Optical spectroscopy of some axial and double acceptors in germanium

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University of Wollongong

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Optical Spectroscopy of some Axial and Double Acceptors in Germanium

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

JOBE PRABAKAR CHELLIAH MSc, MPhil

Department of Engineering Physics
2000
DECLARATION

I, Jobe Prabakar Chelliah, declare that this thesis, submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Engineering Physics, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Jobe Prabakar Chelliah
21 September 2000
Abstract

Zeeman and piezospectroscopic studies have been carried out on samples of germanium cut from single crystal ingots doped with ZnH acceptor complex. For Zeeman studies, magnetic fields were applied with strengths up to 6.5 T along <100>, <111> and <110> crystallographic directions. The spectra were obtained using the Voigt configuration. The effect of uniaxial stress on this complex has been studied for F||<100> and <111>. From the observed Zeeman and piezo transitions of the D line, the behaviour of the ground and excited states has been determined. The excited state behaviour of this complex is the same as that of the group III impurities in Ge. Though this complex constitutes a hydrogenic atom, the presence of H causes the ground state to be very different from that of unperturbed group III impurities. The observed ground state behaviour provides a template for identification of such axial defects.

A new method was adopted to diffuse Mg into Ge. In the process, complexes were introduced. Zeeman studies were carried out with B||<100> for two of these, viz., MgX_1 and MgX_2. From the spectra, the Zeeman behaviour of the ground and excited state have been compared with that of ZnH complex which showed that these are also <111> axial defects. Zeeman and piezo studies have been carried out along <111> and <100> directions respectively, for CuX complex. Observed spectra showed the axial nature of this complex is also like ZnH. This also explained previous Zeeman studies with B||<100>.

The effect of magnetic field on neutral magnesium double acceptor states has been studied for B||<100>, confirming that the ordering of the ground state is the same as for neutral Zn. Also, a prediction is obtained of the Zeeman behaviour of the ground state of Mg'. This result is different than that for Zn'. An attempt has been made to study the Zeeman effect of neutral beryllium in germanium; the magnetic field dependence of the G line for B||<100> has been observed using polarized radiation. The results are very complex, more experimentation being required to simplify the spectra.
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Chapter 1. Introduction

Solids are differentiated according to their electrical properties into three groups: conductors, insulators and semiconductors [1,2]. Conductors have their valence electrons in the conduction band with "free electron" concentrations of $\sim 10^{23}$ cm$^{-3}$ resulting in high electrical conductivity. Under an electric field these electrons move easily and their concentration does not change with temperature. In an insulator virtually all these electrons are contained within the valence band, being bound into its crystalline structure, resulting in a solid with high resistivity.

A semiconductor can change from insulator-like to metal-like, as its free carrier density ranges from about $10^9$ to $10^{21}$ cm$^{-3}$. This variation can be achieved by the addition of impurities to the material or by changing its temperature. Both effect the semiconductor's most characteristic feature, it's forbidden energy gap. Electrically active point defects and impurities [1] introduce energy levels into this gap. The band structure of germanium, a typical semiconductor, is shown schematically in Figure 1.1

![Energy band structure of germanium](image)
Depending upon the energies of the levels introduced, defects may be broadly classified into two categories. The first category, the shallow impurities [3], are produced when atoms from the immediate neighbouring elemental groups are introduced substitutionally into the host atom. Shallow impurities introduce energy levels close to extrema of the energy gap and are responsible for the controlled introduction of electrons or holes into the conduction or valence bands. An example of the second category, the deep impurities, are those in which the levels are formed by transition metal impurities [4]. These defects introduce one or more energy levels relatively far from the extrema of the energy bands and catalyze the recombination of electrons and holes across the energy gap [5].

This work is concerned largely with the optical studies of some shallow defects in Ge. When group III or group V elements are substitutionally introduced into group IVB semiconductors (silicon or germanium), they occupy a site of tetrahedral symmetry, (intrinsic Ge has octahedral symmetry, the presence of the impurity atom reduces its symmetry to tetrahedral) and produces a population of free charge carriers at room temperature, electrons for donors and holes for acceptors. These charge carriers are associated with impurity ions through Coulombic interaction, forming a hydrogen-like system at very low temperatures. The periodic potential and high polarizability described by the static dielectric constant [6] of the host reduces the binding energy of such a hydrogen-like system to well below that of hydrogen. Hydrogen-like bound states lie near either the top of the valence band or the bottom of the conduction band. The binding energy of a “hydrogenic” system can be expressed as

\[ E_n = \frac{-m^* e^4}{2 \hbar^2 \kappa^2 n^2}, \]

where \( m^* \) = effective mass, \( \kappa \) = static dielectric constant and \( n = 1, 2, 3, \ldots \).
This hydrogenic model, is supported by observation of optical transitions analogous to those of the Lyman series of hydrogen. The different methods for the study of impurity energy levels, symmetry properties and transition probabilities for semiconductors doped with shallow impurities are those of infrared spectroscopy, photoconductivity, Raman spectroscopy and luminescence spectroscopy. Detailed study of the impurity energy states can be achieved by application of external perturbations which involves strain and magnetic fields or their combination. External perturbation lifts, partly or completely, the degeneracy and splits the energy states, consequently it splits the corresponding spectral lines.

In the case of an acceptor, $E_n$ represents the acceptor energy levels. The system is viewed as a bound hole moving in a potential of tetrahedral symmetry ($T_d$). The acceptor energy levels belong to the distinct irreducible representations $\Gamma_6$, $\Gamma_7$ and $\Gamma_8$ of the double group $T_d$ (see below). The degeneracy of an acceptor energy level is given by the dimensionality of the representation to which it belongs. Impurity levels with $\Gamma_6$ and $\Gamma_7$ symmetry are two-fold degenerate while those of $\Gamma_8$ symmetry are four-fold degenerate [7]. The ground state wave functions of the acceptor form a basis for $\Gamma_8$ whilst the excited state wave functions may form a basis for $\Gamma_6$, $\Gamma_7$ or $\Gamma_8$ [8]. Since the impurity states are shallow and lie close to the valence band edge, their wave functions are constructed from Bloch functions near the valence band edge. Within the effective mass approximation [9] (see Chapter 2), the wavefunctions of the impurity states are written as

$$\psi(r) = \sum_j F_j(r)\phi_j(r),$$

(1.2)
where $F_j(r)$ are hydrogenic envelope functions, satisfying the appropriate Schrödinger equation and $\phi_j(r)$ are Bloch functions of the top of the valence band, i.e., at $k=0$. Since the $F_j(r)$ are hydrogenic in nature, they are categorised as 1s, 2s, 2p, 3s-like etc, which in the tetrahedral environment of the crystal, are also classified according to the irreducible representations of $T_d$

$$s \leftrightarrow \Gamma_1, \ p \leftrightarrow \Gamma_5, \ d \leftrightarrow \Gamma_3+\Gamma_5, \text{ etc.}$$

From this we conclude that the symmetry of the full acceptor wavefunction $\Psi(r)$ is that of the products of the valence band states and the envelope functions giving

$$s \leftrightarrow \Gamma_1 \otimes \Gamma_8 = \Gamma_8$$

$$p \leftrightarrow \Gamma_5 \otimes \Gamma_8 = \Gamma_6 + \Gamma_7 + 2\Gamma_8$$

$$d \leftrightarrow (\Gamma_3 + \Gamma_5) \otimes \Gamma_8 = 2\Gamma_6 + 2\Gamma_7 + 3\Gamma_8,$$

etc.,

since the $\phi_j(r)$ involved are of $\Gamma_8$ symmetry which includes spin-orbit coupling. Transitions between the $\Gamma_8$, s-like ground state and other energy levels lead to the Lyman spectral series of absorption lines shown in Figure 1.2. It is this series of lines which will be studied for the defects ZnH [10, 11, 12, 13], CuX$^{(o)}$[14], several defects associated with Mg and Mg$^{(o)}$ and Be$^{(o)}$. The techniques of Zeeman and piezospectroscopy have been used to elucidate their properties.
Figure 1.2: Theoretical (EMT) energy levels for the ground state and excited states of group III acceptors in germanium and the allowed optical transitions.
Chapter 2 Theoretical Considerations

2.1 Effective Mass Theory

The simple model of shallow impurities in Ge and Si proposed by Bethe [15] gives an intuitive description of these impurity systems. In this model the electron donated by a group V impurity, substituting for a host atom, is bound Coulombically to the parent ion at low temperatures to form the analogue of a H-atom. The energy states ascribed to such hydrogenic "atoms" (see Equation 1.1) had binding energies of the correct order of magnitude although there was little known about the nature of the effective mass involved. This quantity is not that of an unfettered electron since "free" donor electrons are restricted to Bloch-like states and their group velocity, $<v> = \frac{1}{\hbar} \text{grad}_k \varepsilon(k)$ and acceleration

$<a> = \frac{1}{\hbar} \text{grad}_k \left[ \frac{d\varepsilon(k)}{dt} \right]$,

under an externally applied force, are determined by $k$, their wave-vector, and hence the initial state $\varepsilon(k)$ of the particle. The latter is unique to a given solid being dictated by its periodic potential. The effective mass is determined by the location of the donor electron within the energy band scheme of the crystal and is defined in terms of a second-rank tensor whose components are given by

$$\left( \frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon(k)}{\partial k_i \partial k_j}.$$

The process of thermally ionising a bound donor impurity as the temperature of the host is progressively raised involves the electron moving up its ladder of
energy states until it occupies the lowest continuum state of the solid. When bound it is not unreasonable to describe the hydrogenic system by the wave equation

\[-\frac{\hbar^2}{2m}(\nabla^2 + U_i(r))F(r) = E_nF(r), \tag{2.1}\]

where \(U_i(r)\) is the potential energy of the impurity. However, once in the continuum its property must be that of a Bloch state \(\varphi(r)\), modified by the presence of the defect. Thus the impurity even in its bound states needs to carry the imprint of the Bloch states describing the continuum extremum if, when ionised, it is to blend with the states of the latter. Intuitively, the full state of the impurity is expected to be described by Equation 1.2, where the summation is over either the number of equivalent energy band extrema or the degeneracy of such, the \(F(r)\) being modulated by the \(\varphi(r)\).

The above brief description of thermal ionisation also indicates that the effective mass appropriate to the bound electron is that of the band extremum. Since \(m^*\) is a tensor quantity a more formal approach to the problem is required particularly for the shallow states of group III acceptors whose continuum is that of the valence band which is four-fold degenerate at \(k=0\) since the light and heavy hole bands (see Figure 1.1) coalesce there; these states all have \(j=3/2\).

A formulation particularly useful in describing shallow impurity states is the effective mass approximation. This was successful in determining the band structure of a crystal starting with an extremum whose properties were assumed to be known and then applying perturbation theory [16]. The extension of this to
include $U_j(r)$ in the Hamiltonian of the crystal, taking advantage of the large spatial extend of $U_j(r)$ compared with that of a primitive cell of the solid [9] gave excellent agreement with experiment [6,17] for p-states of the group V donors and some success for acceptors [6, 18, 19]. A brief summary of the results of this approach is given in the following.

In the case of shallow donors states, the $F_j(r)$ were determined from the axial wave equation

$$
\left[ -\frac{\hbar^2}{2m_t} \frac{\partial^2}{\partial z_j^2} - \frac{\hbar^2}{2m_l} \left( \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} \right) - \frac{e^2}{kr} \right] F_j(r) = E_j F_j(r),
$$

(2.2)

where $m_t$ and $m_l$ are the transverse and longitudinal effective masses, respectively, at the conduction band minima. The surfaces of constant energy in $k$-space are ellipsoids of revolution and $j$ labels the different, equivalent conduction band valleys.

For acceptors the degeneracy of the valence bands of silicon and germanium makes the effective mass theory more complicated than for donor states so instead of a single partial differential equation a set of coupled equations are needed.

$$
\sum_{j'=1}^{6} D_{ij'}^{\alpha\beta} \left( \frac{1}{i} \frac{\partial}{\partial x^\alpha} \right) \left( \frac{1}{i} \frac{\partial}{\partial x^\beta} \right) F_{j'}(r) - \lambda \varepsilon_j F_j + \frac{e^2}{kr} F_j(r) = E F_j(r).
$$

(2.3)

Here $D_{ij}^{\alpha\beta}$ = numerical constants characteristic of the material and of the dimension $\hbar^2/m$, $\varepsilon_j$ is defined by $\varepsilon_j = \begin{cases} 0, & j = 1, 4 \\ 1, & j = 5, 6 \end{cases}$, and $\lambda$ is the spin-orbit splitting of the valence band at $k = 0$. 
The binding energy of an acceptor in germanium is \( \sim 10 \) meV which is very much smaller than the spin orbit separation (\( \lambda = 290 \) meV) so to a good approximation that part of Equation 2.3 due to the split-off band can be decoupled from the rest to give

\[
\sum_{j=1}^{4} D_{jj'}^{\alpha \beta} \left( \frac{1}{i} \frac{\partial}{\partial \alpha} \right) \left( \frac{1}{i} \frac{\partial}{\partial \beta} \right) F_{j'}(r) F_{j}(r) + \frac{e^2}{\kappa r} F_{j}(r) = E F_{j}(r),
\]

(2.4)

where \( j = 1, \ldots, 4 \).

Approximate solutions of (2.4) can be obtained by expanding the \( F_j(r) \) in spherical harmonics. For even \( l \) we have

\[
F_j(r) = \sum_{l=0,2,\ldots} \sum_{m} f_{j,l,m}(r) Y_{l,m}(\theta, \phi),
\]

(2.5)

where \( f_{j,l,m}(r) \) is the radial part of the spherical harmonics. The ground state ionization energy so determined, namely 8.9 meV, is in fair agreement with the measured value. Inclusion of \( F_5 \) and \( F_6 \) by perturbation theory increases the ionization energy by less than 1%. The representation of the solution of the above equation is \( \Gamma_8 \) with four-fold degeneracy or \( \Gamma_6 \) and \( \Gamma_7 \) with two-fold degeneracy. The impurity states can be characterized according to the symmetry deduced from the transformation properties of the total wave functions.

A new method was introduced by Baldererschi and Lipari [20], which has the advantage of providing a convenient algorithm for numerical calculations of the energies. In this method effects of the periodic crystal potential on an impurity state are replaced by an equivalent tensor quantity in the effective one-electron equation of motion, this was achieved by separating spherical terms of the effective mass Hamiltonian and considering the cubic terms as perturbations.
They extended the theory by considering the effect of the split-off band and wave vector dependent dielectric screening functions [21]. The outcome of this approach gave excellent agreement with the experimental energies of many of the p-like states of group III acceptors in Ge. The parameterisation of the ground state wave functions permitted transition probabilities to be calculated which also agreed well with the experimental observations.

In a group IV semiconductor, a substitutional impurity finds itself at a site of tetrahedral symmetry, so it is assumed that the impurity atom does not introduce any distortions that might alter the site symmetry. The cubic terms in the acceptor Hamiltonian reduces the symmetry from that of the full rotation group to $\text{O}_h$, the symmetry of the intrinsic material. The s-like states of shallow acceptors in silicon and germanium belong to the four-dimensional representation $\Gamma_8$ under $\text{T}_d$, the true site symmetry, while it is designated as $\Gamma_8^+$ under $\text{O}_h$ and the excited states of the G and D lines, for example, [8] are also designated as $\Gamma_8$ under $\text{T}_d$ and $\Gamma_8^-$ under $\text{O}_h$. An integer starting with 1 is prefixed to the symmetry labels for the lowest state of a given symmetry, thus, under $\text{O}_h$ notation, the unperturbed s-like ground state has the label $1\Gamma_8^+$ and higher-lying s-like states have the labels $2\Gamma_8^+$, $3\Gamma_8^+$, etc., whereas the excited p-like states are $1\Gamma_8^-$, $2\Gamma_8^-$ and so on.

2.2 Effect of Magnetic Field and Stress

As in atomic spectroscopy, external perturbations are used to understand the energy levels of the impurity states which also yields information about the intrinsic properties of the host. The way in which the acceptor Zeeman states are
labeled requires, first, that these display the values of the magnetic quantum number \( m_j = \mu \) corresponding to those of Bhattacharjee and Rodriguez [22] in order to enable the expressions developed by these authors to be used to calculate g-factors. Secondly, the symmetry labels need to be those used by Broeckx [23] and by Schmitt et al. [24] so that comparison can be made between the experimental behaviour of the individual Zeeman states with that predicted theoretically. Thirdly, the g-factors determined for odd parity states by Schmitt et al. [24] under \( \bar{O}_h \) symmetry need to be transformed for comparison with those extracted under \( \bar{T}_d \) symmetry. This is accomplished using the technique developed by Bleaney [25].

The situation is somewhat complicated by the need to correlate the symmetry labels of Bhattacharjee and Rodriguez [22] with those of Koster et al. [8]; the latter has become the standard in this area notwithstanding the number of errors contained in the character tables. Also, in using these, careful note must be taken of the conventions used. The use of Koster et al. [8] was circumvented by Bhattacharjee and Rodriguez [22] who generated their own character tables where needed.

External perturbation such as elastic and magnetic fields or their combination lifts partly or completely the degeneracies of the energy states. Through Zeeman analysis one can obtain g factors and effective-mass parameters, whereas Uniaxial stress analysis yield deformation potential constants related to the relevant band extrema. In the case of axial defects, the symmetry of the impurity potential is reduced from \( T_d \) resulting in different selection rules from those of group III impurities under applied perturbations. For double acceptors the
symmetry is $T_d$ but the ground state is compounded from $\Gamma_8$ orbitals of the two holes and has the symmetry obtained from the antisymmetric product of these two $\Gamma_8$'s and thus these also behave differently to the group III acceptors under external perturbations. Selection rules for axial defects and double acceptors are discussed in their respective sections in $\overline{O}_h$ notation.

2.2.1 The Effect of Magnetic Field

A magnetic field splits a state into its various Zeeman levels. The Hamiltonian of a single hole acceptor in the presence of a magnetic field $B$, is

$$H_z = -\mu_B (1 + 2s)B - \frac{1}{2} m\mu_B^2 [r^2 B^2 - (r\cdot B)^2],$$

where $m$ is the free-electron mass, $\mu_B$ the bohr magneton and $r$ the position operator, while $l$ and $s$ are the orbital and spin angular momenta in units of $\hbar$, respectively.

The correlations given in Table 2.1. have been obtained by taking the above considerations into account and utilising the appropriate compatibility tables of Koster et al [8]. It might be noted that the compatibility tables of Koster et al [8] and Bhattacharjee and Rodriguez [22] can be correlated by matching the irreducible representations whose bases, $|j\mu\rangle$, are the same. In this table where two Zeeman states of the same symmetry result these have been labelled as $\Gamma_{x,1}$ and $\Gamma_{x,2}$. Treating the direction of the magnetic field as the symmetry axis, Table 2.2 shows the reduction in symmetry for $B||<100>$, $<111>$ or $<110>$ crystallographic directions.
Table 2.1: Correlation of the irreducible representations used in the work of Schmitt et al [24] and Broeckx [23] with the values of $\mu$ used by Bhattacharjee and Rodriguez (B&R) [22] for $\mathbf{B}||<100>$, $\mathbf{B}||<111>$ or $\mathbf{B}||<110>$.

| $\mu$ | $\mathbf{B}||<100>$ | $\mathbf{B}||<111>$ | $\mathbf{B}||<110>$ |
|-------|---------------------|---------------------|---------------------|
|       | (Koster)            | (B&R)               | (Koster)            | (B&R)               |
| $\frac{3}{2}$ | $n\Gamma_8^+$   | $\Gamma_8$       | $\Gamma_6$       | $n\Gamma_6^{+1}$  | $\Gamma_6.1$     | $n\Gamma_4^{+1}$ | $\Gamma_4.1$ | $\Gamma_3.2$ |
|       | $S_4$               | $S_4$              | $C_{3i}$          | $C_{3}$            | $C_{2h}$         | $C_s$            | $C_{1h}$     |

**nT8$^+$ state**

| $\mu$ | $\mathbf{B}||<100>$ | $\mathbf{B}||<111>$ | $\mathbf{B}||<110>$ |
|-------|---------------------|---------------------|---------------------|
|       | $n\Gamma_8^-$      | $\Gamma_8$       | $\Gamma_6$       | $n\Gamma_6^{+1}$  | $\Gamma_6.1$     | $n\Gamma_3^{+1}$ | $\Gamma_3.2$ |
|       | $S_4$               | $S_4$              | $C_{3i}$          | $C_{3}$            | $C_{2h}$         | $C_s$            | $C_{1h}$     |

Table 2.2: Reduction of symmetry in $\bar{T}_d$ and $\bar{O}_h$ notation under magnetic field.

<table>
<thead>
<tr>
<th>Direction of $\mathbf{B}$</th>
<th>Site symmetry $\bar{T}_d$</th>
<th>Site symmetry $\bar{O}_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;100&gt;$</td>
<td>$\bar{S}_4$</td>
<td>$\bar{C}_{4h}$</td>
</tr>
<tr>
<td>$&lt;111&gt;$</td>
<td>$\bar{C}_3$</td>
<td>$\bar{C}_{3i}$</td>
</tr>
<tr>
<td>$&lt;110&gt;$</td>
<td>$\bar{C}_{1h}$</td>
<td>$\bar{C}_{2h}$</td>
</tr>
</tbody>
</table>
Bhattacharjee and Rodriguez have carried out a group theoretical analysis on the Zeeman effect of such acceptors using

\[ H_z^{(i)} = \frac{1}{2} \mu_B g_1^{(i)} B \sigma + q^{(i)} B^2 \quad (i = 6, 7), \]  

(2.7)
as the Zeeman Hamiltonian for \( \Gamma_6 \) and \( \Gamma_7 \) states, where \( \sigma \) is the Pauli matrix.

The most general form of the Zeeman Hamiltonian for a \( \Gamma_8 \) state is

\[ H_z^{(8)} = \mu_B g_1 B J + \mu_B g_2 \left( B_x J_x^3 + B_y J_y^3 + B_z J_z^3 \right) + q_1 B^2 + q_2 (B J)^2 
+ q_3 \left( B_x^2 J_x^2 + B_y^2 J_y^2 + B_z^2 J_z^2 \right), \]  

(2.8)

where \( J \) is the angular momentum operator for \( j = 3/2 \) and \( g_1', g_2', q_1, q_2 \) and \( q_3 \) depend on the unperturbed wave functions of the \( \Gamma_8 \) state. Having chosen an appropriate set of basis functions for the above Hamiltonian enables one to find the eigenvalues of the Zeeman substates and relative intensities for transitions to a given manifold of states. This has been carried out for \( B \parallel \langle 100 \rangle \), \( B \parallel \langle 111 \rangle \), and \( B \parallel \langle 110 \rangle \). Symmetry decomposition of \( \Gamma_8 \) for the above three directions of \( B \) is given in Table 2.3. Tables 2.4, 2.5, and 2.6 show the selection rules.

Table 2.7 gives expressions for \( g_1 \) and \( g_2 \), in it \( \Delta_{\pm 3/2} = E_{3/2} - E_{-3/2} = 3 \mu_B \left( g_1 + \frac{9}{4} g_2 \right) B, 2 \mu_B g_2 B \left( \frac{3}{2} p + \frac{23}{2} \right)^2 + \frac{1}{2}, \mu_B g_2 B \left[ \Delta_+ + \Delta_- + 2 \left( \frac{1}{2} p + \frac{7}{8} \right) \right] \)

and \( \Delta_{\pm 1/2} = E_{1/2} - E_{-1/2} = \mu_B \left( g_1 + \frac{1}{4} g_2 \right) B, \mu_B B \left( g_1 + \frac{13}{4} g_2 \right), \mu_B g_2 B \left[ \Delta_+ + \Delta_- - 2 \left( \frac{1}{2} p + \frac{7}{8} \right) \right] \), for \( B \parallel \langle 100 \rangle, B \parallel \langle 111 \rangle, \) and \( B \parallel \langle 110 \rangle \)

respectively. Expressions for \( B \parallel \langle 110 \rangle \) are approximated for small \( B \), where \( p = g_1 / g_2 \) and \( \Delta_\pm = \sqrt{p + \frac{17}{8}} \).
Table 2.3: Symmetry of decomposition of $\Gamma_8$

<table>
<thead>
<tr>
<th>Magnetic Field Direction</th>
<th>Decomposition of $\Gamma_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;100&gt;$</td>
<td>$\Gamma_5 + \Gamma_6 + \Gamma_7 + \Gamma_8$</td>
</tr>
<tr>
<td>$&lt;111&gt;$</td>
<td>$\Gamma_4 + \Gamma_5 + 2\Gamma_6$</td>
</tr>
<tr>
<td>$&lt;110&gt;$</td>
<td>$2\Gamma_3 + 2\Gamma_4$</td>
</tr>
</tbody>
</table>

Table 2.4: Selection rules for $B||<100>$ ($\bar{T}_d$ notation)

<table>
<thead>
<tr>
<th>$\bar{S}_4$</th>
<th>$\Gamma_5$</th>
<th>$\Gamma_6$</th>
<th>$\Gamma_7$</th>
<th>$\Gamma_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_5$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma_6$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
</tbody>
</table>

In $\bar{O}_h$ notation, i.e., ($\bar{C}_{4h}$),

$E_{\parallel}: \Gamma_i \rightarrow \Gamma_f$ for $i=f=5,6,7,8$. $E_{\perp}: \Gamma_i \rightarrow \Gamma_f$ for $|i-f|\neq2$

Table 2.5: Selection rules for $B||<111>$ ($\bar{T}_d$ notation)

<table>
<thead>
<tr>
<th>$\bar{C}_3$</th>
<th>$\Gamma_4$</th>
<th>$\Gamma_{6,1}$</th>
<th>$\Gamma_5$</th>
<th>$\Gamma_{6,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_4$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma_{6,1}$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma_5$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
</tr>
<tr>
<td>$\Gamma_{6,2}$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
</tr>
</tbody>
</table>

In $\bar{O}_h$ notation, i.e., ($\bar{C}_{3i}$),

$E_{\parallel}: \Gamma_i \rightarrow \Gamma_f$ for $i=f=4,5,6$. $E_{\perp}: \Gamma_i \rightarrow \Gamma_f$ for $|i-f|\neq0$
Table 2.6: Selection rules for $\mathbf{B}||<110>$ ($\bar{T}_d$ notation)

<table>
<thead>
<tr>
<th>$\bar{C}_{1h}$</th>
<th>$\Gamma_{3.1}$</th>
<th>$\Gamma_{3.2}$</th>
<th>$\Gamma_{4.1}$</th>
<th>$\Gamma_{4.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{3.1}$</td>
<td>$E\perp B$</td>
<td>$E\perp B$</td>
<td>$E\parallel B$</td>
<td>$E\parallel B$</td>
</tr>
<tr>
<td>$\Gamma_{3.2}$</td>
<td>$E\perp B$</td>
<td>$E\perp B$</td>
<td>$E\parallel B$</td>
<td>$E\parallel B$</td>
</tr>
<tr>
<td>$\Gamma_{4.1}$</td>
<td>$E\parallel B$</td>
<td>$E\parallel B$</td>
<td>$E\perp B$</td>
<td>$E\perp B$</td>
</tr>
<tr>
<td>$\Gamma_{4.2}$</td>
<td>$E\parallel B$</td>
<td>$E\parallel B$</td>
<td>$E\perp B$</td>
<td>$E\perp B$</td>
</tr>
</tbody>
</table>

In $\bar{O}_h$ notation, i.e., $(\bar{C}_{2h})$, $E||\Gamma_i \rightarrow \Gamma_f$ for $i=f=3,4$. $E:\Gamma_i \rightarrow \Gamma_f$ for $|i-f|\neq 0$

2.2.2 The Effect of Uniaxial Stress.

In general, under homogeneous uniaxial stress the symmetry of a crystal is lowered which in turn partially lifts the degeneracy of impurity states, the Kramers' degeneracy being retained. Table 2.8 shows the reduction of $\bar{T}_d$ symmetry under a uniaxial force, $\mathbf{F}$, along $<100>$, $<111>$ or $<110>$ crystallographic directions.

Using deformation potential theory developed by Bardeen and Shockley [26] in the linear approximation, a one particle Hamiltonian can be written as

$$H = H_0 + H' = H_0 + \sum_{\alpha\beta} V_{\alpha\beta} \varepsilon_{\alpha\beta}$$ (2.9)

The symmetric tensor $V$ produces energy shifts and splittings. Here
Table 2.7: $g_1$ and $g_2$ expression for $\mathbf{B}\|<100>$, $\mathbf{B}\|<111>$, and $\mathbf{B}\|<110>$.

<table>
<thead>
<tr>
<th>Magnetic Field</th>
<th>$g_1$</th>
<th>$g_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathbf{B}|&lt;100&gt;$</td>
<td>$\frac{1}{\mu_B B} \left( \frac{9}{8} \Delta_{1/2} - \frac{1}{24} \Delta_{3/2} \right)$</td>
<td>$\frac{1}{6\mu_B B} \left( \Delta_{3/2} - 3\Delta_{1/2} \right)$</td>
</tr>
<tr>
<td>$\mathbf{B}|&lt;111&gt;$</td>
<td>$\frac{-28\Delta_{1/2} - 13 \sqrt{2} (\Delta_{3/2}^2 - \Delta_{1/2}^2)}{24\mu_B B}$</td>
<td>$\frac{4\Delta_{1/2} + \sqrt{2} (\Delta_{3/2}^2 - \Delta_{1/2}^2)}{6\mu_B B}$</td>
</tr>
<tr>
<td>$\mathbf{B}|&lt;110&gt;$</td>
<td>$\mu_B B \left[ \frac{13}{12} (\Delta_{3/2} + \Delta_{1/2}) - \frac{7}{12} \sqrt{\left(\Delta_{3/2} + \Delta_{1/2}\right)^2 - 3\left(\Delta_{3/2} - \Delta_{1/2}\right)^2} \right]$</td>
<td>$\mu_B B \left[ \frac{-3 (\Delta_{3/2} + \Delta_{1/2}) + \sqrt{\left(\Delta_{3/2} + \Delta_{1/2}\right)^2 - 3\left(\Delta_{3/2} - \Delta_{1/2}\right)^2}}{3} \right]$</td>
</tr>
</tbody>
</table>
\[ \varepsilon_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \]
is the strain tensor, where \( u(x_1, x_2, x_3) \) the displacement field.

### Table 2.8: Reduction of \( T_d \) symmetry under uniaxial stress

<table>
<thead>
<tr>
<th>Direction of Force</th>
<th>Site Symmetry (( T_d ))</th>
<th>Site Symmetry (( O_h ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;100&gt;)</td>
<td>( D_{2d} )</td>
<td>( D_{4h} )</td>
</tr>
<tr>
<td>(&lt;111&gt;)</td>
<td>( C_{3v} )</td>
<td>( D_{3d} )</td>
</tr>
<tr>
<td>(&lt;110&gt;)</td>
<td>( C_{2v} )</td>
<td>( D_{2h} )</td>
</tr>
</tbody>
</table>

On applying stress in an arbitrary direction, the \( \Gamma_8 \) states shift and split into two Kramers' doublets, whereas \( \Gamma_6 \) and \( \Gamma_7 \) states merely shift. One can write, using symmetry arguments, \( H' \) for a \( \Gamma_8 \) hole state

\[
H' = -a \sum_i \varepsilon_{ii} - b \sum_i \varepsilon_{ii} \left( J_i^2 - \frac{1}{3} J^2 \right) - \frac{2d}{\sqrt{3}} \sum_{i<j} \varepsilon_{ij} \{J_i J_j\}. \tag{2.10}
\]

Here \( a, b \), and \( d \) are deformation potential constants and the \( J_i \)'s are angular momentum matrices for \( j=3/2 \).

The splitting of a \( \Gamma_8 \) state is given by

\[
\Delta^2 = 2b^2 \left[ (\varepsilon_{11} - \varepsilon_{22})^2 + (\varepsilon_{22} - \varepsilon_{33})^2 + (\varepsilon_{33} - \varepsilon_{11})^2 \right] + 4d^2 \left( \varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2 \right) \tag{2.11}
\]

For uniaxial stress \( \mathbf{F} \) along an axis with direction cosines \( \alpha_x, \alpha_y, \) and \( \alpha_z \)

\[
\Delta^2(\alpha_x, \alpha_y, \alpha_z) = \Delta^2_{100} + 3(\Delta^2_{111} - \Delta^2_{100})K(\alpha_x, \alpha_y, \alpha_z), \tag{2.12}
\]

where \( \Delta_{100} = 2b(s_{11} - s_{12})T \) and \( \Delta_{111} = \frac{d}{\sqrt{3}} s_{44}T \). Here \( s_{11}, s_{12}, \) and \( s_{44} \) are the elastic compliance constants, \( T \) is the applied stress and is positive for a tensile
force and negative for a compressive force, while

\[ K(\alpha_x, \alpha_y, \alpha_z) = \alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2. \]

The eigenstates and the reduced symmetries of a \( \Gamma_8 \) state for \( F||<111> \) and \( <100> \) are given in Table 2.9. Selection rules in \( \bar{T}_d \) notation are given in the Table 2.10, Table 2.11, Figure 2.1 and Figure 2.2.

Table 2.9: Reduced symmetry of \( \Gamma_8 \) and its eigenstates for \( F||<111> \) and \( F||<100> \)

<table>
<thead>
<tr>
<th>Direction of Force</th>
<th>States</th>
<th>Eigenstate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;111&gt;)</td>
<td>( \Gamma_5 + \Gamma_6(\bar{C}_{3v}) )</td>
<td>( a(s_{11} + 2s_{12})T + \left( \frac{d}{2\sqrt{3}} \right)s_{44}T )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_4(\bar{C}_{3v}) )</td>
<td>( a(s_{11} + 2s_{12})T - \left( \frac{d}{2\sqrt{3}} \right)s_{44}T )</td>
</tr>
<tr>
<td>(&lt;100&gt;)</td>
<td>( \Gamma_6(\bar{D}_{2d}) )</td>
<td>( a(s_{11} + 2s_{12})T + b(s_{11} - s_{12})T )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_7(\bar{D}_{2d}) )</td>
<td>( a(s_{11} + 2s_{12})T - b(s_{11} - s_{12})T )</td>
</tr>
</tbody>
</table>
Figure 2.1: Selection rules for $\mathbf{F}||<100>$

Table 2.10: Selection rules for the group $\overline{D}_{2d}$: $\mathbf{F}||<100>$

<table>
<thead>
<tr>
<th>$\overline{D}_{2d}$</th>
<th>$\Gamma_6$</th>
<th>$\Gamma_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_6$</td>
<td>$\mathbf{E} \perp \mathbf{F}$</td>
<td>$\mathbf{E} \perp \mathbf{F}$, $\mathbf{E} \parallel \mathbf{F}$</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>$\mathbf{E} \perp \mathbf{F}$, $\mathbf{E} \parallel \mathbf{F}$</td>
<td>$\mathbf{E} \perp \mathbf{F}$</td>
</tr>
</tbody>
</table>
Figure 2.2: Selection rules for $F||<111>$

Table 2.11: Selection rules for the group $\overline{C}_{3v}$: $F||<111>$

<table>
<thead>
<tr>
<th>$\overline{C}_{3v}$</th>
<th>$\Gamma_4$</th>
<th>$\Gamma_5 + \Gamma_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_4$</td>
<td>$E \perp F$, $E</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_5 + \Gamma_6$</td>
<td>$E \perp F$</td>
<td>$E</td>
</tr>
</tbody>
</table>
Chapter 3  Experimental Techniques.

3.1  Introduction

In dispersive spectroscopy the electromagnetic radiation from the source is separated into its component wavelengths by a monochromator using a grating or prism, and, usually, the monochromatic radiation is passed through the sample and collected by a detector. Scanning of the grating or prism changes the photon energy incident on the sample to give its spectrum. In Fourier transform spectroscopy there is no monochromator to separate the light beam, a broad range of wavelengths is incident on the sample after being passed through an interferometer and the detected signal is in the form of an interferogram which is Fourier transformed to produce the spectrum.

An FTIR (Fourier transform infrared) spectrometer is usually based on the Michelson interferometer and relies on the interference of two beams of radiation to produce the interferogram. The radiation from the source is collimated and then separated into two coherent beams by a beam splitter. One beam is reflected by a stationary mirror, the other by a moving mirror, with both returning to the beam splitter and subsequently superimposed to produce interference. If the source is monochromatic, the detector will record a cosine for the interferogram. Each maximum in the interferogram will correspond to the path difference between the two beams being an integral number of wave lengths. A spectrum can be obtained by a Fourier transform of the interferogram that converts intensity versus mirror travel into intensity versus wavenumber. If a polychromatic source is used the interferogram becomes the sum of the cosines
for each wavelength. At zero path difference all cosines add constructively to produce a "grand maximum" fringe. The fringe intensity drops for increasing value of path difference. The transmission spectrum of a material can be obtained by placing the sample in the recombined section of the beam path before the beam reaches the detector, the loss of intensity at the sharp absorption lines giving rise to modulation in the interferogram.

Since all wavelengths from the source are detected at the same time the signal to noise ratio is very high in FTIR spectroscopy which is the main (Felgett's or Multiplex) advantage over dispersive spectroscopy [27]. Further increase in signal to noise is achieved by either averaging over a number of scans or using a larger time constant and slower scan speed. For the former the reduction in the noise is the square root of the number of scans.

Mathematically the interferogram and the spectrum are represented by:

\[
\text{Interferogram} \quad I(\delta) = \int B(\sigma) e^{2\pi i \sigma \delta} d\sigma \quad -\infty < \sigma < + \infty \quad (3.1)
\]

\[
\text{Spectrum} \quad B(\sigma) = \int I(\delta) e^{-2\pi i \sigma \delta} d\delta \quad -\infty < \delta < + \infty, \quad (3.2)
\]

where \( \delta \) and \( \sigma \) are the retardation and frequency, respectively. Here

\[
\delta = 2vt, \quad (3.3)
\]

where \( v \) is the mirror speed and the time, \( t \), is zero at zero path difference. We can obtain a real spectrum by performing the cosine Fourier transform of \( I(\delta) \)

\[
B(\sigma) = \int I(\delta) \cos 2\pi \sigma \delta \, d\delta \quad -\infty < \delta < + \infty \quad (3.4)
\]

If the function is even, then

\[
B(\sigma) = 2 \int I(\delta) \cos 2\pi \sigma \delta \, d\delta \quad 0 < \delta < + \infty \quad (3.5)
\]
Experimentally, the function to be transformed is sampled at a constant rate, $\Delta$, over a finite range of mirror travel. The sampling interval must be the reciprocal of twice the highest frequency, $f_c$ present (sometimes called the folding or Nyquist frequency), i.e., $f_c = 1/2\Delta$ in order to detect all the frequencies present.

The Fourier transform of the function is defined between $+f_c$ and $-f_c$ the power outside the range being folded back in, i.e., aliased. This effect can be removed by low-pass filtering of the original function before sampling. The final transform will be a discrete Fourier transform.

$$B(f_n) = \Delta \sum_{k=0}^{N-1} I_ke^{-2\pi i kn/N},$$  \hspace{1cm} (3.6)

where $f_n = n/N\Delta$, $n = -N/2, ..., N/2$, $N$ is the input points.

The instruments used in this work were a modified Polytec FTIR for Zeeman studies and a Bomem DA3 FTIR for stress analyses. Both were of the Michelson type.

### 3.2 Interferometer

#### 3.2.1 Polytec FTIR Spectrometer

The Polytec spectrometer is a slow-scan interferometer designed for use in the 10 -1000 cm$^{-1}$ wavenumber region. Figure 3.1 is a block diagram of the spectrometer based on a Polytec FTIR. This consisted of three chambers. In the first chamber the electromagnetic radiation from the source is amplitude modulated by a chopper and collimated before entering the interferometer. The chopper produces the reference signal for synchronous detection. The present
Figure 3.1: Schematic of Polytec FTIR spectrometer.

S  Source
C  Chopper
M_P  Plane mirror
M_oap  Off axis paraboloidal mirror
B  Beam splitter
P  Polarizer
Po  Polypropylene window
M_Pi  Plane mirror
M  Magnet
Sa  Sample space
L_P  Light pipe
D  Detector
PA  Preamplifier
measurements used mylar beam splitters in the interferometer; these were of thickness 6, 12 and 23 μ, covering the ranges 15-370 cm⁻¹, 25-180 cm⁻¹ and 10-110 cm⁻¹, respectively. After passing through a wire grid polariser (gold evaporated onto a polyethylene replica grating as substrate) (used when required), the beam fell on the sample mounted between the split-coil of an Oxford Instruments superconducting (SC) magnet. A plane mirror M₁ between the polariser and the magnet could be rotated to give the Voigt or Faraday configuration. The room temperature and the cold windows of the magnet were polypropylene, one of the former and both the latter were 50μ thick. The room temperature entrance window was a disc 0.8 mm thick with a cone machined into it which reduced the thickness at its apex to 0.4 mm. This was to eliminate channeled spectra. The three thinner windows were unwedged and produced broad but significant fringes. Cooling of the sample was achieved by siphoning liquid helium into the sample chamber where it evaporated. Usually the sample temperature was maintained at near liquid He temperature as indicated by thermometers on the sample stick. The sample space was held at a pressure of ~8 mbar using a vacuum pump. It is believed that this stabilized the temperature by preventing burst of He entering the sample chamber. Two co-axial, contiguous light pipes collected the radiation transmitted by the sample and delivered it to the detector whose window was also a 50μ thick polypropylene film. The light pipe nearer the sample was attached to the nitrogen shield of the SC magnet. It terminated at the thinner of the two room temperature windows of the magnet on the other side of which was the entrance to the room temperature part of this split light pipe. The signal received by an Infrared Laboratories (IRL) silicon bolometer was synchronously detected by a PAR model 124A lock-in amplifier. The DC output of this amplifier was led to a digital computer through a 16 bit A/D
converter to record the interferogram, subsequently this was transformed to obtain the spectrum.

### 3.2.2 Bomem FTIR Spectrometer

The Bomem spectrometer is a rapid scan interferometer producing a sinusoidal intensity variation of the beam with a specific frequency for each spectral element. This is amplified by a broad-band amplifier.

The instrument as used was fitted with a coated mylar beam splitter which covered the spectral range 10-700 cm\(^{-1}\). The cold filter of the bolometer detector determined the spectral regions; these were 10-110 cm\(^{-1}\), 10-370 cm\(^{-1}\) and 50-700 cm\(^{-1}\). The source used was a globar.

A schematic of the Bomem FTIR is given in Figure 3.2. An off-axis ellipsoidal mirror located in the source chamber focuses the radiation on to an adjustable mechanical iris. After divergence the beam is collimated and made incident on the beam splitter to produce two coherent beams of equal intensity. One is directed toward a fixed mirror, while the other towards the moving mirror. Upon respective reflections these return to the beam splitter and the two superimposed, the interfering collimated beams being refocused to a 1:1 image of the iris. The sample is located at this image behind the polarizer. Both a stand-alone tungsten wire grid polarizer\(^1\) and a “pile-of-plates” polyethylene polarizer

---

\(^1\) Manufactured at the National Standards Laboratory of CSIRO; on loan.
Figure 3.2: Schematic of Bomem FTIR spectrometer.
[28] were used for 10-110 cm$^{-1}$ and 10-370 cm$^{-1}$ spectral regions respectively. The beam through the sample is collected by an IRL bolometer via a light pipe.

The sample cryostat was of stainless steel and was composed of a removable stress centre piece which has been described elsewhere [29]. The sample was compressed along its length using lead weights instead of pressurized gas [30]. The method for mounting the sample is also described elsewhere [31].

The signal from the detector was fed to a high speed vector processor where a filter function was automatically generated for a particular spectral range and suppressed the unwanted frequencies by numeric filtering, it also convolved the data with the Fourier transform.

### 3.3 Samples

For Zeeman studies, $B$ was applied across the width of a sample, for piezo-studies $F$ was applied along its length, the radiation propagated through the thickness of the samples, at right angles to either $B$ or $F$. Typical dimensions of Zeeman samples were approximately 19 mm long by 7 mm wide and 4 mm thick. A wire saw was used to cut the samples roughly to size. All samples were ground using 600 grit silicon carbide powder on a wet glass plate to remove the saw marks and then wedged approximately 230 $\mu$ in thickness along their lengths to eliminate transmission interference fringes. Sample faces were polished using 1$\mu$ alumina powder in a water solution. Some of the samples were oriented before grinding, while others had their orientation checked after preparation. For checking orientations, samples were etched for 5-7 minutes at $\sim$ 85°C with 30 wt
% hydrogen peroxide solution. Crystallographic orientations were checked using the optical technique of Hancock and Edelman [32], the lamp being replaced by a 1 mW He-Ne laser. The list of samples used in this work is given in Table 3.1. The energy absorbed by or reflected from a sample will depend upon the two optical constants, refractive index, n, and extinction coefficient, k, and the thickness of the sample. It has been shown by Fan [33] that in the absence of interference fringes, the transmission T can be written as

\[
T = \frac{I}{I_0} = \frac{(1 - R)^2 e^{-\alpha x}}{1 - R^2 e^{-2\alpha x}},
\]

(3.7a)

where

\[
I = \text{transmitted energy}
\]

\[
I_0 = \text{energy incident on the sample}
\]

\[
R = \text{reflectivity} = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]

\[
\alpha = \text{absorption coefficient} = \frac{4\pi k}{\lambda}
\]

\[
x = \text{sample thickness}
\]

\[
\lambda = \text{wavelength of measurement.}
\]

The above equation can be used to calculate the maximum transmission expected for the case where \(\alpha x = 0\) with the result that \(T_{\text{max}} = (1-R)/(1+R)\). \(T_{\text{max}}\) for Ge is \(~48\%\) around \(40\ \text{cm}^{-1}\). Sample spectra were divided by the background spectrum (spectrum taken without sample in the beam) to give transmission spectra. The presence of any fine surface scratches, or any obstructions produced by other plane parallel surfaces within the beam may affect \(T_{\text{max}}\), in that case the background of the percentage transmission spectra would be adjusted to give appropriate transmission. Of the spectra given in this thesis some are presented as transmission spectra, some are presented as absorption spectra.
Table 3.1. Samples used in this thesis work.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Direction of Perturbation</th>
<th>I(mm) ±0.02</th>
<th>w(mm) ±0.02</th>
<th>t(mm) ±0.02</th>
<th>Prepared by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(Zn;ZnH) 394A#1B</td>
<td>B∥&lt;110&gt;</td>
<td>18.75</td>
<td>5.88</td>
<td>1.25</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Zn;ZnH) 394A# 3.1</td>
<td>B∥&lt;100&gt;</td>
<td>19.00</td>
<td>7.14</td>
<td>4.04</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Zn;ZnH) 394A# 3.2</td>
<td>B∥&lt;111&gt;</td>
<td>19.06</td>
<td>6.83</td>
<td>3.69</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Zn;ZnH) 394A# 3.3</td>
<td>B∥&lt;110&gt;</td>
<td>18.91</td>
<td>6.89</td>
<td>3.67</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Zn;ZnH) 394A# 4.1</td>
<td>F∥&lt;111&gt;</td>
<td>20.09</td>
<td>4.21</td>
<td>4.03</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Zn;ZnH) 394A# 4.2</td>
<td>F∥&lt;100&gt;</td>
<td>19.21</td>
<td>4.12</td>
<td>3.76</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Mg;MgX)81-7DSR #2</td>
<td>B∥&lt;100&gt;</td>
<td>18.57</td>
<td>6.59</td>
<td>2.14</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Mg;MgX)81-7-23 #4</td>
<td>B∥&lt;100&gt;</td>
<td>18.75</td>
<td>6.70</td>
<td>2.05</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Mg;MgX)81-7-23 #3</td>
<td>B∥&lt;100&gt;</td>
<td>18.20</td>
<td>3.48</td>
<td>3.00</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Mg)81-7-27</td>
<td>B∥&lt;100&gt;</td>
<td>18.75</td>
<td>6.92</td>
<td>3.71</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Cu;CuX)81-7DSR</td>
<td>F∥&lt;100&gt;</td>
<td>18.99</td>
<td>7.11</td>
<td>3.32</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Cu;CuX)81-7-27</td>
<td>B∥&lt;111&gt;</td>
<td>18.40</td>
<td>6.37</td>
<td>3.43</td>
<td>J.P. Chelliah</td>
</tr>
<tr>
<td>Ge(Cu;CuX)422A(N₂)</td>
<td>B∥&lt;111&gt;</td>
<td>15.37</td>
<td>6.62</td>
<td>2.93</td>
<td>G.J.Takacs</td>
</tr>
<tr>
<td>Ge(Cu;CuX)422A(He)</td>
<td>B∥&lt;111&gt;</td>
<td>15.27</td>
<td>6.63</td>
<td>2.90</td>
<td>G.J.Takacs</td>
</tr>
<tr>
<td>Ge(Be)703#1</td>
<td>B∥&lt;100&gt;</td>
<td>19.19</td>
<td>7.98</td>
<td>3.1, 1.8, 1.15, 0.5, 0.30</td>
<td>J.P. Chelliah</td>
</tr>
</tbody>
</table>
To calculate absorption spectra, Equation 3.7a can be rearranged and solved for $\alpha$. The expression for $\alpha$ is given as

$$\alpha = -\frac{1}{x} \ln \left[ \frac{-(1 - R)^2 + \sqrt{(1 - R)^4 - 4R^2T^2}}{2R^2T} \right].$$

(3.7b)

The spectral line positions were determined by finding the peak position of the line or by using a Lorentzian fit to the line.
Chapter 4

Zeeman and Piezospectroscopy of ZnH in Germanium

4.1 Introduction

In addition to the monatomic substitutional acceptors in Ge, \textit{i.e.}, the groups IB, IIB and IIIA elements, a number of other neutral acceptor complexes have been identified [10, 11]. The recognition of these as distinct neutral acceptors is based on the observation that their Lyman series have line spacings which are identical to those of the elemental set but the lines occur at energies which are different. In particular, it has been demonstrated by Haller and co-workers [10, 11] that samples cut from Zn-doped ingots grown in a reducing atmosphere of hydrogen will give rise to spectral lines whose energy spacings and relative intensities are essentially the same as those characteristic of the lines exhibited by all neutral acceptors in Ge. Confirmation that these result from hydrogen secreted in the host has been made by driving-off the hydrogen \textit{via} an annealing process [10, 11]. It is important to understand the properties of isolated H in semiconductors since it can be either a donor or acceptor. Theoretical calculations shows that interstitial H both in Si and Ge is a deep donor [34, 35]. A number of axial defects in Si and Ge are of interest, particularly those which involve hydrogen as this element plays an important role in passivation of unwanted impurities in various semiconductors. For a review, see [36]. As an acceptor H behaves as a group VII element in accepting a second electron from a donor impurity to become H\(^{-}\) and removing one donor level from the band gap [37]. The other behaviour characteristic of H is the opposite of what was just described: H as a group I element compensates a single electron deficient site then becomes H\(^{+}\) which binds to a negatively charged acceptor. Because of the
electron donation it has been shown that for CuH the hydrogen moves the Cu levels closer to the valence band edge [38].

It has also been demonstrated that [10, 11]

1. The position of H when combined with Zn [39] (see Figure 4.1) is along any one of the four different <111> covalent bond directions of Ge.

2. Optical transitions take place in a time short compared with the tunneling time of the hydrogen atom in a complex from one <111> direction to another thus reducing the site symmetry of the defects from $T_d(O_h)$ [8], that of the monoatomic substitutional impurities, to $C_{3v}(D_{3d})$.

3. As a consequence of the above, the states $n\Gamma_8^\pm$ are reduced to $n\Gamma_4^\pm + (n\Gamma_5^\pm + n\Gamma_6^\pm)$ of $D_{3d}$, where $n = 1, 2, 3, \ldots$, to give two, two-dimensional manifolds $n\Gamma_4^\pm$ and $n\Gamma_5^\pm + n\Gamma_6^\pm \equiv n\Gamma_5^\pm$ (see Figure 4.1; the symmetry labels are those of Koster, et al.[8]). The site symmetries of the defect along <111> axes are reduced separately with respect to the direction of any applied perturbation leading to different selection rules (see Tables 4.1-4.7 and Figures 4.2-4.6) from those of group III impurities.

Spectra exhibited by samples cut from several Zn-doped Ge ingots [40], each exhibiting the C and D lines ascribed to the complex ZnH, were examined. In order to explore further the nature of these entities, detailed Zeeman studies using field strengths of up to 6.5 T, with the magnetic field, $B$, parallel to <100>, <111> and <110> crystallographic directions and piezo-studies with compressive force, $F$,
Figure 4.1: Energy states of group III and axial defects in Ge for $\mathbf{B} \parallel <100>$. 

Substitutional Point Defect-group III Acceptor

Substitutional Axial Defect-ZnH Acceptor
parallel to <100> and <111> directions, were carried out; the findings are presented here.

Table 4.1. Site symmetry of defects along <111> axes under perturbations.

<table>
<thead>
<tr>
<th>Perturbation Direction</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type 1\textsuperscript{a}</td>
</tr>
<tr>
<td>B[100]</td>
<td>[111]</td>
</tr>
<tr>
<td>B[111]</td>
<td>C\textsubscript{i}</td>
</tr>
<tr>
<td>B[110]</td>
<td>C\textsubscript{3i}</td>
</tr>
<tr>
<td>F[100]</td>
<td>C\textsubscript{2h}</td>
</tr>
<tr>
<td>F[111]</td>
<td>D\textsubscript{3d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} see also Figure 4.1

4.2 Unperturbed Spectra

The unperturbed optical absorption spectrum of a Ge sample containing Zn, cut from an ingot grown in an H-atmosphere, is shown in Figure 4.7. Here the full spectrum has been taken at an unapodised resolution, $\Delta \nu$, of 0.36 cm$^{-1}$ while that which is inset has been obtained with a $\Delta \nu = 0.073$ cm$^{-1}$. However, for this sample, the spectrum of the inset was unchanged at a resolution of 0.18 cm$^{-1}$. Both spectra have been obtained with the use of the modified polytec interferometer (See section 3.2.1.) with a He-cooled Si bolometer as detector. In the region beyond $\sim 225$ cm$^{-1}$ is seen the Lyman series of neutral zinc, Zn(0), [41] in which the G, D and C lines occur at $\sim 228.2$, $\sim 242.4$ and $\sim 248.6$ cm$^{-1}$, respectively. The feature at $\sim 225$ cm$^{-1}$ is not a lattice absorption and may be the D* transition from the
Figure 4.2: Selection rules for $\mathbf{B}||<100>$. 

Table 4.2: Equivalent Group III excited states used for labelling the Zeeman components of ZnH in Ge for $\mathbf{B}||<100>$. 

<table>
<thead>
<tr>
<th>Axial Defect</th>
<th>$\Gamma_{2,1}(C_i)$</th>
<th>$\Gamma_{2,2}(C_i)$</th>
<th>$\Gamma_{2,3}(C_i)$</th>
<th>$\Gamma_{2,4}(C_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group III</td>
<td>$\Gamma_8(C_{4h})$</td>
<td>$\Gamma_6(C_{4h})$</td>
<td>$\Gamma_7(C_{4h})$</td>
<td>$\Gamma_5(C_{4h})$</td>
</tr>
</tbody>
</table>
Figure 4.3: Selection rules for \( \mathbf{B} \parallel \langle 111 \rangle \).

Table 4.3: Equivalent Group III excited states used for labelling the Zeeman components of ZnH in Ge for \( \mathbf{B} \parallel \langle 111 \rangle \).

<table>
<thead>
<tr>
<th>Group III</th>
<th>( \Gamma_{-4} (C_3) )</th>
<th>( \Gamma_{-6,1} (C_3) )</th>
<th>( \Gamma_{-5} (C_3) )</th>
<th>( \Gamma_{-6,2} (C_3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial Defect (Type 1 axis)</td>
<td>( \Gamma_{-4} (C_3) )</td>
<td>( \Gamma_{-6,1} (C_3) )</td>
<td>( \Gamma_{-5} (C_3) )</td>
<td>( \Gamma_{-6,2} (C_3) )</td>
</tr>
<tr>
<td>Axial Defect (Types 2-4 axes)</td>
<td>( \Gamma_{-2,1} (C_1) )</td>
<td>( \Gamma_{-2,2} (C_1) )</td>
<td>( \Gamma_{-2,3} (C_1) )</td>
<td>( \Gamma_{-2,4} (C_1) )</td>
</tr>
</tbody>
</table>
Table 4.4: Selection rules for $\mathbf{B}||[111]$ for Type 1\textsuperscript{a} axis.

<table>
<thead>
<tr>
<th>$\Gamma^+<em>{6.1} (C</em>{3i})$</th>
<th>$\Gamma^-<em>{5} (C</em>{3i})$</th>
<th>$\Gamma^-<em>{4} (C</em>{3i})$</th>
<th>$\Gamma^-<em>{6.2} (C</em>{3i})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E\parallel B$</td>
<td>$E \perp B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma^+<em>{5} (C</em>{3i})$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
</tr>
<tr>
<td>$\Gamma^+<em>{4} (C</em>{3i})$</td>
<td>$E \perp B$</td>
<td>$E \perp B$</td>
<td>$E \parallel B$</td>
</tr>
<tr>
<td>$\Gamma^+<em>{6.2} (C</em>{3i})$</td>
<td>$E \parallel B$</td>
<td>$E \perp B$</td>
<td>$E \perp B$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Table 4.1.

For Types 2, 3 and 4 (see Table 4.1) all transitions are allowed for both polarizations.
Figure 4.4: Selection rules for $\mathbf{B}||<110>$. 

Table 4.5: Equivalent Group III excited states used for labelling the Zeeman components of ZnH in Ge for $\mathbf{B}||<110>$. 

<table>
<thead>
<tr>
<th>Group III</th>
<th>$\Gamma_{4.1}(C_{2h})$</th>
<th>$\Gamma_{3.1}(C_{2h})$</th>
<th>$\Gamma_{4.2}(C_{2h})$</th>
<th>$\Gamma_{3.2}(C_{2h})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial Defect (Types 1&amp;2 axes)</td>
<td>$\Gamma_{2.1}(C_1)$</td>
<td>$\Gamma_{2.2}(C_1)$</td>
<td>$\Gamma_{2.3}(C_1)$</td>
<td>$\Gamma_{2.4}(C_1)$</td>
</tr>
<tr>
<td>Axial Defect (Types 3 &amp;4 axes)</td>
<td>$\Gamma_{4.1}(C_{2h})$</td>
<td>$\Gamma_{3.1}(C_{2h})$</td>
<td>$\Gamma_{4.2}(C_{2h})$</td>
<td>$\Gamma_{3.2}(C_{2h})$</td>
</tr>
</tbody>
</table>
Table 4.6: Selection rules for $\mathbf{B}||[110]$ for Types 3 and 4 \textsuperscript{a} axes.

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma^{+}<em>{3.2} (C</em>{2h})$</th>
<th>$\Gamma^{-}<em>{4.2} (C</em>{2h})$</th>
<th>$\Gamma^{-}<em>{4.1} (C</em>{2h})$</th>
<th>$\Gamma^{-}<em>{3.1} (C</em>{2h})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^{+}<em>{3.2} (C</em>{2h})$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
</tr>
<tr>
<td>$\Gamma^{+}<em>{4.2} (C</em>{2h})$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
</tr>
<tr>
<td>$\Gamma^{+}<em>{4.1} (C</em>{2h})$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
</tr>
<tr>
<td>$\Gamma^{+}<em>{3.1} (C</em>{2h})$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
<td>$\mathbf{E}\perp \mathbf{B}$</td>
<td>$\mathbf{E}\parallel \mathbf{B}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Table 4.1.

For Types 1 and 2 \textsuperscript{a} axes (see Table 4.1) all transitions are allowed for both polarizations.
Group III Axial (F=0) Axial (F=<100>)

Figure 4.5: Selection rules for F||<100>.
Table 4.7: Selection rules for $\mathbf{F}||<111>$ for Type 1 axis.

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma_{4}(D_{3d})$</th>
<th>$\Gamma_{5+6}(D_{3d})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{4}^{+}(D_{3d})$</td>
<td>$\mathbf{E}</td>
<td></td>
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<tr>
<td>$\Gamma_{5+6}^{+}(D_{3d})$</td>
<td>$\mathbf{E} \perp \mathbf{B}$</td>
<td>$\mathbf{E}</td>
</tr>
</tbody>
</table>

$^a$See Table 4.1.

For Types 2, 3 and 4 (see Table 4.1) axes all transitions are allowed for both polarizations.
Figure 4.7: Spectrum of zinc-doped Ge containing ZnH complexes. The range 70-270 cm\(^{-1}\) illustrates the spectra of Zn\(^{(0)}\), ZnH and part of those of Al, Ga, P and As. The insert shows the details for the range 60-95 cm\(^{-1}\).
$\Gamma_3 + \Gamma_5$ ground state of Zn$^{(0)}$ [41]. At lower energies there are other features due to contamination by aluminium, gallium, arsenic and phosphorus. The arsenic and phosphorus lines are observable since band-gap radiation from the globar source is also incident on the sample. The two prominent features, designated as D(ZnH) and C(ZnH) occurring at $77.72 \pm 0.01$ cm$^{-1}$ and $83.77 \pm 0.01$ cm$^{-1}$, respectively, are those which have been attributed to ZnH [10, 11]. The asymmetric shape of these two lines is found to become more pronounced as the concentration of Zn increases. Their energy spacing, viz., $\sim 6.05$ cm$^{-1}$ is that which is characteristic of all known neutral acceptors in Ge [7].

4.3 Zeeman spectra and discussion for $B \parallel <100>$

The Zeeman spectra of the C and D lines of ZnH for $B \parallel <100>$ at 0.5T are shown in Figure 4.8 while those of the D line at 2.5 T, 3.0T, 3.5 T, 4.5 T and 6.0 T are given in Figures 4.9 to 4.11, respectively. The Voigt configuration has been used with the radiation plane-polarized either parallel ($E_\parallel$) or perpendicular ($E_\perp$) to $B$; here $E$ is the electric field of the far infrared radiation. Figures 4.12 and 4.13 give an overview of all these spectra for $E_\perp B$ and $E_\parallel B$, respectively. The dependence of the energies of the D components on $B$ ($B = |B|$) is given in Figure 4.14, where the curves are polynomial fits to the data. In the cases where a component is observed for both polarizations, the same order of polynomial is used for the two polarizations. For all the data presented in this work, the dashed curves are the results for $E_\parallel$ while the full ones are for $E_\perp$. The Zeeman components in Figure 4.8 have been labelled in accordance with those observed between 3 and 3.5 T (See Figures 4.9 and 4.10); the detailed meaning of these labels will be given later. In
Figure 4.8: D and C lines of ZnH at 0.5 T. Unapodised resolution is 0.18 cm$^{-1}$. 
Ge(Zn; ZnH) 394A#3.1
B||<100>; 3.0 T

\[ \begin{align*}
\text{E} & \perp \text{B} \\
\text{E} & \parallel \text{B}
\end{align*} \]

\[ T = 3.3 \text{ K} \]

Figure 4.9: D line of ZnH at 3.0 T. Unapodised resolution is 0.18 cm\(^{-1}\).
Ge(Zn; ZnH) 394A#3.1
B∥<100>; 3.5 T

- - - E∥B
- - E⊥B

T = 3.3 K

Figure 4.10: D line of ZnH at 3.5 T. Unapodised resolution is 0.18 cm⁻¹.
Ge(Zn; ZnH) 394A#3.1
B∥<100>; 6.0 T
-- E⊥B
--- E∥B

T = 3.4 K

Figure 4.11: D line of ZnH at 6.0 T. Unapodised resolution is 0.18 cm⁻¹.
Figure 4.12: Magnetic field dependence of $E \parallel B$ of ZnH in Ge for $B < 100 \rangle$. 
Figure 4.13: Magnetic field dependence of $E \parallel B$ of ZnH in Ge for $B<100>$. 
Figure 4.14: Magnetic field dependence of the Zeeman components of the D-line of ZnH in Ge.
identifying the components of ZnH care was necessary in identifying the Zeeman components of the weak C and D lines of the contaminants Al and Ga [42, 43]; one such component is labelled in Figure 4.10. At lower fields, where \(D_3 = (2.2,6)\) and \(D_4 = (2.1,6)\) are not resolved, the relative intensities of these two components at fields where they are resolved are taken into account in assigning the component. Thus, for fields below 3 T the data points for the compound component \(D_3 + D_4 = (2.2,6) + (2.1,6)\) (see Figure 4.14) for \(E_\perp\) is taken to give the energy of the \(D_4 = (2.1,6)\) component in making the fit, whereas for \(E_\parallel\) this compound component is expected to have an energy which is close to the average of the two unresolved components. In this case, the low field data is not used in making either of the two fits. It should be noted that \(D_3 = (2.2,6)\) occurs in both polarizations (see Figure 4.14) and the two fits coincide.

First, the spectra obtained for \(B < 2T\) are essentially identical to those obtained for the C and D lines of group III impurities [42, 43]; both the energy spacings of the components and their relative intensities are almost the same as may be noted by comparison of Figure 4.8 with the results for boron shown in Figure 3 of [42]. Secondly, the serpentine behaviour of several of the components in Figure 4.14 for \(B > 2T\) is the same as that exhibited by some of the D components of group III impurities in Ge [43]. For the latter, this is due to the behaviour of one of the Zeeman states into which the excited state of the D line splits [23, 24, 43]. Thirdly, with the final state, it is found that, at all fields, the splittings of the groups of components "8", "6", "5" and "7" (see Figure 4.14) of D(ZnH) are identical to those observed for the Zeeman components of the D lines of group III impurities; this result is illustrated in Figure 4.15. In this figure, the upper two sets of data points are the splittings obtained from the ZnH components, while the curves
Figure 4.15: Splittings of the Zeeman states of the excited and ground states of the D line of ZnH in Ge. For the excited state (upper two sets of data), the points are those obtained from the observed Zeeman spectra of ZnH, while the curves are fits to the corresponding splittings of the excited states of the D lines of B and Ga in Ge. For the ground state (lowest set of data), the points are from the spectra of ZnH while the dot-dashed line is a linear least squares fit to the experimental data. The meaning of $D_{2,1}$ and $D_{2,2}$ is given in the text.
associated with these points are fits to the splittings of the $\pm 1/2$ and $\pm 3/2$ states of the unperturbed $2\Gamma_8^-$ state of gallium and boron for this orientation of $B$ [43].

Fourthly, a large number of the components, viz., $D_3$ to $D_7$, i.e., $(2.2,6)$ to $(2.1,7)$ are unpolarised at all fields which is not the case for the group III impurities.

Finally, the selection rules for the Zeeman components of the D line of the latter impurities permit only four components for $E_\parallel$, whereas six are observed for ZnH.

In view of the latter point, any attempt to analyse the results for the D line of ZnH as the transition $1\Gamma_8^+ \Rightarrow 2\Gamma_8^-$, which gives rise to the D line of the group III acceptors under $O_h$ symmetry, fails. The explanation for the observation of more than four D components for the $E_\parallel$ polarization requires the ground state to be different to that of the group III impurities since it is clear from the above that the behaviour of the excited state is identical to that of these shallow acceptors.

The results can be understood using the model proposed for ZnH [10,11] and described earlier. Upon the application of $B||<100>$, all site symmetries are reduced to $C_1(C_i)$ (see Table 4.1) and the two Kramers’ states, $\Gamma_4(\Gamma_4^\pm)$ and $\Gamma_{5+6}(\Gamma_{5+6}^\pm)$ of $C_{3v}(D_{3d})$, are each split into pairs of Zeeman states all of which belong to $\Gamma_2(\Gamma_2^\pm)$. If the unperturbed upper ‘ground state’, proposed in the model to be $\Gamma_4(\Gamma_4^\pm)$ is not populated in the present measurements then only the lower one, $\Gamma_{5+6}(\Gamma_{5+6}^\pm)$, produces the observed spectra. Since the induced electric dipole has $\Gamma_1(\Gamma_1^-)$ symmetry for both $E_\parallel$ and $E_\perp$ under the above model, and $\Gamma_2^* \times \Gamma_1 \times \Gamma_2 = \Gamma_1$ (or $\Gamma_2^- \times \Gamma_1^- \times \Gamma_2^+ = \Gamma_1^+$), then all of the eight possible transitions are allowed for each polarization.
The Zeeman splitting of the doublet ground state is obtained from the spacings of $D_\ell$ and $D_u$, where $\ell = u+1$ and $u = 1,3,5,7$. Here the series of four components $D_\ell$ arises from the lower Zeeman ground state while the set $D_u$ originate from the upper. In the following, the symmetry of the lower Zeeman state of $\Gamma_{5+6}^+$ is designated as $\Gamma_{2.1}(\Gamma_{2.1}^+)$ and that of the upper as $\Gamma_{2.2}(\Gamma_{2.2}^+)$. The splitting of the ground state with $B$ is shown in Figure 4.15 as the lowest set of data points; the line through these is the result of a linear least squares fit.

The model also proposes that, unlike the ground state, the splitting of the excited state due to the axial nature of the defect is negligible, i.e., the $\Gamma_4(\Gamma_4^-)$ and $\Gamma_{5+6}(\Gamma_{5+6}^-)$ excited states are essentially degenerate, since these p-like states are not sensitive to the contents of the central cell of the defect. Thus under $B$, the four Zeeman excited states will behave in a way which is independent of the nature of the negatively charged centre. The Zeeman behaviour of such a state is that of the $2\Gamma_8^-$ state of the group III acceptors [23, 24, 43]. Thus, the four $\Gamma_2(\Gamma_2^-)$ Zeeman excited states of the D line have been labeled in order of increasing hole energy (at low fields) as $2\Gamma_8^-$, $2\Gamma_6^-$, $2\Gamma_5^-$ and $2\Gamma_7^-$, the notation for group III point defect, for $B||<100>$ (see Figure 4.14) Thus, the components in all appropriate figures are labeled as the transitions $(i,f)$, where $i = 2.1$, 2.2 and $f = 5$, 6, 7, 8. It should be noted that for $B||<100>$, the upper "axial" ground state, $1\Gamma_4^+(D_{3d})$, is also decomposed into two $\Gamma_2^+(C_1)$ states. Thus, the selection rules alone are not sufficient to legislate which of the two "axial" ground states is the lower.
4.4 Zeeman spectra and discussion for B \parallel <111>

A detailed study has also been made of the behaviour of the D line of ZnH for B\parallel <111>. The effect of B\parallel <111> on part of the spectrum of ZnH in Ge is shown in Figures 4.16-4.18 at fields of 0.5 T, 3.5 T and 6.5 T, respectively. Again the Voigt configuration has been used. The meaning of the labeling of the Zeeman component in these figure is discussed later. Figure 4.19 and 4.20 show all the observed spectra for collectively E_\perp and E_\parallel, respectively. The dependence of the energies of the components on B for fields up to 6.5 T is given in Figure 4.21, where the curves are fits to the data. At all fields below \sim 1.5 T, the Zeeman spectra are identical to those of any one of the five group III acceptors [44]. At fields above this, again like those of group III, the low field Zeeman components of ZnH split into several components. However, unlike the group III spectra, many of the ZnH components have the same energy in both polarizations; this is strictly forbidden by selection rules for the group III elements as was the case for B\parallel <100> [22].

In this case, those defects with axes along B will behave differently from those along the other three <111> directions. The site symmetry of the former reduces from C_{3v}(D_{3d}) to C_{3}(C_{3i}) (Type 1), while the other three have C_{1}(C_{i}) (Types 2-4) symmetry. For impurities of the second type, the selection rules again permit eight unpolarised components while for the other the components are polarised, there being four for each polarization. Thus, overall, twelve components are permitted for each polarization with eight in coincidence for the two directions of polarization permitting a total of sixteen components. Experimentally, a total of twelve components are observed at the higher fields.
Figure 4.16: D and C line of ZnH at 0.5 T. Unapodised resolution is 0.18 cm⁻¹.
Figure 4.17: D line of ZnH at 3.5 T. Unapodised resolution is 0.18 cm\(^{-1}\).
Figure 4.18: D line of ZnH at 6.5 T. Unapodised resolution is 0.18 cm$^{-1}$. 

Ge(Zn; ZnH) 394A#3.2
B∥<111>; 6.5 T
--- E∥B
----- E∥B

T = 4.0 K

Absorption coefficient (cm$^{-1}$)

Photon energy (cm$^{-1}$)
Figure 4.19: Magnetic field dependence of $E_{LB}$ of ZnH in Ge for $B<111>$. 
Figure 4.20: Magnetic field dependence of $E || B$ of ZnH in Ge for $B < 111 >$. 
Figure 4.21: Magnetic field dependence of the Zeeman components of the D-line of ZnH in Ge.
On examination of the data in Figure 4.21, it is noted that the energy spacings between the four groups of components labelled 4, 6.1, 5 and 6.2 are essentially the same as those of the four Zeeman excited states of the $2\Gamma_{8}^{\pm}$ [23, 24, 44] state of group III acceptors for $\mathbf{B}|<111>$. This is the final state of the D line of these impurities. The symmetry labels for these four Zeeman states for $B \geq 1 \, T$ are $2\Gamma_{4}^{-}, 2\Gamma_{6.1}^{-}, 2\Gamma_{5}^{-}$ and $2\Gamma_{6.2}^{-}$ in increasing hole energy; below these fields the first two have their order reversed [23, 24]. These labels are those of the irreducible representations of $\overline{C}_{3i}$, the subgroup of $\overline{O}_{h}$ whose elements are common to the latter and to the group of $\mathbf{B}$ [23, 24]. In detail, it is found that the energy spacings of particular components in two different sets of components are identical to corresponding splittings of the $2\Gamma_{8}^{-}$ state of the group III impurities. This is the origin of the second index in the parenthetical labeling of the ZnH components in all figures. The remaining characteristics of the ZnH spectra can be understood using the model already proposed [10, 11] for this complex and seen to be successful in explaining the Zeeman measurements with $\mathbf{B}|<100>$ [12].

As was assumed in the case of $\mathbf{B}|<100>$, the observed spectral features are taken to have the ground state of $1\Gamma_{5+6}^{+}$ symmetry as their initial state. For $\mathbf{B}|<111>$, the defects of Type 1 (see Table 4.1) have their symmetry reduced from $D_{3d}$ to $C_{3i}$ which causes $1\Gamma_{5+6}^{+}$ to decompose into two $\Gamma_{6}^{+}$ states which will be labeled $1\Gamma_{6.1}^{+}$ and $1\Gamma_{6.2}^{+}$. The $\Gamma_{4}^{-} + \Gamma_{5+6}^{-}$ excited states become $\Gamma_{4}^{-} + \Gamma_{5}^{-} + 2\Gamma_{6}^{-}$; again the two $\Gamma_{6}^{-}$ states will be labelled 6.1 and 6.2. It can be shown that the allowed transitions for the Type 1 complexes are $\Gamma_{6} \rightarrow \Gamma_{6}$ for $E_{\parallel}$ and $\Gamma_{6} \rightarrow \Gamma_{4,5}$ for $E_{\perp}$. Thus four transitions are allowed for both polarizations and, for finite Zeeman splittings of the ground state, all have different energies. For this direction of $\mathbf{B}$, complexes of the Types 2, 3 and 4 (also, see Table 4.1) have their symmetry reduced to $C_{i}$ and all
manifolds decompose into $\Gamma_2$ states. All transitions are now allowed leading to eight different unpolarised pairs. It might be noted that the $1\Gamma_4^+$ state, resulting from the axial nature of the complex, reduces to $1\Gamma_4^+ + 1\Gamma_5^+$ under $C_{3i}$ and to two $\Gamma_2$ states under $C_i$. For Type 1 complexes only two transitions are allowed for $E_\parallel$ while six are permitted for $E_\perp$, the two $E_\parallel$ components having no partners in the $E_\perp$ set. The selection rules for Types 2, 3 and 4 complexes are the same as for the $1\Gamma_5^+ + \Gamma_6^+$ state.

For negligible splittings of the p-like excited states of this axial defect, their behaviour under $B$ will be indistinguishable from that of the corresponding group III states. Thus the Zeeman states of $2\Gamma_8^-$ have been labelled 4, 6.1, 5, and 6.2 for all four types of complexes. As stated above, the splittings of the excited states of the D lines of ZnH and the group III acceptors are the same; this is illustrated in Figure 4.22. In this figure the upper two sets of data points are the experiment splittings of the excited states of the D-line of ZnH while the curves associated with these data are fits to the corresponding splittings obtained experimentally for boron and gallium in Ge. In particular, the larger of these two splittings is that of $\Gamma_{6,1}^-$ and $\Gamma_{6,2}^-$, the $\pm 3/2$ Zeeman states, while the other is for that of $\Gamma_4^-$ and $\Gamma_5^-$, the $\pm 1/2$ states; here the magnetic quantum numbers are those of Ref 22.

A detailed analysis of the data gives an energy level diagram that is consistent with all observed transitions, the selection rules and the two Zeeman ground states associated with both Type 1 and Types 2, 3 and 4 axial complexes. It should be noted that if the unperturbed $1\Gamma_4^+$ ground state were lower in energy than the $1\Gamma_5^+ + \Gamma_6^+$ state then no $E_\parallel$ components associated with the $2\Gamma_{6,1}^-$ and $2\Gamma_{6,2}^-$ final states would be observed contrary to the experimental results. The labeling of the transitions in figures is based on the latter being the original of all transitions at the temperatures
Figure 4.22: Splittings of the excited state of the D line of ZnH (upper two sets of data points) and that of B and Ga (upper two curves) in Ge for $B||[111]$. The lower sets of data and the fits to these are those for type 1 and types 2 to 4 complexes under this field direction (see text).
used. The first index in these labels designates the initial Zeeman state. For example, the $E_\parallel$ transition labeled (6.2, 6.1) arises from the lower Zeeman state $1\Gamma^+_{6.2}$ of Type 1 complex and terminates on the $2\Gamma^-_{6.1}$ excited Zeeman state. The splittings of the ground states for $B_\parallel<111>$ are also given in Figures 4.22. These are the two lower curves and, in these cases, the lines through the data points are fits to these.

It needs to be pointed out that for $B_\parallel<111>$, at $B \approx 5$ T, a strong interaction occurs between the $2\Gamma^-_{6.2}$ Zeeman state of group III acceptors and higher lying states of the same symmetry [23, 24, 44]. This same effect is observed for ZnH with the mixings occurring in the range $\approx 4.75$ to $\approx 5.75$ T. No details of this are given here; the fits shown in Figure 4.21 for the 6.2 set of components ignores this hybridization as does the labeling of the component at $\approx 86$ cm$^{-1}$ in Figure 4.18. For this reason, in Figure 4.22, the splitting of the $\pm 3/2$ states, $2\Gamma^-_{6.1}$ and $2\Gamma^-_{6.2}$, has not been shown beyond 4.5 T for either ZnH or the group III acceptors.

4.5 Zeeman spectra and discussion for $B_\parallel<110>$

Samples Ge(Zn, ZnH)394A#1B and Ge(Zn, ZnH)394A #3.3 were used to study the Zeeman behaviour for $B_\parallel[110]$. Sample Ge(Zn, ZnH)394A#1B was prepared from the bottom of the ingot and the spectral lines of ZnH exhibited high impurity concentration broadening effects [3] compared to the other sample, which was from the middle of the ingot. Spectra have been recorded with polarised light in the Voigt geometry for the applied magnetic fields from 0.5 Tesla up to 6.0 T. The Zeeman spectra of the D line for 0.5 T, 3.5 T and 6.0 T are shown in Figures 4.23-4.25.
Figure 4.23: D and C lines of ZnH at 0.5 T. Unapodised resolution is 0.18 cm$^{-1}$. 

Ge(Zn; ZnH) 394A#1B 
B|$<110>$; 0.5 T 
--- E|$\perp$B 
... E|$\parallel$B 

T = 2.7 K
\textbf{Ge(Zn; ZnH) 394A#3.3}
\textbf{B∥<110>; 6.0 T}
\begin{itemize}
  \item \textbf{E⊥B}
  \item \textbf{E∥B}
\end{itemize}
\textbf{T ≈ 3.8 K}

Figure 4.25: D line of ZnH at 6.0 T. Unapodised resolution is 0.18 cm$^{-1}$. 
The full curves are for $E_\perp$ while the dashed curves are for $E_\parallel$. All the $E_\parallel$ and $E_\perp$ components of the samples Ge$(\text{Zn}, \text{ZnH})394\text{A#3.3}$ and Ge$(\text{Zn}, \text{ZnH})394\text{A #1B}$ for various magnetic field are shown in Figures 4.26-4.29, respectively. The labelling of the components is as before with the details given below. The dependence of the energies on $B$ is given in Figure 4.30.

For $B\parallel [110]$, the symmetry $D_{3d}$ is reduced to $C_i$ for Types 1 and 2 defects, while for Types 3 and 4 the reduction is to $C_{2h}$. The selection rules for $C_{2h}$ and $C_i$ symmetries are shown in Figure 4.4 and Table 4.4. At low fields, particularly for $B \leq 1$ Tesla, the Zeeman spectra are essentially identical to those of group III impurities in Ge [45]. For larger fields, the components split into several components like those of the group III impurities in Ge. Selection rules for group III acceptors for $B\parallel<110>$ permit eight components for each polarization with different energy values for a given $B$, but for Ge$(\text{ZnH})$ six perpendicular and nine parallel components are observed, among these five components appeared with the same energy for both polarizations. For this direction of $B$, $1\Gamma_{5+6}^+$ states of defects of the Types 1 and 2 decompose into $1\Gamma_{4,1}^+$ and $1\Gamma_{3,2}^+$ under $C_{2h}$ symmetry. The selection rules permit four components for both polarizations all with different energies. For Types 1 and 2, $1\Gamma_{5+6}^+$ of $D_{3d}$ decomposes into two $1\Gamma_2^+$ states $1\Gamma_{2.1}^+$ and $1\Gamma_{2.2}^+$ with $C_i$ symmetry; the selection rules permit eight components for both polarizations with each component being allowed.

Proceeding as for the previous two directions of $B$, in Figure 4.30 it is noted that the D components are grouped into four distinct sets. The spacings of these are those of the Zeeman states of the $2\Gamma_8^-$ level of the group III acceptor, Al, in Ge [45], thus the sets have been designated by the symmetry labels of the Zeeman
Figure 4.26: Magnetic field dependence of $E||B$ of Ge(ZnH)394A#3.3 for $B<110>$. 
Figure 4.27: Magnetic field dependence of $E_{1B}$ of Ge(ZnH)$_3$ for $B<$110$>$. 
Figure 4.28: Magnetic field dependence of $\mathbf{E} \parallel \mathbf{B}$ of Ge(ZnH)$_3$ for $\mathbf{B} \parallel <110>$. 
Figure 4.29: Magnetic field dependence of $\mathbf{E} \perp \mathbf{B}$ of Ge(ZnH)394A#1B.
Figure 4.30: Magnetic field dependence of the Zeeman components of the D-line of ZnH in Ge.
levels of this group III state. The splittings of ZnH and Al are compared quantitatively in Figure 4.31, where the upper two sets of data are those for ZnH while the two smooth curves associated with these data are the splittings of the ± 1/2 states (upper curve) and the ± 3/2 states (lower curve) for $2\Gamma_8^-$ of Al. The actual labels for the excited Zeeman states of ZnH of the D-line are $2\Gamma_{4.1}$, $2\Gamma_{3.1}$, $2\Gamma_{4.2}$, $2\Gamma_{3.2}$ for $\overline{C}_2h$ symmetry (Types 1 and 2) and $2\Gamma_{2.1}$, $2\Gamma_{2.2}$, $2\Gamma_{2.3}$, $2\Gamma_{2.4}$ for $\overline{C}_1$ symmetry (Types 3 and 4). As in the case for $B\parallel<100>$ and $B\parallel<111>$, the labels of the group III Zeeman states of $2\Gamma_8^-$ are used as the second index in the parenthetical labeling of the ZnH components. Thus it is seen that each of the four groups of transitions in Figure 4.30 correspond to excitations from the Zeeman levels of the split ground states of $\overline{C}_2h$ and $\overline{C}_1$ symmetries to one of the Zeeman states of the split excited states.

Care was necessary to eliminate the Zeeman components of the weak C lines of Ga. One such $E_\perp$ component is identified in Figure 4.25. Identification of the initial states of the D components has been made by applying the selection rules and comparing the energy spacings of components with common excited states. This analysis provides the first of the two indices in the labels of the components. Thus, it is seen that transitions from both Zeeman states of Types 3 and 4 defects are observed while only those from the $1\Gamma_{3.1}^+$ states of Types 1 and 2 are detected. The dependence on $B$ of the splitting of the $1\Gamma_{2.1}^+$ and $1\Gamma_{2.2}^+$ states is given in Figure 4.31. The line is a linear least squares fit to these data.
Figure 4.31: Splittings of the excited state of the D line of ZnH and Al in Ge for $B\parallel<110>$. The lower sets of data and the fit to the Types 1 and 2 complexes under this field direction.
4.6 Piezospectroscopy of ZnH in Germanium for \( F\parallel<100> \)

Previous piezospectroscopic studies on this complex were carried out using unpolarized radiation [10, 11] while the experimental results for a uniaxial force, \( F \), along \(<100>\) were not presented in detail anywhere. Infrared absorption measurements for \( F\parallel<100> \) and \( F\parallel<111> \), using polarized radiation are presented here for \( F \) compressive. Figure 4.32 shows a series of such spectra for the \( C \) and \( D \) lines at different compressive stresses with \( F\parallel<100> \); the full curves are for \( \mathbf{E}\perp \mathbf{F} \) while the dashed curves are for \( \mathbf{E}\parallel \mathbf{F} \). The experimental technique for these observations has been presented in Chapter 3; the Bomem instrument was used. The stress dependence of the \( D \) components is shown in Figure 4.33.

Using the model of ZnH which was successful in explaining the Zeeman data, the symmetry of all four types of defects is reduced from \( \overline{C}_{3v} (\overline{D}_{3d}) \) to \( \overline{C}_s (\overline{C}_{2h}) \), which decomposes the representations \( \Gamma^\pm_{5+6} \) into \( \Gamma^\pm_{3+4} \) with each type being effected in the same manner. All observed transitions originate from the \( 1\Gamma^+_{5+6} \) ground state as established from the results for \( B\parallel<111> \). Noting that this is a Kramers' doublet while the excited state consists of two Kramers' doublets, the selection rules allow two transitions for both polarizations. Thus, two \( D \) components should be observed in both polarization. Experimentally this is what is detected as can be seen in Figure 4.32. The spacing of these two components directly gives the stress dependence of the splitting, \( \Delta_{100}^D \), of the excited state; this is shown in Figure 4.34. The slope of the straight line fit to this splitting yields a value for \( b_D \) (see Equation 2.12 in Chapter 2) of \( 0.55\pm0.01 \) eV, which is to be compared with that of \( 0.53\pm0.03 \) eV obtained for the \( 2\Gamma^-_8 \) state of Ga in Ge [46].
Figure 4.32: Piezo-spectra of the C and D lines of ZnH in Ge for \( F\parallel<100> \) at an unapodised resolution of 0.22 cm\(^{-1}\).
Figure 4.33: Stress dependence of D line of ZnH in Ge for $\mathbf{F} || <100>$. 
Figure 4.34: Splitting of the excited state of the D line of ZnH in Ge for $\mathbf{F}||<100>$. 
4.7 Piezospectroscopy of ZnH in Germanium for $F||<111>$

Sample Ge(Zn, ZnH)394A#4.1 has been used to study the effect of $F||<111>$ on the spectrum of ZnH. The results obtained for the C and D lines are illustrated in the spectra of Figures 4.35 and 4.36 for $E||F$ and $F \perp F$. Again, the dashed curves are for the former and the full curves are for the latter. Two of the panels of Figures 4.35 and 4.36 are shown on a larger scale in Figure 4.37 and 4.38. These are the results at 9.1 and 31.3 Mpa, respectively and shown the detailed labeling of the components. The energies of the D components as a function of $S$ are given in Figure 4.39. The energies of the C components have not been given, however, in Figures 4.35 and 4.36, it is seen that with increasing stress the low energy C component for $E \perp F$ splits into $C_1$ and $C_2$. At high stresses, these overlap the high energy D components with $C_1$ crossing the latter; see also Figure 4.38. The curves through the data in Figure 4.39 are polynomial least squares fits, although these are not truly representative for $D_3$ and $D_4$ since these are not resolved in either polarization for $S$ below ~23 Mpa. An inspection of Figure 4.38 suggests that it is this which causes the upper two curves in Figure 4.39 to be closer together than is the case for the lower two since for the latter, $D_1(||)$ and $D_2(\perp)$ are single components. At the higher stresses the energies of the shoulders to $D_3(\perp)$ and $D_4(||)$ labeled $D_4(\perp)$ and $D_3(||)$, respectively. (see Figure 4.38), have not been determined and hence are not included as data points in Figure 4.39.

The data for the D components can be understood from the selection rules of Figure 4.6 as applied to the $<111>$ axial defect model of ZnH. With $1Gamma_{5+6}^+$ as the lower ground state and the behaviour of the excited state to be that of a group III acceptor $D_1(||)$ and $D_1(\perp)$ are the two allowed transitions from defects with Type 1
Figure 4.35: Spectra of ZnH in Ge, at a resolution of 0.22 cm$^{-1}$. 
Figure 4.36: Continuation of previous figure.
Figure 4.37: D line of ZnH at 9.110 Mpa. Unapodised resolution is 0.22 cm\(^{-1}\).
Figure 4.38: D and C lines of ZnH at 31.339 Mpa. Unapodised resolution is 0.22 cm$^{-1}$. 
Ge(Zn; ZnH)394A#4.1
F||[111]
 Orbit labels:
• E^⊥F
• E||F

Figure 4.39: Stress dependence of D line of ZnH in Ge for F||<111>.
orientation, viz., axes parallel to $F$, while $D_3$ and $D_4$, which occur in both polarizations (see Figure 4.38), are those allowed from ground states of Types 2, 3 and 4. The asymmetry in the shift of the ground state of Type 1 defect relative to those of Type 2, 3 and 4 illustrates that the former needs to shift with $S$ at 3 times the rate of the latter if the "centre of gravity" is to be maintained. It is also noted that $D_1$ and $D_2$ are significantly weaker than $D_3 + D_4$ for the two polarizations. This is to be expected if the matrix elements between the excited states and the two ground state types are comparable since there are three times as many defects of Types 2, 3 and 4 than Type 1. This has been noted in the original report on the piezospectra of ZnH [10, 11].

In Figure 4.6, it can be seen that if the $1\Gamma_4^+$ state were lower than the $1\Gamma_{5+6}^+$ state the lowest energy transition would be for $E_\perp$ rather than $E_\parallel$ as is observed thus confirming the conclusion reached from the $B_{||<111>}$ data that $1\Gamma_{5+6}^+$ is the lower. This illustrates the advantage of using polarized radiation for these studies. Figure 4.40 shows the stress components of the D line as observed with unpolarized radiation. Clearly the details of the behaviour of the four states involved cannot be extracted from such data. In particular the stress dependence of the excited state cannot be determined. Although small, the deformation potential constant, $b_D$, of the $2\Gamma_5^-$ state of group III acceptors in Ge is not zero [47, 48] but similar to that of Zn in Ge [49]. In addition, significant interaction between the stress induced state $2\Gamma_{5+6}^-$ of $2\Gamma_8^-$ and those of other levels produces behaviour similar to that exhibited by other single hole acceptors in Ge. This is clearly seen in Figures 4.39 and 4.41. The latter figure shows the dependence on $S$ of the splitting of the final state of the D line of ZnH as determined from the difference in energy of $D_1(\parallel)$ and $D_2(\perp)$. The linear term in the polynomial fit to this data (see Figure 4.41) yields a value for $d_D$
Figure 4.40: Stress dependence of D line of ZnH in Ge for F|[111] with unpolarised radiation.
Figure 4.41: Splittings of the excited state of the D line of Zn$^-$ and ZnH in Ge for $\mathbf{F} \parallel <111>$. 
of 0.65± 0.02 eV, which is to be compared with that of ~ 0.06 eV for Ga in Ge and for Zn in Ge. It is not clear why these are so different.

4.8 Conclusion

Zeeman and piezo spectroscopy have been performed on Ge(ZnH) to analyse the nature of its ground state. Analysis confirmed that ZnH is a single acceptor has trigonal symmetry $C_{3v}(D_{3d})$. It was found that the behaviour of the excited state, $2\Gamma_4^- + 2\Gamma_5^{+6}$, is essentially identical to that of $2\Gamma_8^-$ the group III impurities in Ge. The symmetry reduction resulting from the presence of H splits the ground state $1\Gamma_8^+$ into two two-fold states, $1\Gamma_4^+(D_{3d})$ and $1\Gamma_5^{+6}(D_{3d})$. Observations for both B and F parallel to <111>, using polarized radiation, confirm that the $1\Gamma_5^{+6}(D_{3d})$ state is the lower of these two.
Chapter 5  Other Axial Defects in Ge

5.1  Introduction

In intrinsic Ge, acceptors can be introduced as substitutional impurities [3], complexes [10-13, 38, 50, 51], or dislocations [52, 53]. The diffusion of known impurities such as Cu, Mg, etc., into Ge, followed by quenching, introduces a variety of unknown defects [54] of which many can be detected by observing their far infrared Lyman spectra; some exhibit classic neutral acceptor spectra, others do not [14, 54, 55]. Three defects which have D lines [7] of energies 101.52, 163.71 and 225.21 cm\(^{-1}\) have been examined in this work. The first two are named as MgX\(_1\) and MgX\(_2\), respectively, since they appear when Mg is diffused. Here the D and C lines of MgX\(_1\) are those designated as lines 3 and 4, respectively, in Figure 7 of [54]. The spectrum of MgX\(_2\) has not been reported before while for the third, named CuX [14, 55], Zeeman results for \(\mathbf{B}||\langle100\rangle\) have been presented elsewhere, the interpretation of which was uncertain [14]. The purpose of the present studies is to determine the types of centres giving these spectra.

5.2  Spectra of MgX\(_1\) in Ge

5.2.1  Unperturbed Spectrum

Two samples have been used to study the D line of MgX\(_1\) in Ge. A modification of the procedure of [56] was adopted for diffusing the magnesium. A sandwich
was made of the sample with 130 μMg foil inserted between it and its two covers; this replaced the evaporated Mg coating described in [56]. The centre of the sandwich was the sample, originally intrinsic Ge, to be diffused while the two outer covers consisted of two other pieces of intrinsic Ge. Nylon thread was used to bind the covers, magnesium foils and Ge crystals together. This sandwich was encapsulated in an evacuated fused quartz ampoule and then heated at 850° C for about 48 hours after which it was quenched by dropping the capsule into a dewar of liquid nitrogen. The main Ge crystal was designated as Ge(Mg;MgX₁)81-7-23DSR #4 while one of the covers was labelled as Ge(Mg;MgX₁)81-7-23DSR #3.

The unperturbed optical absorption spectrum of the Ge(Mg; MgX₁)81-7-23DSR #4 sample is shown in Figure 5.1. Here the spectrum has been taken at an unapodised resolution, Δν, of 0.07 cm⁻¹ with the use of the Polytec FTIR spectrometer previously described in Chapter 3.2.1. In the range 60-100 cm⁻¹ the D, C and B lines of Ga along with two unknown features at 86.45 and 92.56 cm⁻¹ appear which have the D-C energy spacing. Beyond ~100 cm⁻¹ is seen the Lyman series of MgX₁ in which the D, C and B lines occur at 101.52 and 107.59 cm⁻¹ and 112.62 cm⁻¹, respectively. Some lines which have been reported in Ref [48] as 7 and 8 are also seen at 152 cm⁻¹ and 158.5 cm⁻¹, respectively. At higher energies D and C of Zn(⁰) are observed at 242.70 cm⁻¹ and 248.82 cm⁻¹, respectively. The G, D, C, and B lines of Mg(⁰) appear 251.87, 265.75, 271.77 and 277.02 cm⁻¹, respectively.
Figure 5.1: Spectrum of Ge containing MgX₁ complex. The insert shows the details for the range 95-115 cm⁻¹.
5.2.2 Zeeman Spectra of MgX₁ for B||<100>.

Sample Ge(Mg, MgX₁)81-7-23DSR#4 has been used to obtain the Zeeman spectra of MgX₁ in Ge. Only a few fields were used to study sample Ge(Mg, MgX₁)81-7-23 DSR#3; its Zeeman components were found to be in agreement with those obtained from Ge(Mg, MgX₁)81-7-23DSR#4. The Zeeman spectra of the C and D lines of MgX₁ for B||<100> at 0.5 T are shown in Figure 5.2. The Zeeman spectra of the D line for 2.0 T, 4.0 T, 5.0 T, and 6.0 T are given in Figures 5.3 to 5.6. The Voigt configuration has been used with the radiation plane-polarized with either Eᵧ or E±. The magnetic field dependence of the Zeeman D components of MgX₁ is shown in Figure 5.7. In all the figures, the dashed curves are the results for Eᵧ while the full ones are for E±. The curves in Figure 5.7 are polynomial fits to the data. In the case where a component is observed for both polarizations, the same order of polynomial is used for both polarizations.

In several aspects, the Zeeman behaviour of MgX₁ is very similar to that of ZnH. At lower fields (B < 2.0T), like ZnH, the components are essentially identical to those obtained for the C and D lines of group III impurities in Ge [42, 43]. Unlike ZnH, at low fields, the Zeeman components are better resolved. The Zeeman dependence of some of the D components for B>2T exhibit serpentine behaviour, which is same as that shown by some of the D components of group III impurities [43] and the <111> axial defect ZnH in Ge (see Section 4.3). It is found that, at all fields, the splittings of several pairs of the components of D(MgX₁) are identical to those observed for the D lines of group III impurities. This result is shown in Figure 5.8. In this figure, the upper two
Figure 5.2: C and D lines of MgX in Ge at 0.5 T. Unapodised resolution is 0.18 cm$^{-1}$. 

Ge(Mg: MgX) 81-7-23#4
B∥<100>; 0.5 T

T = 3.4 K
Figure 5.3: D line of MgX$_1$ in Ge at 2.0 T. Unapodised resolution is 0.18 cm$^{-1}$.
Figure 5.4: D line of MgX$_1$ in Ge at 4.0 T. Unapodised resolution is 0.18 cm$^{-1}$. 

Ge(Mg; MgX$_1$) 81-7-23#4

$B$$\parallel$$<100>$$; 4.0$ T

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T = 3.3 K
Figure 5.5: D line of MgX₁ in Ge at 5.0 T. Unapodised resolution is 0.18 cm⁻¹.
Figure 5.6: D line of MgX in Ge at 6.0 T. Unapodised resolution is 0.18 cm$^{-1}$. 

$\text{Relative transmission}$

$\text{Photon energy (cm}^{-1}).$
Figure 5.7: Magnetic field dependence of the Zeeman components of the D-line of MgX₁ in Ge.
Figure 5.8: Splittings of the excited state of the D line of MgX₁ (upper two sets of data points) and that of B and Ga (upper two curves) in Ge for $\mathbf{B} \parallel \langle 100 \rangle$. For the ground state (lowest set of data), the points are from the spectra of MgX₁ while the dot-dashed line is a linear least squares fit to these data.
sets of data points are the splittings obtained from the MgX$_1$ components, while
the curves associated with these points are fits to the splittings of the ±1/2 and
±3/2 states of the 2Γ$_8^{-}$ state of gallium and boron for this orientation of B [43].
This figure shows that just as was the case for ZnH, the p-like excited states of
MgX$_1$ are very like those of group III acceptors and that they are insensitive to
the contents of the central cell of the defect. The existence of unpolarized
transitions, the number of observed components and their magnetic field
dependence are close to those of ZnH which suggests that the behaviour of the
ground state of this defect is similar to that of the latter in all respect except for its
splitting. The splitting of the ground state with applied magnetic field is shown in
Figure 5.8 as the lowest set of data points; the line through these is a linear least
squares fit. From these results it is deduced that MgX$_1$ is an axial defect with its
axis along any one of the <111> covalent bonds.

5.3 Spectra of MgX$_2$ in Ge.

5.3.1 Unperturbed Spectrum

Sample Ge(Mg; MgX$_2$)81-7DSR#2 was used to study MgX$_2$ in Ge. The
procedure for introducing the Mg in this case was different to that described in
Section 5.3.1. Here, the sample and a Mg sheet of 3x2x0.13 mm$^3$ were located
separately in the same sealed, evacuated quartz tube, heated at 850°C for about
48 hours and then quenched in a dewar of liquid nitrogen. The unperturbed
optical absorption spectrum of this sample is shown in Figure 5.9. This
spectrum has been obtained using the Polytec spectrometer described previously
at an unapodised resolution, of 0.14 cm$^{-1}$. In the range of 100 cm$^{-1}$ to 150 cm$^{-1}$
Figure 5.9: Spectrum of Ge containing MgX₂. The insert shows the details for the range 160-180 cm⁻¹.
a number of transitions are observed. None of these have energy spacings related to those of the Lyman spectrum of neutral acceptors. Also, none can be identified with those reported previously [54]. Beyond 150 cm\(^{-1}\), a Lyman series is seen with lines at 150 cm\(^{-1}\) (G), 163.71 cm\(^{-1}\) (D), 169.78 cm\(^{-1}\) (C), 174.86 cm\(^{-1}\) (B) and 177.57 cm\(^{-1}\) (A\(_3\)). The neutral acceptor giving rise to this series has been designated MgX\(_2\). Very little Mg\(^{(0)}\) has been introduced as in evidence by its weak D line at 265.8 cm\(^{-1}\). Beyond 300 cm\(^{-1}\), the Cu\(^{(0)}\) Lyman series is also seen with G, D, C, and B at 311.83 cm\(^{-1}\), 325.55 cm\(^{-1}\), 331.64 cm\(^{-1}\) and 336.74 cm\(^{-1}\), respectively.

### 5.3.2 Zeeman Spectra of MgX\(_2\) for B\(\parallel\)<100>\>

Figure 5.10 shows the C and D lines of MgX\(_2\) at 0.5 T while the Zeeman components of the D line of this centre at 3.0 T, 3.5 T, 5.0 T and 6.0 T are given in Figures 5.11 to 5.14 respectively. Voigt geometry has also been used here with plane polarized infrared radiation. Figure 5.15 shows the field dependence of the components of the D line of MgX\(_2\). The number of Zeeman components, relative intensities and magnetic field dependence are the same as for MgX\(_1\) and ZnH except that the magnitude of the ground state splitting is different. This splitting for MgX\(_2\) is given by the lowest set of data points in Figure 5.16; the straight line through these points is a least squares fit. The upper two sets of data points give the splitting of the final state of the D line of MgX\(_2\), while the curves associated with those are the fits to the splittings of the \(\pm 1/2\) and \(\pm 3/2\) states of \(2\Gamma\)\(_8\)\(^-\) of Ga and B in Ge.
Figure 5.10: C and D lines of MgX\textsubscript{2} in Ge at 0.5 T. Unapodised resolution is 0.29 cm\textsuperscript{-1}.
Figure 5.11: D line of MgX₂ in Ge at 3.0 T. Unapodised resolution is 0.29 cm⁻¹.
Figure 5.12: D line of MgX₂ in Ge at 3.5 T. Unapodised resolution is 0.29 cm⁻¹.
Figure 5.13: D line of MgX₂ in Ge at 5.0 T. Unapodised resolution is 0.29 cm⁻¹.
Ge(Mg; MgX₂)81-7DSR#2

B∥<100>; 6.0 T

--- E⊥B

--- E∥B

T ≈ 3.7 K

Figure 5.14: D line of MgX₂ in Ge at 6.0 T. Unapodised resolution is 0.29 cm⁻¹.
Figure 5.15: Magnetic field dependence of the Zeeman components of the D-line of MgX$_2$ in Ge.
Figure 5.16: Splittings of the excited state of the D line of MgX$_2$ (upper two sets of data points) and that of B and Ga (upper two curves) in Ge for B||100>. For the ground state (lowest set of data), the points are from the spectra of MgX$_2$ while the dot-dashed line is a linear least squares fit to the experimental data.
5.4 Spectra of CuX in Ge

5.4.1 Unperturbed Spectrum
The procedure discussed in Ref [57] was adopted to diffuse Cu in Ge. In a number of instances, not only was the substitutional triple acceptor $\text{Cu}^{(0)}$ introduced but also another defect whose Lyman spectrum occurred at an energy which was $\sim 100 \text{ cm}^{-1}$ lower than that of $\text{Cu}^{(0)}$. This defect has been labelled CuX [14, 55]. Here, the sample designated as Ge(Cu; CuX)81-7 DSR has been used to study CuX in Ge. The unperturbed spectrum of this sample is shown in Figure 5.17 which is that of a neutral acceptor. This has been obtained with the use of the Polytec FTIR spectrometer described previously and at an unapodised resolution, of 0.36 cm$^{-1}$. The Lyman series of CuX is in the range 210 to 245 cm$^{-1}$. The G, D, C, B, three A and two I lines are seen. Of these, the first four occur at 211.43, 225.2, $\sim 231.25$ and 236.46 cm$^{-1}$, respectively. The two strongest lines, C and D, have an energy spacing 6.05 cm$^{-1}$ which is characteristic of all neutral acceptors in Ge [7]. Beyond 300 cm$^{-1}$ the Lyman series of $\text{Cu}^{(0)}$ is observed [57].

5.4.2 Zeeman Spectra of CuX for B||<100>
Zeeman studies of CuX for B||<100> have been reported elsewhere [14]. Figure 5.18 shows the field dependence of the energies of the components of the D line (see Fig.5, Ref.[14]). At the time of these earlier measurements the Zeeman behaviour of <111> axial defects was not known quantitatively. Comparison of these results with those for ZnH, MgX$_1$ and MgX$_2$ clearly shows that CuX is the same type of neutral single acceptor as these three but with a different ground
Figure 5.17: Spectrum of Ge containing CuX. The insert shows the details for the range 210-250 cm\(^{-1}\).
Figure 5.18: Magnetic field dependence of the Zeeman components of the D-line of CuX.
state splitting. That CuX is an axial defect was one of the interpretations presented previously but no details had been deduced. It is now possible to determine the ground state splitting for CuX. This is shown as a function of field strength in Figure 5.19 as the lowest set of data points along with the linear least squares fit to these. This splitting is also shown in Figure 5.20 (a) along with the ground state splittings of ZnH, MgX₁ and MgX₂. It is interesting to note that splitting increases with increasing binding energy of the defect as is shown in Figure 5.20 (b). The binding energy is obtained by adding to the energy of the D line the theoretical value of that of the 2Γ₈⁻ state of group III impurities [54].

5.4.3 Zeeman Spectra of CuX for B||<111>

In order to confirm the <111> axial nature of CuX, Zeeman measurements have now been made with B||<111>. The spectra have been recorded in the Voigt configuration using plane polarized Infrared radiation with applied magnetic fields from 0.5 T to 6.0 T. The Zeeman spectra of the C and D lines of CuX in Ge at 1.5 T is shown in Figure 5.21 while those of the D line at 3.5 T and 5.5 T are shown in Figures 5.22 and 5.23, respectively. The full curves are for \( E_\perp \) while dashed ones are used for \( E_\parallel \). The dependence of the energies of the D components on B is given in Figure 5.24.

At low fields the spectra are very similar to those of group III impurities [44] and the axial defect ZnH. Above these fields, the Zeeman components split into several components. Unlike the group III acceptors, many of the CuX Zeeman components exhibit unpolarized transitions in the same manner as was observed for ZnH for this orientation of B. In fact all the data can be understood using the
Figure 5.19: Splittings of the Zeeman states of the excited and ground states of the D line of CuX in Ge for $\mathbf{B}||<100>$. For the excited state (upper two sets of data), the points are those obtained from the observed Zeeman spectra of CuX, while the curves are fits to the corresponding splittings of the excited state of the D lines of B and Ga in Ge (see Figure 4 of [37]). For the ground state (lowest set of data), the points are from the spectra of CuX while the dot-dashed line is a linear least squares fit to the experimental data.
Figure 5.20: (a) Ground state splittings of ZnH, MgX₁, MgX₂, and CuX for $B\parallel<100>$ and (b) variation of phenomenological g factor with binding energy.
Figure 5.21: C and D lines of CuX in Ge at 1.5 T for $B \parallel <111>$. Unapodised resolution is 0.18 cm$^{-1}$. 
Figure 5.22: D line of CuX in Ge at 3.5 T for $\mathbf{B}\parallel<111>$. Unapodised resolution is 0.18 cm$^{-1}$. 
Figure 5.23: D line of CuX in Ge at 5.5 T for $\mathbf{B} \| <111>$. Unapodised resolution is 0.18 cm$^{-1}$. 
Figure 5.24: Magnetic field dependence of the Zeeman components of the D-line of CuX in Ge for $\mathbf{B} \parallel <111>$. 

Ge(Cu; CuX)81-7-27

$\mathbf{B} \parallel [111]$
axial defect model that was ascribed to ZnH (see Chapter 4), assuming for this
defect only the lower ground state, \( \Gamma_{5+6}(\Gamma_{5+6}^+) \) is populated at He temperature as
is the case of ZnH.

Figure 5.25 illustrates that the splitting of the excited state of the D line of this
centre behaves the same as that of group III acceptors [23, 24, 44]. The upper
two sets of data points give the CuX splittings while the curves are the fits to the
\( \pm 1/2 \) and \( \pm 3/2 \) Zeeman excited state splitting of boron and gallium in Ge. The
splitting of the ground states of Type 1 and Types 2-4 under B are shown as the
lower two curves, where in this case the straight lines are fits to the data.
Comparison of these latter splittings with the corresponding ones for ZnH (see
Figure 5.26) shows that the much deeper impurity, CuX, has a much larger
ground state splittings just as was the case for B\(||<100>\) (see Figure 5.20 (a)).
The non linear behaviour of the Type 1 ground state of ZnH, since it is shallower
than that of Types 2-4, may be due to an interaction with the Zeeman states of the
first excited state. This could be significantly smaller for CuX.

5.5 Piezospectroscopy of CuX for F\(||<100>\)

In addition to the Zeeman measurements just described, piezospectroscopic
observations have been made for F\(||<100>\). Stresses up to \( \sim 30 \) Mpa were
applied using lead masses and the behaviour of the G, D, C and B lines analysed.
Spectra for six different stresses are shown in Figure 5.27 to 5.29. The stress
dependences of the energies of the components of the above four lines are given
Figure 5.25: Splittings of the excited state of the D line of CuX (upper two sets of data points) and that of B and Ga (upper two curves) in Ge for $\mathbf{B}||<111>$ [44]. The lower two sets of data and the linear fits to these given by the dot-dashed lines are those for Type 1 and Types 2 to 4 complexes under this field direction.
Figure 5.26: Splittings of the ground states of the D line of ZnH and CuX in Ge for $\mathbf{B} \parallel [111]$. The sets of data and the fits to these are those for type 1 and types 2 to 4 complexes under this field direction.
Figure 5.27: G, D, C and B lines of CuX in Ge for $\mathbf{F}||<100>$. Unapodised resolution is 0.15 cm$^{-1}$. 
Figure 5.28: Continuation of previous figure.
Figure 5.29: Figure 5.28: Continuation of previous figure.
in Figure 5.30. The curves through the data points in the latter figure are polynomial least squares fits. In these figures, the results for radiation polarized parallel to the applied force (E||F), are shown as dashed curves while for E⊥F they are solid curves.

Just as was the case for ZnH with F||<100>, the spectra show very little change in the relative intensities of their components over the range of stresses involved. This indicates that the ground state does not split as would be the case if the initial state is a Kramers' doublet. Further, with F||<100>, the defects will have the same symmetry for all four <111> axial defect sites (see Table 4.1). The splitting can be attributed to the excited state and for the D line is shown in Figure 5.31 as a function of stress. Also shown on this figure is the corresponding result for ZnH (see Figure 4.34). Thus, the splitting of the excited state of the D line of both ZnH and CuX is the same and from the deformation potential constant obtained (see Section 4.6) is identical to that of the 2Γ₈⁻ state of group III acceptors and hence, in Figure 5.31, is so labelled.

Unlike ZnH the spectrum of CuX contains well-defined G and B lines whose excited states are also of Γ₈⁻ symmetry and their piezospectroscopy should be close to that of the G and B lines of group III impurities. Figure 5.31 shows the splittings of the final states of the G and B lines of CuX. The deformation potential constants extracted from these data are 0.223±0.005 eV and 0.648±0.005 eV for b_G and b_B, respectively. These are to be compared with 0.247±0.007 eV and 0.65±0.03 eV, respectively, the same quantities for group III impurities [45].
Figure 5.30: Stress dependence of G, D, C and B lines of CuX in Ge with \( F \parallel <100> \).
Figure 5.31: Excited State Splitting of ZnH and CuX in Ge for \( \mathbf{F}||<100> \).
5.6 Conclusion

Zeeman and piezo-spectroscopy have been performed on the acceptor complexes \( \text{MgX}_1, \text{MgX}_2 \) and \( \text{CuX} \) in Ge. Using ZnH in Ge as a "template", it has been demonstrated that these other acceptor are of the same nature, viz., they are axial defects with their axes along the \( <111> \) bond directions of Ge. It is also found that the behaviour of the excited state of the D line of these three defects under applied perturbations is the same as that of the \( 2\Gamma_8^- \) state of group III impurities in Ge. The data for \( \mathbf{F}||<111> \) for ZnH demonstrates that the \( 1\Gamma_{5+6}^+ \) ground state is the one populated at He temperature and, thus, it is concluded that this also the case for these other three \( <111> \) axial acceptors.

The chemical element which is the counterpart of the H in ZnH has not been determined. The difference between these defects is in the magnitude of the Zeeman splittings of the ground states. For \( \mathbf{B}||<100> \), these states split linearly with field, the splitting increasing with binding energy.
Chapter 6 Neutral Double Acceptors

6.1 Introduction

Substitutional group II impurities in germanium bind two holes at low temperatures and constitute a solid state analog of the helium atom. The ground state of a hydrogen-like atom created by a neutral group III impurity in germanium reflects the complexity of the valence band. In the case of a neutral double acceptor (NDA), the ground state is expected to be even more complex because of the mutual interaction between its two bound holes. The experimental results show that the energy, spacings and the relative intensities of the p-like excited states of group II impurities are close to those of substitutional group III impurities [54, 58-60]. The electronic states of an NDA in which a single hole is excited can be represented as a product of two single-hole states, provided the mutual Coulomb interaction between the two holes is assumed to be small. For a single acceptor, the ground state wave functions generate the irreducible representation \( 1\Gamma_8^+ \) of \( O_h \) symmetry [3, 54], and its excited states wavefunctions generate \( \Gamma_6^-, \Gamma_7^- \), and \( \Gamma_8^- \) representations. Here the notation and the representations of [8] are used. The symmetry of the ground state of an NDA can be written as the antisymmetric direct product of two single hole representations, i.e., \( \{1\Gamma_8^+ \times 1\Gamma_8^+\}=1\Gamma_1^++1\Gamma_3^++1\Gamma_5^+ \). Hund’s rule suggests that the \( 1\Gamma_3^++1\Gamma_5^+ \) state is bound more tightly than the \( 1\Gamma_1^+ \) state, but in the case of neutral zinc, it has been demonstrated experimentally [58-61] and theoretically [62] that the \( 1\Gamma_1^+ \) state is the lowest. Excitation of one of the two holes to a p-like state allows one to represent the excited states by \( 1\Gamma_8^+ \times n\Gamma_e^- \), where \( n = 1, 2, \ldots \) and \( e = 6, 7, 8 \). For example, with \( e = 8 \), the excited states are \( \Gamma_8^+ \times \Gamma_8^- = \Gamma_1^- + \Gamma_2^- + \Gamma_3^- + 2\Gamma_4^- + 2\Gamma_5^- \).
The degeneracy of the ground state may be lifted because of hole-hole interaction [63, 64], however, for the excited states with one hole in a p-like orbital and the other still with an s-like orbital, these effects are expected to be insignificant. For Zn\(^{(0)}\), the properties of the unexcited hole have been shown to be the same [59, 60] as that of the ground state of Zn\(^{-}\). Zeeman studies have been carried out to study the nature of NDA's on the basis of the above model. A preliminary Zeeman study has also been made of neutral Be in Ge.

6.2 Results and Discussion for Mg\(^{(0)}\).

Samples Ge(Mg,MgX\(_{1}\))81-7-27#4 and Ge(Mg)81-7-27 were used to study the Zeeman effect of the G and D lines of Mg\(^{(0)}\) with \(B||<100>\). No samples were prepared for other orientations of \(B\).

6.2.1 D Line

6.2.1a Unperturbed Spectrum

The unperturbed spectrum of one of the samples used to study the D of Mg\(^{(0)}\) line is given in Figure 6.1 (see also Ref. 54). The unperturbed spectrum of the other Mg-doped sample has already been given (see Figure 5.1). This sample was prepared in the same way as that used to obtain the sample used to study MgX\(_{1}\) except that the Mg ribbon was from a different source (see Section 5.2.1). Comparison of the spectrum of any NDA with that of a group III impurity demonstrates that for an NDA only a single-hole optical excitation is involved. It might be noted that three
Ge(Mg) 81-7-27
$\Delta v = 0.18 \text{ cm}^{-1}$.

Figure 6.1: Spectrum of Ge containing Mg. The insert shows the details for the range 250-285 cm$^{-1}$. 
other groups of features were observed for this sample. These were clustered around 100 cm$^{-1}$, 130 cm$^{-1}$ and 190 cm$^{-1}$. Some of these have already been recorded in Ref [54] many others have not. No detailed study of the effect of $B||<100>$ on these has been made.

6.2.1b Zeeman Spectra with $B||<100>$

Zeeman spectra of the D line of Mg$^{(0)}$ at 2.0 T, 4.0 T and 6.0 T are given in Figures 6.2 to 6.4, respectively. The spectra of Figures 2 T and 4 T are from sample Ge(Mg)81-7-27 while that of Figure 6.4 is from the other sample. Some of the components, particularly 8x6, were better defined than for the latter sample as can be seen. The dependence of the energies of the D components of B is given Figure 6.5; this includes data from both samples. The detailed meaning of the labeling in these figures is described below. The result in Figure 6.5 is very similar to that obtained for Zn$^{(0)}$ [65].

As already mentioned, the NDA excited state wave function is a product of the ground state wavefunction of the singly ionised impurity and that of a group III excited state. Under a uniform magnetic field, $B$, along a $<100>$ crystallographic direction, the symmetry $\overline{O}_h$ of the host is reduced to $\overline{C}_{4h}$ and $\Gamma_8^+(\overline{O}_h)$ decomposes into $\Gamma_5^+ + \Gamma_6^+ + \Gamma_7^+ + \Gamma_8^+$ of $(\overline{C}_{4h})$. The symmetry of an excited state is expressed as $\Gamma^{-} = \Gamma_u^+ \times \Gamma_e^-$, where $u, e = 5, 6, 7, 8$ while $f = 1, 2, 3, 4$. For a hole excited to a $\Gamma_8^-$ orbital, the excited state can be any one of those four sets (ladders) of states, each ladder containing four states. These ladders will be displaced from each other by an amount equal to the splitting of the four orbitals possible for the unexcited hole, which is the same as the splitting of the ground state of a singly ionised NDA.
Figure 6.2: D line of Mg in Ge at 2.0 T. Unapodised resolution is 0.18 cm⁻¹.
Figure 6.3: D line of Mg in Ge at 4.0 T. Unapodised resolution is 0.18 cm\(^{-1}\).
Figure 6.4: D line of Mg in Ge at 6.0 T. Unapodised resolution is 0.18 cm$^{-1}$. 

Ge(Mg; MgX$_1$)81-7-23#4
B\parallel<100>; 6.0 T

- - - E\parallel B
--- E\perp B

T = 3.7 K
Figure 6.5: Magnetic field dependence of the Zeeman components of the D-line of Mg in Ge for $\mathbf{B} \parallel <100>$. 
Within a given ladder the ordering and Zeeman splittings are those of any group III impurity. These excited states are shown in Figure 6.8. It is assumed that order of the Zeeman ground states of Mg$^-$ is the same as that of Zn$^-$ [60]. The order of the group III Zeeman states is that of the $2\Gamma_8^-$ state (the excited state of the D line) for $B>4.5$ T [60]. The four ladders of four states in Figure 6.6(b) are compounded from the states shown in (a) with those shown in (c). The labels on these states, without the parity signs, are those used to label the transitions.

\begin{align*}
7^+ & \quad 6^+ & \quad 5^+ & \quad 8^+ \\
6^+ & \quad 5^+ & \quad 8^+ & \quad 7^+ \\
5^+ & \quad 8^+ & \quad 5^+ & \quad 7^+ \\
8^+ & \quad 7^+ & \quad 6^+ & \quad 6^+ \\
& \quad 8^+ & \quad 5^+ & \quad 5^+ \\
& \quad 8^+ & \quad 6^+ & \quad 6^+ \\
& \quad 8^+ & \quad 8^+ & \quad 8^+ \\
(a) & & & (b) & (c)
\end{align*}

Figure 6.6: Zeeman states for an NDA in Ge for $B\parallel<100>$. (a) these dotted lines give the Zeeman splittings of ground state of Mg$^-$ in Ge (b) the full lines show the Zeeman excited states of an NDA in Ge, (c) these dotted lines give the Zeeman states of the $2\Gamma_8^-$ state of group III acceptors in Ge for $B>4.5$ T.

Since the $1\Gamma_1^+$ ground state of an NDA retains this label under $B$, the selection rules for $B\parallel<100>$ are $1^+ \rightarrow 1^-$ for $E_\parallel$ and $1^+ \rightarrow 3^-$, $4^-$ for $E_\perp$, thus permitting four transitions for $E_\parallel$ and eight for $E_\perp$. Three transitions for $E_\parallel$ and six for $E_\perp$ are
observed. It might be noted that if the observed transitions were from the $\Gamma_3 + \Gamma_5$ states, the other ground states, then, from the selection rules, one expects the total number of transitions to be 24 and 48 for $E_{||}$ and $E_{\perp}$, respectively.

6.2.2 G Line

The Zeeman measurements which were carried out for MgX$_1$ also yielded the Zeeman behaviour of the G line of (Mg$^{(0)}$) (see Section 5.2.1). As already mentioned, the details of the unperturbed spectrum are given in Section 5.2.1.

Zeeman spectra of the G line of Mg$^{(0)}$ at 1.0 T, 2.0 T, 3.0 T, 4.0 T, 5.0 T and 6.0 T are given in Figures 6.7 to 6.12 respectively. The magnetic field dependence of the energies of the G components with $B_{||}<100>$ is given Figure 6.13, is found to be very similar to that of Zn$^{(0)}$ in germanium [58]. Since the excited and ground state representations used to label the Zeeman transitions of the D line are the same for the G line except for the order interchange in the top two excited states of group III acceptors at high fields, the same electric-dipole selection rules can be used to label the transitions and to understand the magnetic field dependence of G components.

The transitions allowed are 4 for $E_{||}$ and 8 for $E_{\perp}$, just as was the case for the D line. Three for $E_{||}$ and six for $E_{\perp}$ were observed for the G line. For the determination of the splittings of the orbitals of the unexcited hole both the D and G Zeeman data were used; these gave essentially the same results as can be seen in Figure 6.14. The data in this figure is for the splittings of the $\pm 3/2$ and $\pm 1/2$ orbitals of the unexcited hole where the linear term of the fits through the data have been used to
Figure 6.7: G line of Mg in Ge at 1.0 T. Unapodised resolution is 0.18 cm\(^{-1}\).
Figure 6.8: G line of Mg in Ge at 2.0 T. Unapodised resolution is 0.18 cm\(^{-1}\).
Figure 6.9: G line of Mg in Ge at 3.0 T. Unapodised resolution is 0.18 cm⁻¹.
Figure 6.10: G line of Mg in Ge at 4.0 T. Unapodised resolution is 0.18 cm$^{-1}$. 
Figure 6.11: G line of Mg in Ge at 5.0 T. Unapodised resolution is 0.18 cm$^{-1}$. 

Ge(Mg, MgX)81-7-23#4
B||<100>; 5.0 T
--- E||B
--- E⊥B

T = 3.4 K
Figure 6.12: G line of Mg in Ge at 6.0 T. Unapodised resolution is 0.18 cm\(^{-1}\).
Figure 6.13: Magnetic field dependence of the Zeeman components of the G-line of Mg in Ge for $\mathbf{B}||<100>$. 
Figure 6.14: Splittings of the $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$ orbitals of the unexcited hole of Mg and Zn in Ge.
determine the g-factors. Unlike Zn$^-$ in Ge with $B\parallel<100>$, the splittings between the ground states of Mg$^+$ are not equal [60], but at the same time they appear to be linear with respect to field strength (see Figure 6.14). The experimental data yield slopes of $0.327\pm0.002$ and $0.843\pm0.002$ cm$^{-1}$/T, respectively. These value yield $g_1'=\ -0.712\pm0.004$ and $g_2'=0.294\pm0.014$. For Zn$^-$ a single g-value is obtained, viz., $0.5355$ [60].

6.3. Results and Discussion for Be$^{(0)}$ in Ge

6.3.1 Unperturbed Spectrum

The sample used to obtain the unperturbed and Zeeman spectra of Be in Ge was cut from a disc of material approximately 28 mm in diameter and just over 3 mm thick. This part of the original ingot is labelled Ge(Be)703-11.5; the $<113>$ growth axis of the boule was taken to be [113] and the sample cut so that $B$ could be applied along the [010] direction while retaining approximately the full thickness of the slab. After mounting the sample on its holder and inserting this into the superconducting magnet, the holder was rotated about its vertical axis through $\sim17.5^0$ to give $B\parallel[010]$ since this direction is tilted out of the (113) plane by $17.55^0$.

The unperturbed spectrum of Be in Ge is shown in Figure 6.15; this has been taken at a unapodized resolution of $0.15$ cm$^{-1}$ using the slow-scan FTIR Polytec described previously. Measurement at four times this resolution gave essentially the same result. The Lyman series of Be$^{(0)}$ appears beyond 155 cm$^{-1}$, while the D and C
Figure 6.15: Spectrum of Ge containing Be. The insert shows the G line of Ge(Be).
lines of Al are seen at 66.81 and 72.88 cm$^{-1}$, respectively; also, a trace of B was detected. The inset to Figure 6.17 shows the details of the G line more clearly; this is the same result as that obtained elsewhere [66]. For the sample thickness of 3.1 mm, the transmission was too low to reveal any of the structure reported by others [41, 67] for the D, C, B, and A lines.

It has been established by the latter workers and others previous to them [68, 69] that, unlike Zn$^{(0)}$ and Mg$^{(0)}$, for Be$^{(0)}$, the ground state multiplet consisting of $1\Gamma_1^+$, $1\Gamma_3^+$, and $1\Gamma_5^+$, is closely spaced, with all three states contributing to the Lyman spectrum even at liquid He temperatures, although the $1\Gamma_1^+$ state is still the deepest. The energies of these states relative to the latter are 0.055 and 0.15 meV, i.e., 0.44 and 1.21 cm$^{-1}$. It is not clear which of the other two is the lower but in what follows, for explicitness, it will be assumed that these are in the order of $1\Gamma_3^+$ and $1\Gamma_5^+$. However, even with three ‘ground states’, this cannot account for five or more G lines.

It is known that the D line possesses at least six components and thus its excited state, of symmetry $\Gamma_8^+ \times \Gamma_8^- = \Gamma_1^- + \Gamma_2^- + \Gamma_3^- + 2(\Gamma_4^- + \Gamma_5^-)$, must also be split [41, 67]. The excited state of the G line is of the same symmetry as that of the D line and also the B line; the lower lying the state the larger is its splitting [41, 67], thus the lowest lying excited state, that of the G line, should have the largest splitting. For Zn$^{(0)}$ in Ge, with $\Gamma_1^+$ as ground state, the observation of two G lines is deduced to be due to the splitting of the two $\Gamma_4^-$ states; the value of this splitting is 0.24 cm$^{-1}$ [59]. This is based on the electric dipole selection rules for double acceptors [63]; in $O_h$ notation these are as follows:

$$\Gamma_1^+ \Rightarrow \Gamma_4^-$$
\[
\Gamma_3^+ \Rightarrow \Gamma_4^-, \Gamma_5^-
\]
\[
\Gamma_5^+ \Rightarrow \Gamma_2^-, \Gamma_3^-, \Gamma_4^-, \Gamma_5^-
\]

thus permitting a total of 12 transitions. Since the binding energy of Be\(^{(0)}\) is smaller than that of Zn\(^{(0)}\), the splitting of the two \(\Gamma_4^-\) excited states of the G line of Be\(^{(0)}\) is expected to be larger than 0.24 cm\(^{-1}\).

The energies of the G lines in Figure 6.15 have been determined by fitting five Lorenzian profiles to the combined set. The values obtained are 160.00 (G\(_1\)), 160.50 (G\(_2\)), 161.25 (G\(_3\)), 161.75 (G\(_4\)) and 162.00 (G\(_5\)) cm\(^{-1}\). In addition, approximate values for the very weak shoulders to \(G_3\), viz, \(G_{3a}\) and \(G_{3b}\), are 161 and 161.5 cm\(^{-1}\), respectively. The energy level scheme, with transitions, which fit these data is given in Figure 6.16. In this figure, the numbers in parentheses on the ground states are those given above as deduced by others [41, 67]; all the other numbers are from the present data and its interpretation. It should be emphasized that the scheme given in Figure 6.16 is only one possible interpretation of the unperturbed data.

It appears that the origins of the lines \(G_1\), \(G_2\), \(G_3\) and \(G_4\) are well substantiated, giving excellent agreement with the splitting of the two ground states involved as determined previously [41, 67]. The splitting of the two \(\Gamma_4^-\) excited states is seen to be 0.50 cm\(^{-1}\), about twice that obtained for Zn\(^{(0)}\). The aspect which is disturbing is that in order to explain the \(G_5\) transition, the intermediate ground state has an energy which is significantly different from that believed to be the case.
6.3.2 Zeeman Spectra of Be$^{(0)}$

The Zeeman studies for this orientation were again made in the Voigt configuration with radiation polarized either parallel ($E_\parallel$) or perpendicular ($E_\perp$) to $B$. Since the radiation is incidence on the sample at an angle of $\sim 17^\circ$, its electric vector inside the sample for $E_\parallel$ is no longer parallel to $B$. Using the refractive index of Ge of 3.925 at liquid He temperature in the spectral region of interest [70], it is determined that $E_\parallel$ is at an angle of 13.14° to $B$. Thus, there is a component of $E_\perp$ present for the “$E_\parallel$” polarization; this is estimated to be 5.2% of the total intensity of $E_\parallel$. The problem does not arise for $E_\perp$. 

---

Figure 6.16: Energy level scheme for the G line of Be in Ge.
In Figures 6.17. to 6.19 are shown some of the Zeeman spectra of a preliminary study of $\text{Be}^{(0)}$ in Ge with $\mathbf{B}||<100>$, while Figure 6.20 gives the dependence of the energies of the Zeeman components of the $G$ line on field strength. The spectra of Figures 6.17 to 6.19 have been obtained with a sample thickness of 3.1 mm. Subsequent to these observations, the sample was thinned down, successively, to 1.8 mm, 1.18 mm, 0.50 mm and, finally, to 0.31 mm. The data obtained for these different thicknesses have been included, where possible, in Figure 6.20. It might be noted that the energies of the four strong Zeeman $D$ components of Al for $\mathbf{E}_||$ with $\mathbf{B}||<100>$ agree to within 0.01 cm$^{-1}$ of the known values at 6 T [45], thus confirming that the orientation of $\mathbf{B}$ is correct.

It is seen that the Zeeman spectra, although complex, consist of sharp components. However, it has not been possible to determine which of the five $G$ lines gives rise to which components. Part of this problem is presumably due to the degree of hybridization which will take place between adjacent ground state Zeeman levels of the same symmetry as well as within the excited Zeeman states of the $G$ lines. Under this direction of $\mathbf{B}$, the site symmetry is $C_{4h}$ and the three ground states reduce as follows:

$$
\Gamma_1^+ \rightarrow \Gamma_1^+
$$

$$
\Gamma_3^+ \rightarrow \Gamma_1^+, \Gamma_2^+
$$

$$
\Gamma_5^+ \rightarrow \Gamma_2^+, \Gamma_3^+, \Gamma_4^+
$$

while, for example,

$$
\Gamma_4^- \rightarrow \Gamma_1^- + \Gamma_3^- + \Gamma_4^-
$$

$$
\Gamma_5^- \rightarrow \Gamma_2^- + \Gamma_3^- + \Gamma_4^-.
$$
Figure 6.17: G line of Be in Ge at 1.0 T and 2 T.
Figure 6.18: G line of Be in Ge at 3.0 T and 4 T.
Figure 6.20: Magnetic field dependence of Zeeman components of the G-line of Be in Ge.
Thus, a significant amount of mixing between Zeeman states could take place at relatively small fields which would make it difficult to follow the intensities of the Zeeman components as a guide to identifying their parent lines. It has been thought that a comparison of the Zeeman spectra of Mg\(^{(0)}\) and Zn\(^{(0)}\) with those of Be\(^{(0)}\) might have provided a way to separate out the transitions from the \(\Gamma_1^+\) ground state from those of the other two ground states but this also seems to be thwarted by the mixing between Zeeman states of the same symmetry. Further Zeeman studies with the sample at different and lower temperatures could help to identify the ground state involved in the different Zeeman transitions; this has not yet been done.
Chapter 7 Concluding Remarks

A set of neutral acceptor complexes in Ge has been studied. Having established in detail how one of these, ZnH, a $<111>$ axial defect, behaves under applied perturbations, this behaviour has been used to characterise three other unknown complexes designated as MgX$_1$, MgX$_2$ and CuX. All three match the template provided by ZnH demonstrating that all are $<111>$ axial defects. They also exhibit spectra from only one of their Kramers' ground state doublets so that, like ZnH, no experimental measure of the energy separation of the $\Gamma^+_{5+6}$ and $\Gamma^+_{4}$ ground states has been obtained. For $\mathbf{B}|<100>$, these states split linearly with field, the splitting increasing with the binding energy of the complex. The splitting of the two different types of ground states for both ZnH and CuX for $\mathbf{B}|<111>$ is also found to increase with their binding energy. It has been established for ZnH that the $\Gamma^+_{5+6}$ ground state is the lower. It is assumed that this is true for the other three and that only spectra from this ground state are observed at liquid He temperature. Thus no experimental value has been obtained for the separation of these two states. The application of a magnetic field should produce piezo-Zeeman-like spectra. For piezo-Zeeman studies using both applied magnetic fields and forces, the realistic configuration is that for which $\mathbf{B}$ is chosen to be perpendicular to $\mathbf{F}$. It is for such configurations that eigenvalues have been determined [71]. Of the three orientations of $\mathbf{B}$ used for the study of ZnH, the case of $\mathbf{B}|[110]$ has this geometry for the Types 3 and 4 defects, i.e., axes and hence $\mathbf{F}_{\text{effective}}$ along the $[\bar{1}1\bar{1}]$ and $[1\bar{1}1]$ directions, respectively. However, the ground state splitting for these types was not observed and hence the eigenvalues could not be applied to find $\mathbf{F}_{\text{effective}}$ and the splitting produced by it.
It would be of interest to carry out Zeeman experiments on the $\Gamma_{4}^{+}$ ground state of an axial defect. The most likely candidate for this is BeH in Ge for which transitions are observed from both ground states at He temperature [10, 11]. These states are split by ~4 cm$^{-1}$ [10, 11], thus the intensities of the transitions from this state could be significantly reduced by cooling the sample to simplify the spectrum and identify from which ground state each arises.

Zeeman studies on neutral Mg$^{(0)}$ in Ge for $B_{||<100>}$ have confirmed that $\Gamma_{1}^{+}$ is the lowest of the three possible ground states; this the same as for Zn$^{(0)}$. Both these neutral double acceptors show similar Zeeman spectra. Analysis of the data is simplified by the knowledge that the excited hole has orbitals which are the same as those of a group III acceptor. In addition, the unexcited hole assumes any one of the four tightly bound orbitals of the ground state of the singly ionised impurity. Proceeding in this manner allows the $g$-factors of the latter to be predicted. Unlike Zn$^{(-)}$, the splitting for Mg$^{(-)}$ is not given by one $g$-value but requires two in the same way that all the single-hole group III acceptors require except that the values of $g_1$ and $g_2$ for Mg$^{(0)}$ are very much larger than is the case for the shallow acceptors.

Preliminary studies have been made of Be$^{(0)}$ in Ge. The unperturbed G line consists of at least five separate transitions. These are interpreted as being excitations from the three closely-spaced ground state manifolds to a central-cell split excited state. Some agreement is obtained with other observations. The Zeeman spectra of the G lines for $B_{||<100>}$ are very complex. Because of the multiplicity of the various states, the intensities of a given component is difficult to follow with field due, presumably, to interactions between Zeeman states of the same symmetry. Additional measurements at lower temperatures might produce some simplification.
References


[8] The symmetry labels are those of G.F. Koster, J.O. Dimmock, R.G. Wheeler and H. Statz, *Properties of the Thirty-Two Point Groups*, MIT Press, Cambridge, Mass., 1963. The site symmetry of substitutional acceptors in Ge is $T_d$. This point group, its labels and those of its subgroups have been used to
describe the behaviour of the impurity states under applied uniaxial forces (S. Rodriguez, P. Fisher and F. Barra, Phys. Rev. B, 5, 2219, 1972). However, in the theory of unperturbed acceptor states as developed by Baldereschi and Lipari (see A.K. Ramdas, and S. Rodriguez, Rep. Prog. Phys. 44, 1297, 1981 for a review), the point group symmetry of the host, $O_h$, is used to describe the impurity states under a spherical Coulomb potential. This notation is carried over to the models for the Zeeman effect of the group III acceptors (see [23, 24] below).


[39] Note that in [10, 11] this acceptor defect has been designated by A(ZnH).

[40] These ingots were grown at Purdue University by the late Ms Louise Roth; a reducing atmosphere of hydrogen was used in the furnace.


