ times the atomic unit $k$ (a being the lattice parameter in atomic unit). The value of energy in this expansion is given in the unit of electron volts. The determined coefficients of the expansion (5-8) are listed in Table IV for all the bands considered.

The effective mass related to the cyclotron resonance is given by

$$m^* = \frac{\hbar^2}{2\pi} \frac{dA(E_F)}{dE_F} \tag{5-9}$$

where $E_F$ is the Fermi energy and $A(E_F)$ is the extremal cross sectional area of the Fermi surface perpendicular to the applied magnetic field. In atomic units, we rewrite it as

$$\frac{m^*}{m_o} = \frac{1}{\pi} \frac{dA(E_F)}{dE_F} = \frac{1}{2\pi} \int_0^{2\pi} \frac{k_F^2(E_F, \theta)}{dE_F} d\theta \tag{5-10}$$
where \( k_F(E_F, \theta) \) is the value of \( k \) vector on the Fermi surface and the integral is performed on the surface perpendicular to the applied magnetic field. In the present investigation, we considered the effective masses associated with three different directions of applied magnetic field, namely, the \([100]\), \([110]\), and \([111]\) directions. From (5-8), the Fermi level is determined by

\[
Z = A k_F^2 + B k_F^3 + C k_F^4 + D k_F^6 + \cdots
\]

where

\[
Z = E_F(k_F) - E_0,
\]

\[
A = E^{(1)}_2 + E^{(2)}_2 T_2,
\]

\[
B = E_3 T_3,
\]

\[
C = E^{(1)}_4 + E^{(2)}_4 K_{4,1},
\]

\[
D = E^{(1)}_6 + E^{(2)}_6 K_{4,1} + E^{(3)}_6 K_{6,1}.
\]

Inverting (5-11), we obtain

\[
k_F^2 = F_1 Z + F_2 Z^{3/2} + F_3 Z^2 + F_4 Z^{5/2} + F_5 Z^3 + \cdots
\]

where

\[
F_1 = \frac{4}{A}, \quad F_2 = -\frac{B}{A^{5/2}}, \quad F_3 = \frac{3}{2} \frac{B^2}{A^4} - \frac{C}{A^3},
\]

\[
F_4 = -\frac{21}{8} \frac{B^3}{A^{11/2}} + \frac{7}{2} \frac{BC}{A^{9/2}}
\]

\[
F_5 = 5 \frac{B^4}{A^7} - 10 \frac{B^2 C}{A^6} + 2 \frac{C^2}{A^5} - \frac{D}{A^4}.
\]
The effective mass is calculated by

\[
\frac{m^*}{m} = \frac{1}{2\pi} \left[ \int_{0}^{2\pi} F_1 \, d\theta + \frac{3}{2} \int_{0}^{2\pi} F_2 \, d\theta + 2 \int_{0}^{2\pi} F_3 \, d\theta \right.
\]
\[
+ \frac{5}{2} \int_{0}^{2\pi} F_4 \, d\theta + 3 \int_{0}^{2\pi} F_5 \, d\theta \right].
\]

(5-13)

All the integrals involved in (5-13) were performed numerically on the surfaces perpendicular to the directions [100], [110], and [111]. The calculated effective mass versus Fermi energy curves obtained by (5-13) are given in Fig. 3 through Fig. 6 for the conduction, light hole, heavy hole and split-off bands. The upper and lower bands split by inversion asymmetry are separately considered for conduction band and light hole band.

To obtain the carrier concentration dependency of the effective mass, we need to find the carrier concentration as a function of Fermi energy for electrons and holes. The carrier concentration occupying states near \( k=0 \) is given by

\[
\mathcal{F} = \frac{2}{(2\pi)^3} \int_{E_F} d^3k = \frac{1}{12\pi^3} \int_{k_F}^3 d\Omega.
\]

(5-14)

In this expression, we neglected the inversion asymmetry splitting of the band. The expression \( k_F^3 \), which can be obtained from (5-12) contains a complicated angular dependency and therefore the evaluation of the angular integral over the entire solid angle appears to be very involved. On the other hand, it is expected
that the anisotropy near $k=0$ would not affect too much the relation between carrier concentration and Fermi energy. To carry out a simple evaluation of the angular integration in (5-14) under this assumption, we made another representation of the energy bands using only the Kubic harmonic expansion (5-1). The coefficients in (5-1) were determined by another least square procedure and, as expected, the resulting energy representation turned out to be good for large energy values while the anisotropy for small energy values was not satisfactorily represented. By inverting this expansion, we obtain the expression of $k_F^3$ which contains only Kubic harmonics for the angular part. Making use of the orthonormality of Kubic harmonics [the Kubic harmonics given in (5-2) and (5-3) are normalized to $4\pi$], we find a simple expression for $\rho$:

$$
\rho (z_F) = \frac{1}{3\pi^2} z_F^{3/2} \left\{ 1 - \frac{3}{2} \alpha z_F + \left[ \frac{27}{8} (\alpha^2 + \beta) - \frac{3}{2} \gamma \right] z_F^2 \right\}
$$

where

$$
z_F = \frac{E_F (k) - E_0}{E_2^{(u)}}, \quad \alpha = \frac{E_4^{(u)}}{E_2^{(u)}}, \quad \beta = \frac{E_4^{(2)}}{E_2^{(u)}}, \quad \gamma = \frac{E_6^{(2)}}{E_2^{(u)}}.
$$

For the conduction band, as the Fermi level crosses over the energy of L minima, the states near L points begin to be occupied. We assume that the energy surfaces in the vicinity of L points are ellipsoidal and thus obtain an expression for the concentration of carriers occupying the states near L minima:
\[ P_L = \frac{4}{3\pi} (E_F - E_L)^{3/2} m_L \sqrt{m_R} . \] (5-16)

\( E_L \) is the energy level at L point and \( m_L \) and \( m_R \) are longitudinal and tangential effective mass associated with L points. In our calculation, we have used the results obtained by Zhang and Callaway (1968) for these values. The carrier concentration of electrons for the Fermi energy higher than \( E_L \) is expressed as a sum of (5-15) and (5-16).

We have calculated the carrier concentration for holes by applying (5-15) to both the heavy hole and light hole bands. While the hole concentration is contributed by both of these bands, the contribution from the heavy hole band is dominant because of the large density of states in this band.

The calculated conduction band effective mass as a function of conduction electron concentration is given in Fig. 7. In Fig. 8 and Fig. 9, we present the light hole and heavy hole effective masses as functions of hole concentration. The effective mass presented in each of these figures corresponds to the lower one of the two bands split by inversion asymmetry.

Finally, an evaluation has been made for the conduction band effective mass defined by

\[ \frac{m^*}{m_o} (E_F) = \left[ \frac{1}{2} \left( \frac{d^2 E(k)}{dk^2} \right)_{E_F} \right]^{-1}. \] (5-17)
This effective mass plotted as a function of carrier concentration is presented in Fig. 10. From Fig. 7 and Fig. 10, we notice that the effective mass defined by (5-17) has much stronger dependency on the carrier concentration than the corresponding cyclotron resonance effective mass. The difference between these two effective masses is mainly due to the higher order terms than $k^2$ in the energy expansion. The remarkable difference in carrier concentration dependency between the two effective masses, therefore, indicates the importance of including higher order terms in energy representation for the analysis of the effective masses.

The calculated cyclotron resonance effective mass for the conduction band makes a reasonable agreement with experiment both in Fermi energy dependency and anisotropy. In Table V, a comparison is made between calculated and experimentally measured values of conduction band effective mass. The set of the experimental values cited in this table is a collection of values measured by a number of different investigators with different methods. Therefore, it is not possible to extract the precise Fermi energy dependency of the effective mass from these experimental data. In this table, we present the values of effective mass in three different directions for both lower band and upper band split by inversion asymmetry.

The calculated anisotropy of the conduction band effective mass is compared with a recent measurement by Seiler and Becker (1969) in Table VI. Since the correlation between the effective mass and Fermi energy is not uniquely given in their experiment, we compared the experimental values of effective mass with calculated ones which
would make best agreement in [100] direction. From this comparison, we find that, while the anisotropy of the lower band agrees with experiment nicely, the agreement for the upper band is poor in the angular variation between [110] and [111] directions.

For the heavy hole effective mass, we find only a qualitative agreement with experiment. The absolute values of the heavy hole mass turned out to be significantly larger than the values measured by Stradling (1966). However, a remarkable agreement is found in the anisotropy. A comparison between calculated heavy hole mass (for the hole concentration $10^{18}$ cm$^{-3}$) and the experimental values of Stradling (1966) is given in Table VII. Although both heavy hole mass and light hole mass are sensitive to the Fermi level, they are not very sensitive to the hole concentration due to the large density of states in the valence bands. The light hole mass shows a stronger degree of anisotropy than the conduction band effective mass but not as strong as the anisotropy of the heavy hole mass. The splitting of the light hole band due to the inversion asymmetry is the largest among the bands considered here and the effect of this on the effective mass is shown in Fig. 4. The calculated magnitude of the light hole mass turned out to be a little smaller than the measured value 0.052$m_o$ of Stradling (1966). Stradling did not observe any anisotropy of light hole mass in his measurements in three different directions, but the calculated anisotropy is within the range of uncertainty of his measurement.

The Fermi energy dependence of the split-off band effective mass shown in Fig. 6 does not have much physical significance because it
is very unlikely for a significant number of holes to occupy states in this band to form a meaningful Fermi level. (The Fermi level in this context is defined only for the holes occupying this band.) Since the top of this band locates at the level about 0.8 eV lower than the top of other valence bands, the effective mass in the split-off band is virtually independent of the hole concentration. The calculated value of the split-off band mass shows slight anisotropy and the magnitude about 0.17\( m_0 \) coincides with the calculated value for this mass by Higginbotham et al. (1968). There is no available experimental information for the value of the split-off band mass.
CHAPTER VI
OPTICAL PROPERTIES

The imaginary part of the dielectric constant is expressed by

\[ \varepsilon_2(\omega) = \frac{\hbar^2 e^2}{3\pi m^2 \omega^2} \sum_{n, \ell} \int d^3k \left| M_{n\ell}(\varepsilon_k) \right|^2 \delta(E_n - E_{\ell} - \hbar \omega) \]  \hspace{1cm} (6.1)

where the subscripts \( n \) and \( \ell \) denote the conduction bands and the valence bands, respectively, and the momentum matrix element \( M_{n\ell}(\varepsilon_k) \) is given by

\[ M_{n\ell}(\varepsilon_k) = \int d^3r \, U^*_n(\varepsilon_k, r) \nabla U_\ell(\varepsilon_k, r). \]  \hspace{1cm} (6.2)

Here \( U_n(\varepsilon_k, r) \) is the periodic part of the wave function for the energy level \( n \) at the point \( k \) in the Brillouin zone.

To evaluate \( \varepsilon_2(\omega) \) we constructed a cubic mesh whose scale was determined by dividing the [100] axis into 24 equal sections. This mesh generates 1505 points in the 1/48 of the Brillouin zone including the points on the surface of this section. It takes, however, more than a practical amount of the computer time to calculate the energy levels and the wave functions at all these mesh points using the method mentioned in Chapter IV. We therefore employed the \( k \cdot p \) extrapolation method, which was introduced by Saravia and Brust (1968). From the 1505 mesh points, we selected 89 basic points, which corresponded to a coarser mesh with a linear scale three times as large as the original mesh. At each of these basic
points, we calculated the energy bands by diagonalizing the $\sim 30 \times 30$ dimensional pseudo-Hamiltonian matrix constructed for that $k$-value. The energy bands at the remaining mesh points were obtained by the $k \cdot p$ perturbation method using the values of the energy levels and the wave functions calculated already at the nearest basic points. In this $k \cdot p$ perturbation procedure, however, we ignored the contributions from the nonlocal pseudopotential terms and spin-orbit interaction terms such as $Q_{mn}$ and $S_{mn}$ in (4.4). Thus, at a mesh point $k$, near a basic point $k_0$, a $16 \times 16$ $k \cdot p$ Hamiltonian matrix is obtained with the elements

$$H_{nn'} = 2 (k - k_0) \cdot p_{nn'} \quad \text{for } n \neq n'$$

and

$$H_{nn} = E_n (k_0) + 2 k_0 \cdot (k - k_0) + (k - k_0)^2 + 2 (k - k_0) \cdot p_{nn}$$

$$+ \sum_{l=N+1}^{N'} \frac{H_{nl} H_{ln}}{E_n (k_0) - E_l (k_0)}$$

where

$$p_{nn'} = \int d^3 r \, U_n^* (k_0, r) \nabla U_{n'} (k_0, r).$$

Here $N$ is the dimension of the matrix at the major point $k_0$, and $N'$ is that of the $k \cdot p$ Hamiltonian which is taken as 16. This $16 \times 16$ Hamiltonian is diagonalized to yield the lowest eight energy levels (without counting the levels split from Kramers' degeneracy separately).

The integral in (6.1) was performed numerically, being replaced by a finite sum. In atomic units, we have the following expression:
\[ \varepsilon_2(\omega) \Delta \omega = \frac{8}{3\pi} \left( \frac{\pi}{12 a} \right)^3 \frac{1}{\omega^2} \sum_{k} \Delta \omega \left| M_{n\ell}(k) \right|^2 \]  

(6.3)

The superscript on the summation sign indicates that the summation is performed over values of \( k \) which satisfy

\[ \omega - \frac{\Delta \omega}{2} \leq E_n(k) - E_{\ell}(k) \leq \omega + \frac{\Delta \omega}{2} \]

It is known that the value of \( |M_{n\ell}(k)|^2 \) is, in general, slowly varying with respect to \( k \). We calculated \( |M_{n\ell}(k)|^2 \) at each of the 89 basic points and, for the remaining \( k \) values, we used those values of \( |M_{n\ell}(k)|^2 \) at the nearest basic points.

The calculated imaginary part of the dielectric constant is shown in Fig. 11 for the energy range from 0 eV to 6 eV. Some conduction bands other than the lowest eight levels we calculated have the energy values just above 6 eV from the highest valence band at the center of the Brillouin zone. Therefore, the imaginary part of the dielectric constant for the energy range over 6 eV cannot be obtained unless we include more energy levels in our calculation. In this calculation, we have used the pseudo-Hamiltonian parameters listed in Table VIII rather than those in Table I. After finishing this part of calculation, we readjusted the parameters and obtained the set given in Table I. The two band structures obtained from these two sets of parameters are not much different from each other. But it is expected that the positions of the peaks might generally be shifted slightly (order of 0.1 eV) toward higher energy region.
The real part of the dielectric constant $\varepsilon_1(\omega)$ and the reflectivity $R(\omega)$ are obtained by the relations:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\nu \varepsilon_2(\nu)}{\nu^2 - \omega^2} d\nu$$  \hspace{1cm} (6.4)

$$R(\omega) = \frac{[\eta(\omega) - 1]^2 + \kappa^2(\omega)}{[\eta(\omega) + 1]^2 + \kappa^2(\omega)}$$  \hspace{1cm} (6.5)

where $\eta(\omega)$ and $\kappa(\omega)$ are the real and imaginary parts of $[\varepsilon_1(\omega) + i \varepsilon_2(\omega)]^{\frac{1}{2}}$. In order to use the Kramers-Kronig relation, (6.4), to calculate $\varepsilon_1(\omega)$, it is necessary to know the imaginary part of the dielectric constant for all energies. On the other hand, it is known that $\varepsilon_2(\omega)$ decreases monotonically as the energy increases above the energy range in which we calculated it explicitly (Phillipp and Ehrenreich, 1963). Moreover, the general shape of the reflectivity vs. energy curve does not critically depend on the values of $\varepsilon_2(\omega)$ for the range of energy over 6 eV. We artificially extrapolate the value of $\varepsilon_2(\omega)$ for the energy over 6 eV in two extreme cases: (1) rapidly decreasing, (2) slowly decreasing, namely,

1. $\varepsilon_2(\omega) = \varepsilon_2(6) \cdot \exp(-0.43 \omega)$ \hspace{1cm} for $6 < \omega \leq 40$,

2. $\begin{cases} \varepsilon_2(\omega) = \varepsilon_2(6) \cdot \exp(-0.43 \omega) & \text{for } 6 < \omega \leq 8 \\ \varepsilon_2(\omega) = \varepsilon_2(8)/\omega & \text{for } 8 < \omega \leq 40, \end{cases}$
where the energy $\omega$ is measured in the unit of eV. The corresponding curves for the real part of the dielectric constant $\varepsilon_1(\omega)$ and the reflectivity $R(\omega)$ are given in Fig. 12 and Fig. 13, respectively. In Fig. 13, the reflectivity measured by Cardona (1961) at room temperature is also given for comparison.

From the calculated reflectivity vs. energy curve in Fig. 13, we observe peaks at 0.9 eV, 2.1 eV, 2.5 eV, 3.3 eV, 3.7 eV, 4.3 eV, 4.8 eV, and 5.6 eV. Most of them correspond very nicely to the experimentally observed peaks at 2.08 eV, 2.55 eV, 3.74 eV, 4.33 eV, 4.70 eV and 5.70 eV. In the usual interpretation, the highest peak located at 4.33 eV is due to the level separations $E(X_{6c}) - E(X_{7\nu})$ and $E(X_{6c}) - E(X_{6\nu})$. But consulting the calculated energy bands in Fig. 2, we see that the highest peak in our calculation located at 4.3 eV is due to a number of separations:

\[ E(X_{6c}) - E(X_{7\nu}), E(X_{6c}) - E(X_{6\nu}), E(\Gamma_{8c}) - E(\Gamma_{8\nu}), \text{ and} \]

\[ E(\Sigma_{3c}, \Sigma_{4c}) - E(\Sigma_{3\nu}, \Sigma_{4\nu}). \]

In our calculated band structure, the level separations $E(L_{6c}) - E(L_{4\nu}, L_{5\nu})$ and $E(L_{6c}) - E(L_{6\nu})$ are 2.0 eV and 2.4 eV rather than 1.4 eV and 1.9 eV. The peaks corresponding to these level separations do not appear in the calculated reflectivity curve. They are believed to be buried in the shadow of more intense peaks around 2.1 eV and 2.5 eV. Meanwhile a slight prominence at 1.3 eV is noticed which might be due to $E(\Gamma_{6c}) - E(\Gamma_{7\nu})$.

Experimental measurements of the reflectivity at low temperature over a large range of photon energies would be desirable in order to permit a Kramers-Kronig analysis to determine $\varepsilon_2$ directly from
experimental data. This would enable a much more precise comparison between pseudopotential theory and experiment.
CHAPTER VII
PRESSURE DEPENDENCE OF THE BAND STRUCTURE

In this chapter we will consider the effect of hydrostatic pressure on the band structure of GaSb. This is interesting in view of the measurements of Kosicki et al. (1966a, 1966b). That work has determined experimental pressure coefficients of the three principal energy level separations $E(\Gamma_{6c}) - E(\Gamma_{8v})$, $E(L_{6c}) - E(\Gamma_{6c})$, $E(X_{6c}) - E(\Gamma_{6c})$. A calculation of these pressure coefficients presents an interesting challenge to the pseudopotential method, since it is necessary to determine more completely the variation of pseudopotential parameters with respect to the reciprocal lattice vector $K$. Previously, a number of authors have investigated this question for Germanium and Silicon [Foroff and Kleinman (1963), Kleinman (1963), Bassani and Brust (1963), Cardona and Pollak (1966), Herman et al (1966)]. Bassani and Brust (1963) in particular, obtained an expression for the change in pseudopotential parameters due to the change in lattice parameter by relating the pseudopotential parameters to the OPW calculation. In the present work, however, we followed a rather different approach to obtain the change in pseudopotential parameters due to the hydrostatic pressure.

In the pressure range of the practical interest, the change in the lattice parameter is reasonably small (less than 1%) and it should be a good approximation to assume that the properties of the individual atoms in the crystal remain unchanged under the pressure.
in the experimental range. This consideration leads us to make a basic assumption concerning the pressure dependence of the pseudo-Hamiltonian, that the contributions from individual atoms are independent of the pressure exerted on the crystal. In this approximation we ignore any possible change in the atomic self-consistent field. The expressions for the change in matrix elements of the pseudo-Hamiltonian are then obtained from the relation between the atomic pseudo-Hamiltonian and the crystal pseudo-Hamiltonian.

The change in lattice parameter under pressure is obtained using the known compressibility, \((0.56 \times 10^6 \text{ kg/cm}^2)^{-1}\) for GaSb. (Keyes, 1960).

The dependence of the kinetic energy matrix elements on the lattice parameter \(a\) is straightforward. We must determine the dependence of the potential parameters on \(a\). Let \(v^{III}(r)\) and \(v^V(r)\) be the atomic contributions to the local pseudopotential from the two kinds of atoms, Ga(III) and Sb(V). These are assumed to be spherically symmetric. The local pseudopotential parameters \(V^S(K)\) and \(V^A(K)\) in (3.6) are related to \(v^{III}(r)\) and \(v^V(r)\) by

\[
V^S(K) = \frac{1}{\Omega} \int e^{i K \cdot r} \left[ v^{III}(r) + v^V(r) \right] d^3r
\]

\[
V^A(K) = \frac{1}{\Omega} \int e^{i K \cdot r} \left[ v^{III}(r) - v^V(r) \right] d^3r
\]

We notice here that the lattice parameter dependence of \(V^S(K)\) and \(V^A(K)\) comes through \(\Omega\) and \(K\) which are related to the lattice parameter \(a\) by
\[ \Omega = \frac{a^3}{4}, \quad K = \frac{2\pi}{a} \left( N_x, N_y, N_z \right) \]

where \( N_x, N_y \) and \( N_z \) are integers. \( V^S \) and \( V^A \) are functions of the magnitude of \( K \) only. We therefore obtain

\[ \frac{dV^S}{da} = -\frac{3}{a} V^S - \frac{K}{a\Omega} \frac{d}{dK} \int e^{i\frac{K\cdot r}{\Omega}} \left[ V^\text{III}(r) + V^V(r) \right] d^3r \]

(7.2)

\[ \frac{dV^A}{da} = -\frac{3}{a} V^A - \frac{K}{a\Omega} \frac{d}{dK} \int e^{i\frac{K\cdot r}{\Omega}} \left[ V^\text{III}(r) - V^V(r) \right] d^3r \]

Let us consider the integral, with \( v(r) \) representing either \( v^\text{III}(r) \) or \( v^V(r) \),

\[ \frac{d}{dK} \int e^{i\frac{K\cdot r}{\Omega}} v(r) d^3r = \frac{4\pi}{K} \int v(r) \cos(Kr) r^2 dr - \frac{1}{K} \int e^{i\frac{K\cdot r}{\Omega}} v(r) d^3r \]

(7.3)

The second term is just the local pseudopotential of (7.1). However, an explicit functional form for \( v(r) \), the atomic contribution to the local pseudopotential, is needed to evaluate the first term. To obtain \( v(r) \), it is not sufficient just to know the local pseudopotential parameters because we do not have the Fourier coefficients \( V(q) \) for cases in which \( q \) is not a reciprocal lattice vector. There are, in principle, many different sets of local atomic pseudopotential \( v^\text{III}(r) \) and \( v^V(r) \), which yield the same set of the local pseudopotential parameters. We are therefore in need
of additional information about the local pseudopotential to calculate the pressure effects. In practice, however, it is almost impossible to find a single set of the atomic pseudopotentials exactly reproducing the local pseudopotential parameters we already have determined. We will therefore choose an explicit function for \( v(r) \) according to the following two criteria:

(1) The functional form of \( v(r) \) should be physically reasonable.

(2) The local pseudopotential parameters produced by \( v(r) \) should be in good agreement with already determined values, or, equivalently, the calculated band structure using this new \( v(r) \) should agree with previously calculated one using the known parameters.

We have assumed the atomic local pseudopotential to be in the form (in atomic units)

\[
v(r) = \frac{A}{r} e^{-B r} - \frac{2Z}{r} - C r \quad (7.4)
\]

for \( r < r_o \), where \( Z \) is the charge of the core and \( r_o \) is a small distance less than the core radius. For \( r < r_o \), we artificially set

\[
v(r) = P + Q r^2 \quad (7.5)
\]

to avoid the singularity at \( r = 0 \). The first term in Eq. (5.4) is roughly regarded as the repulsive potential due to orthogonalization while the second term is a slightly screened form (with \( C \ll B \)) of the Coulomb potential due to the core charge. The coefficients \( P \) and \( Q \)
are determined by the continuity conditions at \( r = r_0 \) and therefore not considered to be adjustable constants. We can then evaluate the desired integral

\[
\int_0^\infty v(r) \cos(Kr) r^2 dr
\]

with the parameters \( A, B, C, r_0 \) which are still to be determined from the second criterion listed above.

The parameters \( A, B, C, r_0 \) define a model local pseudopotential. The local part of the crystal pseudopotential is the sum of the assumed local atomic pseudopotentials of (7.4) and (7.5). A temporary set of the parameters \( A, B, C, r_0 \) are determined such that the Fourier coefficients of the model local pseudopotential yield the nearest possible values to those of the actual local pseudopotential. The largest disagreement between these two sets of the Fourier coefficients turned out to be order of 0.03 (15% of the largest local pseudopotential parameters). We then readjust the values of \( A, B, C, r_0 \) in a way similar to that described in Sec. III. We calculate the band structure without including the spin-orbit interaction, using the model local pseudopotential instead of the actual local pseudopotential (the kinetic energy and the nonlocal pseudopotential parts remaining the same as determined in Chapter IV). We have repeated this band calculation varying the values of the parameters \( A, B, C, r_0 \) until the resulting band structure turns out to be in a reasonable agreement with the corresponding band structure calculated by the actual pseudopotential. The four parameters in the model local pseudopotential we have determined are listed in Table IX. In Table X,
some characteristics of the band structure as calculated neglecting
spin-orbit coupling are presented and compared with those of pseudo-
potential determined in Chapter IV. (As the case of Chapter VI, we
have used the pseudo-Hamiltonian parameters listed in Table VIII rather
than those in Table I in this Chapter.)

Since we have used the tight binding approximation for the crystal
core states in the calculation of the nonlocal pseudopotential and
pseudo-spin-orbit interaction, we can easily relate the parameters
of the nonlocal pseudopotential and pseudo-spin-orbit interaction to
those of the corresponding atomic pseudo-Hamiltonians which are
assumed to be pressure independent. The lattice parameter dependence
of the nonlocal pseudopotential matrix elements given in (3.8) comes
only through such factors as $W_{\ell}^{(1)}$, $W_{\ell}^{(V)}$, $B_{q}^{(1)}(|k+K_{q}|)$ and $B_{q}^{(V)}(|k+K_{q}|)$. The parameter $W_{\ell}^{(1)}$, for example, is related to $G_{q}^{(1)}$, which is
considered to be independent of the pressure, by

$$W_{\ell}^{(1)} = \frac{4\pi (2l+1)}{\Omega} G_{q}^{(1)}$$

with $\Omega$ being $a^3/4$. Therefore, the nonlocal parameters under pressure
$W_{\ell}^{(1)}$ and $W_{\ell}^{(V)}$ are obtained by

$$W_{\ell}^{(1)} = (\frac{a}{a'})^3 W_{\ell}^{(1)}, \quad W_{\ell}^{(V)} = (\frac{a}{a'})^3 W_{\ell}^{(V)}$$

where $a'$ is the changed lattice parameter due to the pressure. It
is known that (Weisz, 1966) $B_{q}^{(1)}(|k+K_{q}|)$ and $B_{q}^{(V)}(|k+K_{q}|)$ are, in a
reasonable approximation, proportional to $|k+K_{q}|^\lambda$ and therefore,

$$B_{q}^{(1)}(1|k+K_{q}|) = (\frac{a}{a'})^l B_{q}^{(1)}(1|k+K_{q}|), \quad B_{q}^{(V)}(1|k+K_{q}|) = (\frac{a}{a'})^l B_{q}^{(V)}(1|k+K_{q}|)$$
where the primed quantities are changed values due to the pressure.

Almost the same argument is held for the pseudo-spin-orbit matrix elements given in (3.11). The spin-orbit parameters \( \lambda^S \) and \( \lambda^A \) are changed to \( \lambda^{S'} \) and \( \lambda^{A'} \) as

\[
\lambda^{S'} = \left( \frac{a}{a'} \right)^3 \lambda^S, \quad \lambda^{A'} = \left( \frac{a}{a'} \right)^3 \lambda^A
\]

The lattice parameter dependence of the matrix elements in Eq. (2.9) through the factors such as \((k + K_1)\) is obvious.

Edwards and Drickamer (1961) obtained a value 12.0x10^{-6} eV/bar for \( \frac{d[E(E_{6\text{c}}) - E(\Gamma_{8\text{c}})]}{dP} \), the pressure coefficient of the fundamental optical gap, by measuring the shift of the optical absorption. More recently Kosicki (1967) measured this pressure coefficient and obtained a value 14.5x10^{-6} ev/bar. For the pressure coefficient of the energy level separation between the conduction band minima located at L and \( \Gamma_6 \), \( E(L_{6\text{c}}) - E(\Gamma_{6\text{c}}) \), Sagar (1960) estimated a value -10x10^{-6} ev/bar to explain the measured pressure dependences of Hall effect and conductivity. This value has been conformed by Keyes and Pollak (1960) who explained the pressure effect on Piezoresistance. Finally, for the pressure coefficient of the energy separation \( E(X_{6\text{c}}) - E(\Gamma_{6\text{c}}) \), no direct experimental information is available. Paul, (1961) however, summarized all the pressure coefficients of the energy bands of IV and III-V semiconductors and concluded that the pressure coefficient of X minimum was negative, which means that

\[
\frac{d[E(X_{6\text{c}}) - E(\Gamma_{6\text{c}})]}{dP} < \frac{d[E(\Gamma_{6\text{c}}) - E(\Gamma_{8\text{c}})]}{dP}
\]
The calculated pressure coefficients for this three energy separation are given in Table V, together with the experimental values estimated by Kosicki et al. (1966b). In this calculation, we have proceeded straightforwardly from the basic assumption we have made at the beginning. The only nontrivial approximation made in the process was the use of the model local pseudo-potential which did not exactly agree with the actual local pseudopotential. From (7.2) and (7.3), it is observed that the term containing the model local pseudopotential contributes to the pressure dependence of local pseudopotential only in a small fraction. Therefore, the accuracy of the model pseudopotential is not felt sensitively at the final result.
In the present investigation, we have constructed a pseudo-Hamiltonian and determined its parameters using experimental information. This calculation does have the disadvantage that there are a large number of parameters to be determined (14 in the present case). It is not possible to explore systematically the effect of all possible parameter variations on the band structure in a reasonable amount of computer time. Therefore, there is a definite possibility that the obtained results make an accidental agreement with experiment only for the quantities taken as references in the parameter determining procedure. But this possibility reduces rapidly as we increase the number of reference values. It is not easy, however, to estimate the necessary number of reference values to determine a given number of parameters. One thing that is obvious from our experience is that it is far from trivial to obtain a band structure which will agree with experiment for a given number of reference values using the same number of adjustable parameters. This is especially true for the case in which one has a large number of parameters to determine.

In our calculation, we set up almost equal number of reference values as the number of adjustable parameters in the parameter determining procedure, and obtained excellent agreements between the calculation and experiment except for a few quantities whose experimental results are subject to some uncertainty. The results
of the analysis of effective mass, optical properties, and pressure
dependence of the band structure provide additional and decisive
justifications for our calculated energy bands.

The present calculation is, however, subject to further
refinement as more reliable and precise experimental information is
advanced in the future. In particular, the further experimental
investigation of the reflectivity would be of great value in assessing
the accuracy of the calculation. At present, this calculation
provides many aspects of information concerning the energy band
structure of GaSb with a precision comparable to most of the
present experimental measurements. At the same time, we conclude that
the empirical pseudopotential method can give a rather good fit to a
band structure whose basic features are established with some
precision.
BIBLIOGRAPHY


## TABLE I

Pseudo-Hamiltonian parameters in atomic units

<table>
<thead>
<tr>
<th>Local Parameters</th>
<th>Nonlocal Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_3^S )</td>
<td>-0.199</td>
</tr>
<tr>
<td>( v_3^A )</td>
<td>0.090</td>
</tr>
<tr>
<td>( v_4^S )</td>
<td>0.026</td>
</tr>
<tr>
<td>( v_8^S )</td>
<td>0.015</td>
</tr>
<tr>
<td>( v_{11}^S )</td>
<td>0.045</td>
</tr>
<tr>
<td>( v_{11}^A )</td>
<td>0.030</td>
</tr>
<tr>
<td>( w_0^{III} )</td>
<td>-0.0018</td>
</tr>
<tr>
<td>( w_1^{III} )</td>
<td>-0.0010</td>
</tr>
<tr>
<td>( w_2^{III} )</td>
<td>-0.0012</td>
</tr>
<tr>
<td>( w_0^V )</td>
<td>-0.0025</td>
</tr>
<tr>
<td>( w_1^V )</td>
<td>-0.0035</td>
</tr>
<tr>
<td>( w_2^V )</td>
<td>-0.0006</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spin-orbit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda^S )</td>
</tr>
<tr>
<td>( \lambda^A )</td>
</tr>
</tbody>
</table>
Some important energy level separations and effective mass in GaSb. The energy levels are designated according to the conventional double group notations. The energy values are given in electron volts.

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{6c}-\Gamma_{8v}$</td>
<td>0.81</td>
</tr>
<tr>
<td>$\Gamma_{8c}-\Gamma_{7c}-\Gamma_{8v}$</td>
<td>4.26, 3.82</td>
</tr>
<tr>
<td>$\Gamma_{8v}-\Gamma_{7v}$</td>
<td>0.78</td>
</tr>
<tr>
<td>$L_{6c}-L_{4v}$</td>
<td>1.98</td>
</tr>
<tr>
<td>$L_{6c}-L_{6v}$</td>
<td>2.42</td>
</tr>
<tr>
<td>$L_{4c}, L_{6c}-L_{4v}$</td>
<td>5.71, 5.48</td>
</tr>
<tr>
<td>$L_{4c}, L_{6c}-L_{6v}$</td>
<td>6.15, 5.92</td>
</tr>
<tr>
<td>$X_{6c}-X_{7v}, X_{6v}$</td>
<td>4.26, 4.30</td>
</tr>
<tr>
<td>$X_{7c}-X_{6c}$</td>
<td>0.38</td>
</tr>
<tr>
<td>$\Lambda_{6c}^{(1)}-\Lambda_{4v}$</td>
<td>2.1</td>
</tr>
<tr>
<td>$\Lambda_{6c}^{(1)}-\Lambda_{6v}$</td>
<td>2.6</td>
</tr>
<tr>
<td>$L_{6c}-\Gamma_{6c}$</td>
<td>0.08</td>
</tr>
<tr>
<td>$X_{6c}-\Gamma_{6c}$</td>
<td>0.32</td>
</tr>
<tr>
<td>$m^*(\Gamma_{6c})$</td>
<td>0.040 $m_o$</td>
</tr>
</tbody>
</table>

** The interpretation of these pair of faint peaks in the reflectivity spectrum is not well established.
TABLE III

Energy values of the conduction band near \( k=0 \). \( E^+_0(k) \) and \( E^-_0(k) \) represent the upper spin band and lower spin band obtained by energy band calculation; \( E^+(k) \) and \( E^-(k) \) are the corresponding energy values obtained by least square procedure. The unit of \( k \) in this table is \( 112x(a/2\pi) \) times the atomic unit of \( k \).

<table>
<thead>
<tr>
<th>( k )</th>
<th>( E^-_0(k) )</th>
<th>( E^-_0(k) )</th>
<th>( E^+_0(k) )</th>
<th>( E^+(k) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,0,0</td>
<td>0.008089</td>
<td>0.008088</td>
<td>0.008089</td>
<td>0.008089</td>
</tr>
<tr>
<td>2,0,0</td>
<td>0.031654</td>
<td>0.031644</td>
<td>0.031654</td>
<td>0.031648</td>
</tr>
<tr>
<td>3,0,0</td>
<td>0.068626</td>
<td>0.068646</td>
<td>0.068626</td>
<td>0.068651</td>
</tr>
<tr>
<td>4,0,0</td>
<td>0.116121</td>
<td>0.116096</td>
<td>0.116121</td>
<td>0.116033</td>
</tr>
<tr>
<td>1,1,0</td>
<td>0.015970</td>
<td>0.015988</td>
<td>0.016095</td>
<td>0.016106</td>
</tr>
<tr>
<td>2,1,0</td>
<td>0.038942</td>
<td>0.038946</td>
<td>0.039311</td>
<td>0.039304</td>
</tr>
<tr>
<td>3,1,0</td>
<td>0.075034</td>
<td>0.075024</td>
<td>0.075753</td>
<td>0.075750</td>
</tr>
<tr>
<td>4,1,0</td>
<td>0.121360</td>
<td>0.121392</td>
<td>0.122465</td>
<td>0.122535</td>
</tr>
<tr>
<td>2,2,0</td>
<td>0.060480</td>
<td>0.060429</td>
<td>0.061363</td>
<td>0.061296</td>
</tr>
<tr>
<td>3,2,0</td>
<td>0.094305</td>
<td>0.094332</td>
<td>0.095842</td>
<td>0.095880</td>
</tr>
<tr>
<td>4,2,0</td>
<td>0.138251</td>
<td>0.138287</td>
<td>0.140532</td>
<td>0.140572</td>
</tr>
<tr>
<td>3,3,0</td>
<td>0.125236</td>
<td>0.125236</td>
<td>0.127734</td>
<td>0.127709</td>
</tr>
<tr>
<td>1,1,1</td>
<td>0.023847</td>
<td>0.023832</td>
<td>0.023847</td>
<td>0.023844</td>
</tr>
<tr>
<td>2,1,1</td>
<td>0.046301</td>
<td>0.046275</td>
<td>0.046644</td>
<td>0.046610</td>
</tr>
<tr>
<td>3,1,1</td>
<td>0.081543</td>
<td>0.081580</td>
<td>0.082382</td>
<td>0.082432</td>
</tr>
<tr>
<td>4,1,1</td>
<td>0.127120</td>
<td>0.127077</td>
<td>0.128539</td>
<td>0.128514</td>
</tr>
<tr>
<td>2,2,1</td>
<td>0.067416</td>
<td>0.067423</td>
<td>0.068065</td>
<td>0.068079</td>
</tr>
<tr>
<td>3,2,1</td>
<td>0.100701</td>
<td>0.100699</td>
<td>0.102040</td>
<td>0.102056</td>
</tr>
<tr>
<td>3,3,1</td>
<td>0.131199</td>
<td>0.131172</td>
<td>0.133395</td>
<td>0.133367</td>
</tr>
<tr>
<td>2,2,2</td>
<td>0.087834</td>
<td>0.087890</td>
<td>0.087834</td>
<td>0.087871</td>
</tr>
<tr>
<td>3,2,2</td>
<td>0.119368</td>
<td>0.119338</td>
<td>0.120321</td>
<td>0.120292</td>
</tr>
</tbody>
</table>
TABLE IV

Coefficients of the energy expansion given by (5.8). The unit of \( k \) used in this expansion is \( 10\times(a/2\pi) \) times the atomic unit of \( k \). The energy values in this expansion are given in electron volts.

<table>
<thead>
<tr>
<th></th>
<th>Conduction Band</th>
<th>Light hole band</th>
<th>Heavy hole band</th>
<th>Split-off band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower</td>
<td>Upper</td>
<td>Upper</td>
<td>Lower</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>1.0222</td>
<td>1.0222</td>
<td>0.8556</td>
<td>0.8555</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>0.0117</td>
<td>0.0136</td>
<td>0.2871</td>
<td>0.2793</td>
</tr>
<tr>
<td>( E_3 )</td>
<td>-0.0578</td>
<td>0.0533</td>
<td>0.1068</td>
<td>-0.0853</td>
</tr>
<tr>
<td>( E_4 )</td>
<td>-1.147</td>
<td>-1.147</td>
<td>-1.0116</td>
<td>-0.9891</td>
</tr>
<tr>
<td>( E_4 )</td>
<td>0.0840</td>
<td>0.0870</td>
<td>0.0603</td>
<td>0.0459</td>
</tr>
<tr>
<td>( E_6 )</td>
<td>1.2534</td>
<td>1.1308</td>
<td>0.5309</td>
<td>0.5833</td>
</tr>
<tr>
<td>( E_6 )</td>
<td>-0.2707</td>
<td>-0.2716</td>
<td>0.0470</td>
<td>0.1033</td>
</tr>
<tr>
<td>( E_6 )</td>
<td>0.0266</td>
<td>-0.0083</td>
<td>-0.0299</td>
<td>-0.0473</td>
</tr>
</tbody>
</table>
TABLE V

Comparison of calculated effective masses with experimentally measured values for conduction band.

<table>
<thead>
<tr>
<th>Fermi Energy* (eV)</th>
<th>Experimental $(m^*/m_o) \times 10^2$</th>
<th>Calculated $(m^*/m_o) \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>lower band</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[100] [110] [111]</td>
</tr>
<tr>
<td>0.031</td>
<td>4.2±0.6 a</td>
<td>4.240 4.252 4.266</td>
</tr>
<tr>
<td>0.035</td>
<td>3.9±0.4, 4.1±0.6 a</td>
<td>4.278 4.292 4.307</td>
</tr>
<tr>
<td>0.044</td>
<td>3.9±0.5 a</td>
<td>4.364 4.385 4.404</td>
</tr>
<tr>
<td>0.046</td>
<td>4.9±0.5 b</td>
<td>4.384 4.406 4.425</td>
</tr>
<tr>
<td>0.050</td>
<td>4.4±0.6, 4.3±0.3 a</td>
<td>4.424 4.449 4.469</td>
</tr>
<tr>
<td>0.067</td>
<td>4.7±0.3 c</td>
<td>4.597 4.634 4.660</td>
</tr>
<tr>
<td>0.080</td>
<td>5.2±0.2 d</td>
<td>4.734 4.782 4.813</td>
</tr>
<tr>
<td></td>
<td></td>
<td>upper band</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[100] [110] [111]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.197 4.218 4.214</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.231 4.256 4.252</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.311 4.344 4.339</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.329 4.364 4.359</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.366 4.404 4.399</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.526 4.579 4.575</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.655 4.720 4.716</td>
</tr>
</tbody>
</table>

* Values of Fermi energy are taken from Yep and Becker (1966)

a Yep and Becker (1966)
b Piller (1963)
c Zwerdling et al. (1959)
d Becker et al. (1961)
TABLE VI

Anisotropy of conduction band effective mass. The experimental values are taken from Seiler and Becker (1969).

<table>
<thead>
<tr>
<th>Direction</th>
<th>Experimental $(m^*/m_o)\times10^2$</th>
<th>Calculated $(m^*/m_o)\times10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Lower band</strong></td>
</tr>
<tr>
<td>[100]</td>
<td>$4.66\pm0.08$</td>
<td>4.660</td>
</tr>
<tr>
<td>[110]</td>
<td>$4.69\pm0.06$</td>
<td>4.701</td>
</tr>
<tr>
<td>[111]</td>
<td>$4.74\pm0.07$</td>
<td>4.730</td>
</tr>
</tbody>
</table>
Comparison of calculated heavy hole masses with experimental values.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Experimental $m^*/m_0$</th>
<th>Calculated $m^*/m_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>0.36±0.03</td>
<td>0.61</td>
</tr>
<tr>
<td>[110]</td>
<td>0.36±0.03, 0.38±0.03</td>
<td>0.62</td>
</tr>
<tr>
<td>[111]</td>
<td>0.26±0.04</td>
<td>0.44</td>
</tr>
</tbody>
</table>
TABLE VII

Pseudo-Hamiltonian parameters in atomic units. These parameters were used in Chapters VI and VII.

<table>
<thead>
<tr>
<th>Local Parameters</th>
<th>Nonlocal Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^S_3$</td>
<td>$W^{III}_0$</td>
</tr>
<tr>
<td></td>
<td>$W^{III}_1$</td>
</tr>
<tr>
<td></td>
<td>$W^{III}_2$</td>
</tr>
<tr>
<td>$V^A_3$</td>
<td>$V^V_0$</td>
</tr>
<tr>
<td>$V^A_4$</td>
<td>$V^V_1$</td>
</tr>
<tr>
<td>$V^A_8$</td>
<td>$V^V_2$</td>
</tr>
<tr>
<td>$V^S_{11}$</td>
<td>$W^{V}_{0}$</td>
</tr>
<tr>
<td>$V^A_{11}$</td>
<td>$W^{V}_{1}$</td>
</tr>
<tr>
<td></td>
<td>$W^{V}_{2}$</td>
</tr>
</tbody>
</table>

Spin-orbit parameters

<table>
<thead>
<tr>
<th>$\lambda^S$</th>
<th>0.0075</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda^A$</td>
<td>0.0050</td>
</tr>
</tbody>
</table>
TABLE IX

Parameters of the model local pseudopotentials for Ga and Sb atoms. All values are in atomic units.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ga</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16.00</td>
<td>16.20</td>
</tr>
<tr>
<td>B</td>
<td>1.63</td>
<td>1.38</td>
</tr>
<tr>
<td>C</td>
<td>0.28</td>
<td>0.42</td>
</tr>
<tr>
<td>r_0</td>
<td>0.20</td>
<td>0.10</td>
</tr>
</tbody>
</table>
TABLE X

Band structure calculated by model pseudopotential and by actual pseudopotential. Spin-orbit interaction is not included. The energy levels are designated according to the conventional single group notations. The energy values are given in electron volts.

<table>
<thead>
<tr>
<th></th>
<th>By model pseudopotential</th>
<th>By actual pseudopotential</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_1 - \Gamma_{15} )</td>
<td>0.63</td>
<td>0.91</td>
</tr>
<tr>
<td>( \Gamma_{15} - \Gamma_1 )</td>
<td>2.98</td>
<td>3.31</td>
</tr>
<tr>
<td>( L_1 - L_3^v )</td>
<td>1.85</td>
<td>1.99</td>
</tr>
<tr>
<td>( L_3^c - L_1 )</td>
<td>3.26</td>
<td>3.61</td>
</tr>
<tr>
<td>( X_1 - X_5 )</td>
<td>3.63</td>
<td>3.85</td>
</tr>
<tr>
<td>( X_3 - X_1 )</td>
<td>0.17</td>
<td>0.39</td>
</tr>
<tr>
<td>( L_1 - \Gamma_1 )</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>( X_1 - \Gamma_1 )</td>
<td>0.16</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Pressure coefficients of some of the important energy level separations. The experimental values are from Kosicki et al. (1966b)

<table>
<thead>
<tr>
<th>$\frac{dE}{dP}$</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{6c} - \Gamma_{8v}$</td>
<td>$12.7 \times 10^{-6}$ eV/bar</td>
<td>$14.5 \times 10^{-6}$ eV/bar</td>
</tr>
<tr>
<td>$\Lambda_{6c} - \Gamma_{6c}$</td>
<td>$-9.6 \times 10^{-6}$ eV/bar</td>
<td>$-9.5 \times 10^{-6}$ eV/bar</td>
</tr>
<tr>
<td>$\chi_{6c} - \Gamma_{6c}$</td>
<td>$-17.9 \times 10^{-6}$ eV/bar</td>
<td>$-15.5 \times 10^{-6}$ eV/bar</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Procedure of determining pseudo-Hamiltonian parameters and calculating band structure.

Fig. 2. Calculated energy bands of GaSb along important symmetry axes. The energy levels are designated according to the conventional double group notations.

Fig. 3. Effective mass versus Fermi energy for conduction band. Solid lines and dashed lines represent lower band and upper band, respectively, which are split due to inversion asymmetry. The values of the upper band effective mass in [110] direction and [111] direction are almost identical and therefore are not shown separately.

Fig. 4. Effective mass versus Fermi energy for light hole band.

Fig. 5. Effective mass versus Fermi energy for heavy hole band.

Fig. 6. Effective mass versus Fermi energy for split-off band.

Fig. 7. Effective mass versus carrier concentration for conduction band. Dashed lines represent the case in which the effect of the L minima is neglected.

Fig. 8. Effective mass versus carrier concentration for light hole band.

Fig. 9. Effective mass versus carrier concentration for heavy hole band.

Fig. 10. Effective mass defined by (5.17) versus carrier concentration for conduction band. Dashed lines represent the case in which the effect of the L minima is neglected.
Fig. 11. Imaginary part of the dielectric constant of GaSb. The dots represent actually calculated values and the line connects the dots avoiding the unnecessary statistical noise.

Fig. 12. Real part of the dielectric constant of GaSb. The solid line is obtained by the extrapolation (1) of $\epsilon_2(\omega)$ and the dashed line is obtained by the extrapolation (2) of $\epsilon_2(\omega)$.

Fig. 13. Reflectivity of GaSb as a function of photon energy. The solid line is obtained by the extrapolation (1) of $\epsilon_2(\omega)$ and the dashed line is obtained by the extrapolation (2) of $\epsilon_2(\omega)$. The dots represent Cardona's measurement with n-type GaSb sample.
Fig. 1
Fig. 2
Fig. 5
Fig. 7
Fig. 10

\[ \left( \frac{m^2}{m_0} \right) \times 10^2 \]

\[ \text{ELECTRON CONCENTRATION (cm}^{-3} \text{)} \]
Fig. 11
Fig. 12
Fig. 13
APPENDIX A

STRUCTURE FACTORS IN ZINC-BLENDE STRUCTURE

Let us define the plane wave states $|k, K_n, R_{\mu j}\rangle$ associated with the reciprocal lattice vector $K_n$ and the position vector of an atomic site $R_{\mu j}$ by

$$
\langle r | k, K_n, R_{\mu j} \rangle = \frac{1}{\sqrt{N\Omega}} e^{i(k + K_n) \cdot (r - R_{\mu j})}
$$

(A-1)

where $N$ is the total number of unit cells in the whole crystal and $\Omega$ is the volume of the unit cell. $\mu$ represents the lattice point in the face centered cubic structure and $j$ denotes the sites of the two different atoms in the unit cell.

Let $W$ be an operator (nonlocal in general) expressed as summation of the operators $W_j(R_{\mu j})$ which are associated with the atomic sites $R_{\mu j}$,

$$
W = \sum_{\mu j} W_j(R_{\mu j}) \quad (j = 1, 2)
$$

(A-2)

where $W_j(R_{\mu j})$ have such a property that the matrix elements

$$
\langle r | k, K_n, R_{\mu j} | W_j(R_{\mu j}) | k, K_n, R_{\mu j} \rangle \equiv \frac{1}{N} W_j(k, K_n, K_n')
$$

(A-3)

are independent of the lattice index $\mu$.

Let us specify the vector $R_{\mu j}$ in such a way that
\[ R_{\mu 1} = R_\mu + \xi, \quad R_{\mu 2} = R_\mu - \xi \]  

(A-4)

where \( R_\mu \) is the real lattice vector. Then the matrix element of \( W \) can be written as

\[
< \mathbf{k}, \mathbf{K}_n | W | \mathbf{k}', \mathbf{K}'_n > \equiv < \mathbf{k}, \mathbf{K}_n, \mathbf{R}_0 | W | \mathbf{k}', \mathbf{K}'_n, \mathbf{R}_0 > \\
= \sum_{n,j} < \mathbf{k}, \mathbf{K}_n, \mathbf{R}_0 | W_j (R_{\mu j}) | \mathbf{k}, \mathbf{K}'_n, \mathbf{R}_0 > \\
= \sum_{n,j} e^{i(K'_n - K_n) \cdot R_{\mu j}} < \mathbf{k}, \mathbf{K}_n, \mathbf{R}_{\mu j} | W_j (R_{\mu j}) | \mathbf{k}, \mathbf{K}'_n, \mathbf{R}_{\mu j} > \\
= \frac{1}{N} \sum_n \left\{ e^{i(K'_n - K_n) \cdot (R_{\mu} + \xi)} W_1 (\mathbf{k}, \mathbf{K}_n, \mathbf{K}'_n) + e^{-i(K'_n - K_n) \cdot (R_{\mu} - \xi)} W_2 (\mathbf{k}, \mathbf{K}_n, \mathbf{K}'_n) \right\} \\
= S_1 (K'_n - K_n) W_1 (k, K_n, K'_n) + S_2 (K'_n - K_n) W_2 (k, K_n, K'_n) \]  

(A-5)

where the structure factors \( S_1(K'_n - K_n) \) and \( S_2(K'_n - K_n) \) are defined by

\[
S_1 (K'_n - K_n) = e^{i(K'_n - K_n) \cdot \xi} \\
S_2 (K'_n - K_n) = e^{-i(K'_n - K_n) \cdot \xi} \]  

(A-6)

If we further introduce the symmetric and antisymmetric components as

\[
S^S (k) = \frac{1}{2} [ S_1 (k) + S_2 (k) ] = \cos (k \cdot \xi) \\
S^A (k) = \frac{1}{2} [ S_1 (k) - S_2 (k) ] = \sin (k \cdot \xi) \]  

(A-7)
and

\[
W_S (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n') = W_1 (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n') + W_2 (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n')
\]

\[
W_A (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n') = W_1 (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n') - W_2 (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n')
\]

we obtain

\[
\langle \mathbf{\kappa}, \mathbf{\kappa}_n | W | \mathbf{\kappa}, \mathbf{\kappa}_n' \rangle
\]

\[
= S_S (\mathbf{\kappa}_n' - \mathbf{\kappa}_n) W_S (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n') + i S_A (\mathbf{\kappa}_n' - \mathbf{\kappa}_n) W_A (\mathbf{\kappa}, \mathbf{\kappa}_n, \mathbf{\kappa}_n')
\]

We observe that the matrix elements of a general operator \(W\), which satisfies the above mentioned conditions, can be expressed as a linear combination of its atomic components in a specific way given in (A-5) or (A-9) including the structure factors. We will only consider the simple lattice in the following Appendices just to avoid the complications due to the structure of the cells. But all the results are trivially extended for the zinc-blende structure if we take into account the above arguments.
APPENDIX B
SOME PROPERTIES OF PROJECTION OPERATOR

We prove here two simple lemmas concerning the projection operator we have used in Chapter II and Chapter III. These lemmas relate the crystal pseudopotential to the atomic pseudopotentials.

Let N be the total number of unit cells in the whole crystal and define the Wannier function $|a_{\mu \mu} >$ associated with the lattice site $R_{\mu}$, in terms of Bloch states $|\phi_{tk} >$ by

$$|a_{\mu \mu} > = \frac{1}{\sqrt{N}} \sum_{k} e^{-i k \cdot R_{\mu}} |\phi_{tk} >$$  \hspace{1cm} (B-1)

The inverse relation is easily seen to be

$$|\phi_{tk} > = \frac{1}{\sqrt{N}} \sum_{\mu} e^{i k \cdot R_{\mu}} |a_{\mu \mu} >$$  \hspace{1cm} (B-2)

Define also the plane wave states $|k, k_{n}, R_{\mu} >$ associated with the reciprocal lattice vector $k_{n}$ and lattice site $R_{\mu}$ by

$$< r |k, k_{n}, R_{\mu} > = \frac{1}{\sqrt{N \Omega}} e^{i (k \cdot x + k_{n} \cdot n - R \cdot \mu)}$$  \hspace{1cm} (B-3)

Now, define the generalized projection operators $Q_{k}$ and $Q_{\mu}$ associated with the Bloch states and Wannier states, respectively,

$$Q_{k} = \sum_{\mu} F_{\mu} |\phi_{tk} > < \phi_{tk} |$$  \hspace{1cm} (B-4)
with the same set of constants $F_t$ in both cases.

Then we have the following lemma.

**LEMMA I**

$$ Q_{\mu} = \sum_t F_t |a_{t\mu}^\dagger < a_{t\mu}| $$

(8-5)

Proof: Let $R_0 = 0$ for convenience.

$$ \langle \phi, R_0 | Q_{\mu} | \phi, R_0 \rangle = \sum_{\mu} \langle \phi, R_0 | Q_{\mu} | \phi, R_0 \rangle $$

(8-6)

Let the operator $U$ be the summation of $U$, which is associated with a lattice site $R_\mu^\dagger$, with the property
We then have the second lemma.

**LEMMA II**

\[ U | a_{x \mu} \rangle = \sum_{\mu'} U_{\mu} | a_{x \mu'} \rangle = U_{\mu} | a_{x \mu} \rangle \]  \hspace{1cm} (B-7)

The proof of this lemma is very similar to that of the previous one and will not be given here.

We notice that the nonlocal pseudopotential defined in (3.3) has exactly the form of the generalized projection operator of (B-4). In the tight binding approximation, the Wannier states in (B-1) reduce to the atomic states and, consequently, the projection operator defined in (B-5) becomes the atomic nonlocal pseudopotential. Therefore, in the limit of the tight binding approximation, LEMMA I is interpreted that the crystal nonlocal pseudopotential is obtained by the summation of the atomic nonlocal pseudopotentials over all the lattice sites. The fact that the same set of constants appears in both crystal and atomic nonlocal pseudopotential should be noted.

The spin-orbit interaction \( H^S \) in (3.9) has the properties of the operator \( U \) in (B-7) since in a good approximation it satisfies

\[ \mathbf{S} \cdot \mathbf{h}_\mu | U_{\mathbf{k}} (\mathbf{r}_{\mu'}) \rangle = 0 \quad \text{for} \quad \mu \neq \mu' \]
and the second term of pseudo-spin-orbit interaction in (3.4) has the form of $UQ_K + Q_K U$. LEMMA II then reads that, in tight binding approximation, the crystal pseudo-spin-orbit interaction is obtained by the summation of the atomic pseudo-spin-orbit interaction over all the lattice sites.
APPENDIX C

CANCELLATION PROPERTY OF PSEUDO-SPIN-ORBIT INTERACTION

Since the spin-orbit interaction operator $H^S$ has singularity near nuclei (one order higher singularity than the potential singularity), it is highly desirable to make it smooth within the core region by the pseudopotential formalism. In Appendix B, it is shown that the pseudo-spin-orbit interaction can be expressed as a summation of atomic pseudo-spin-orbit interactions, which can be written as

$$H^S_{\mu} = \frac{1}{2} \left\{ H^S_{\mu} \sum_{\tau} |a^\tau_{\mu}\rangle \langle a_{\mu}\tau| + \sum_{\tau} |a^\tau_{\mu}\rangle \langle a_{\mu}\tau| H^S_{\mu} \right\} \quad (C-1)$$

Here $H^S_{\mu}$ is the atomic spin-orbit interaction and $|a^\tau_{\mu}\rangle$ is the Wannier state associated with the atomic site $R_{\mu}$. The Wannier states $a^\tau_{\mu}(r)$, which can be replaced by the atomic orbitals in tight binding approximation, have the property that

$$a^\tau_{\mu}(r) \approx 0 \quad \text{for} \quad |r - R_{\mu}| \geq r_c$$

where $r_c$ is a constant in the order of core radius.

In ordinary crystals, there are reasonably large number ($M$) of core states so that any function localized in the core region can be well represented by them. Therefore, any arbitrary function $\phi(r)$ can be decomposed into two functions such that
\[ \phi(r) = \phi^c(r) + \phi'(r) \]  \hspace{1cm} (C-2) 

where \[ \phi^c(r) = \sum_{\mu} a_{\mu}^* (r) \int a_{\mu}^* (r') \phi^c(r') d^3r' \]  \hspace{1cm} (C-3) 

\[ \phi'(r) = 0 \quad \text{for} \quad |r - \vec{R}_\mu| < r_c \]  \hspace{1cm} (C-4) 

and also

\[ H^s_{\mu} \phi^c(r) \]  \hspace{1cm} (C-5) 

\[ \simeq \sum_{\mu} a_{\mu}^* (r) \int a_{\mu}^* (r') H^s_{\mu} (r') \phi^c(r') d^3r' \] 

If we apply the atomic pseudo-spin-orbit interaction operator (C-1) to \( \phi(r) \), we obtain

\[ H^s_{\mu} (r) \left[ \phi^c(r) + \phi'(r) \right] - \frac{1}{2} \left\{ H^s_{\mu} (r) \sum_{\mu} a_{\mu}^* (r) \right. 
\times \int a_{\mu}^* (r') \left[ \phi^c(r') + \phi'(r') \right] d^3r' + \sum_{\mu} a_{\mu}^* (r) 
\times \int a_{\mu}^* (r') H^s_{\mu} (r') \left[ \phi^c(r') + \phi'(r') \right] d^3r' \left\} \right. 
\simeq H^s_{\mu} (r) \phi^c(r) + H^s_{\mu} (r) \phi'(r) - \frac{1}{2} \left\{ H^s_{\mu} (r) \phi^c(r) + H^s_{\mu} (r) \phi'(r) \right\} 
\simeq H^s_{\mu} (r) \phi^c(r) \]  \hspace{1cm} (C-6)
The last result implies that the pseudo-spin-orbit interaction is cancelled out in the region $|\mathbf{r} - \mathbf{R}_\mu| \leq r_c$. 
We attempt to generalize the argument made in Chapter II to obtain a Hermitian pseudo-Hamiltonian which has more general form and therefore permits more freedom in selecting parameters.

Instead of defining $P_t$ and $Q$ as in (2.3) and (2.4), let us define $P_{tt'}$ and $Q$ as

$$P_{tt'} = |\Psi_t^c \rangle \langle \Psi_{t'}^c|$$

$$Q = \sum_{t=1}^{M} \sum_{t'=1}^{M} g_{tt'} |\Psi_t^c \rangle \langle \Psi_{t'}^c| = \sum_{t,t'} g_{tt'} P_{tt'}$$

To make $Q$ Hermitian, we require that the coefficients satisfy $g_{tt'} = g_{t't}^*$. If we consider the solution of

$$[H^0 + H^s + Q] |\Phi\rangle = E |\Phi\rangle$$

with the representation

$$|\Phi\rangle = \sum_{t=1}^{M} \alpha_t |\Psi_t^c\rangle + \sum_{n=1}^{\infty} \beta_n |\Psi_n\rangle$$
we obtain

\[ \sum_{n=1}^{N} \left( (E_n^c - E) \alpha_n + \sum_{k=1}^{M} g_{nk} \alpha_k \right) | \Phi_n \rangle = 0 \]  

(D-5)

or

\[(E_n - E) \beta_n = 0 \quad \text{for} \quad n = 1, \ldots, \infty \]  

(D-6)

\[(E_n^c - E) \alpha_n + \sum_{k=1}^{M} g_{nk} \alpha_k = 0 \]  

for \( t = 1, \ldots, M \)  

(D-7)

From (D-7), we find that, if \( a_t (t=1, \ldots, M) \) are not all zero, \( g_{tt'} \) should satisfy

\[ \det \begin{bmatrix} (E_t^c - E) \delta_{tt'} + g_{tt'} \end{bmatrix} = 0 \]  

(D-8)

In other words, one of the eigenvalues of this \( M \)-dimensional secular equation should coincide with the energy eigenvalue \( E \) we are looking for. If we set \( g_{tt'} = g_{tt} \delta_{tt'} \), it reduces to the result we obtained in Chapter II:

\[ g_{tt} = E - E_t^c \]

The coefficients \( \alpha_t \) are not independent one another but determined by (D-7). However the ratio between \( \beta_n \) and any one of \( \alpha_t \) remains arbitrary.

In actual calculation, it is almost impossible to expect that
$g_{tt'}$ have such values that (D-8) is satisfied with actual eigenvalues $E$. In most of the cases, however, it is good enough to have the values of $g_{tt'}$ such that the $M$ eigenvalues of (D-8) are densely distributed over a range of energy in which the energy values sought are located. The range of eigenvalue distribution becomes wider as we change the values for $g_{tt'}$ from

$$g_{tt'} = (E - E_{tc}) S_{tt'}$$

which would give us a single $M$-fold degenerate eigenvalue for (D-8). This kind of departure from the pseudo-Hamiltonian given in Chapter II is desirable because we need to obtain a number of energy levels by diagonalizing a single Hamiltonian matrix.

Starting from this generalized pseudo-Hamiltonian, we can also obtain the parametrized form of pseudo-Hamiltonian given in Chapter III by following similar procedure of reduction. The properties of this pseudo-Hamiltonian, which can be a subject of more detailed study, are expected to be much the same as the usual pseudo-Hamiltonian given in Chapter II.
VITA

Hwe Ik Zhang was born on May 14, 1938 in Yechon, Korea. He graduated from Chong Ju Technical High School, Chong Ju, Korea, in 1957. He received the degree of Bachelor of Science in Physics from Seoul National University, Seoul, Korea, in 1961. He is now a candidate for the degree of Doctor of Philosophy in the Department of Physics and Astronomy.
EXAMINATION AND THESIS REPORT

Candidate: Hwe Ik Zhang

Major Field: Solid State Physics

Title of Thesis: Energy Band Structure of Gallium Antimonide

Approved:

[Signatures]

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: May 8, 1969