ESR STUDY OF ANTIMONY DOPED CADMIUM SULPHIDE

by

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We accept this thesis as conforming to the
required standard

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October, 1969
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Date Nov. 12, 1969
ABSTRACT

The electronic g-tensor in antimony doped cadmium sulphide has been measured at 1.1°K. A sample doped to a room temperature resistivity of 3.3 ohm-cm exhibited an anisotropic g-tensor with $g_\parallel = 1.788$ and $g_\perp = 1.770$.

A single asymmetric line was observed. The asymmetry of this line was found to decrease with decreasing incident power. Further experiments to study this line shape are indicated.
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CHAPTER I

Introduction

This thesis is concerned with electron spin resonance (ESR) in antimony doped cadmium sulphide. The sulphides and selenides of cadmium and zinc are semiconductors with a wurtzite structure, and are especially important as photoconductors and phosphors.

Electron spin resonance experiments have provided valuable information on the structure of the energy bands and on the effect of impurities in semiconductors. A review of the results from extensive studies of semiconductors by ESR techniques has been given by Ludwig and Woodbury.\(^1\)

ESR signals due to shallow donors in silicon and germanium exhibit a hyperfine structure due to the interaction of the electron spin with the donor nuclear magnetic moment.\(^2\) On the other hand, shallow donors in compound semiconductors usually do not show a hyperfine structure. This is to be expected since the available compound semiconductors normally have impurity concentrations in a region where impurity banding takes place. The electrons are mobile even at low temperatures and tend to average out any hyperfine structure. A single line ESR spectrum was observed at approximately 1.1°K in cadmium sulphide doped with antimony. This is believed to form a shallow donor in CdS and the present measurements
were made to determine the g-tensor.

Roth\(^{(3)}\) has given a derivation of the g-value from the band structure, and using these methods Cardona\(^{(4)}\) has calculated the g-value for the common germanium-like semiconductors. By treating wurtzite type materials as cubic, and neglecting the anisotropy, he was able to account for about one-half of the observed shift from the free electron g-value.

Chapters 2 and 3 give a description of the experimental arrangement. Chapter 4 contains an attempt, based on the quasi-cubic model of Hopfield\(^{(5)}\), to calculate the valence band contribution to the g-shift taking anisotropy into account.
CHAPTER 2

Principles of Operation

Magnetic dipole transitions can be induced in a paramagnetic material by placing it in a microwave cavity, in the microwave magnetic field, and applying a suitable D.C. magnetic field perpendicular to the microwave field.

The impedance of a microwave cavity at a detuned short position is given by:

\[ Z = Z_0 \frac{Q_0}{Q_{ex}} \frac{Z_s}{R_s} \]  

where \( Z_0 \) is the characteristic impedance of the transmission line connecting the cavity to the signal source and \( Q_0 \) is the Q-value of the unloaded cavity. The external Q-value, \( Q_{ex} \), measures the power reradiated through the coupling hole. \( R_s \) and \( Z_s \) are the resistance and total impedance respectively of the series equivalent circuit (see Fig. 2.1).

A small paramagnetic sample placed in the cavity changes the self inductance from \( L_0 \) to \( L \) where

\[ L = L_0 \left( 1 + FX \right). \]  

The filling factor, \( F \), is a function of the ratio of the sample to cavity volumes and the cavity shape. The complex rf susceptibility
Figure 2.1 Series Equivalent Circuit of a Resonant Cavity
is a function of the D.C. magnetic field for any given frequency. Tuning the signal source to the resonance frequency of the empty cavity, \( W = \sqrt{\frac{1}{L_0 C}} \), transforms the impedance to

\[
Z = Z_0 \frac{Q_o}{1 + iF_0 (X' - iX'')} \quad 2.4
\]

The real and imaginary parts of the susceptibility can be measured separately by using a microwave bridge. Since the real part represents a detuning of the cavity from resonance, it is possible to compensate for \( X' \) by allowing the signal source frequency to follow that of the cavity. In practice this is accomplished by locking the klystron frequency to the resonant frequency of the cavity.

The superposition of a small modulation field on the D.C. magnetic field will result in a corresponding modulation of the impedance \( Z \) at the same frequency. The amplitude of the impedance modulation is proportional to \( \frac{dX''}{dH} \), the derivative of the imaginary part of the susceptibility with respect to the magnetic field.

A display of \( \frac{dX''}{dH} \) can be obtained by tuning the detector circuit to the modulation frequency and slowly sweeping the D.C. magnetic field. The output of the detection system will then give \( \frac{dX''}{dH} \).
Apparatus

The main features of the spectrometer used are shown in Figure 2.2. The microwave power source is a Varian Associates Reflex Klystron, type V-153/6315. It generates approximately 70mw over the frequency range 8.5 - 10 GHz.

The operating frequency of the klystron was measured with a Hewlett Packard 5245L electronic counter equipped with a 5255 A frequency converter plug-in unit. This unit was capable of measuring frequencies from 3 GHz up to 12.4 GHz.

A $\text{TE}_{102}$ rectangular cavity was used. It was made of standard brass waveguide and gold plated with an immersion type gold solution produced by Sigmund Cohn Co. Inc.* This cavity was undercoupled at room temperature, but was very nearly critically coupled at the operating temperature of 1.1 °K. The samples were placed against the end wall of the cavity and held in place with vacuum grease.

The crystal detector was a 1N23B low noise diode from Microwave Associates. The detector was an integral part of the preamplifier. The preamplifier had an A.C. gain of 40 db ± 3 db over the range 100 Hz to 1 MHz, and was constructed around the crystal mount to reduce the noise introduced in transferring the signal to the Lock-in Amplifier.

---

*Mount Vernon, N. Y., U.S.A.
Figure 2.2: Block Diagram of Spectrometer
The reflector voltage of the klystron was modulated at 10 KHz. This frequency was detected by the crystal and passed on to the A.F.C. (Automatic Frequency Control) where it was amplified and rectified by a phase sensitive detector. Any signal at 10 KHz would then result in a correction voltage being applied to the reflector voltage. In this manner the klystron frequency was made to follow that of the cavity.

The output of the preamplifier also contained the 400 Hz field modulation frequency which carried the resonance signal. This was fed into an Electronics, Missiles and Communications Inc. Model RJB Lock-in Amplifier, with the output going to a Moseley 680 chart recorder.

The magnet was a Newport Instruments Type D 8" electromagnet. The magnetic field was modulated at 400 Hz by a pair of coils mounted on the pole faces and driven by an audio oscillator and amplifier. The maximum amplitude of this modulation field was about 12 gauss.

The magnetic field was measured with a marginal oscillator similar to one produced by Magnion Associates. A glycerine proton sample was mounted on one of the pole faces. Calibration, using DPPH as a standard, showed that there was a difference of \( \approx 4 \) gauss between the sample position in the cavity and the proton sample. The frequency of the marginal oscillator was counted with the Hewlett Packard counter, while the resonance itself was monitored.
on an oscilloscope. A pen marker on the E.M.C. Lock-in Amplifier made it possible to mark the recorder output as the proton resonance crossed the centre of the oscilloscope trace.

The cavity and sample were immersed in liquid helium contained in a glass dewar. It was possible to attain temperatures of \( \approx 1.1^\circ\text{K} \) by pumping on the helium to reduce its vapour pressure.
CHAPTER 3

Sample

The crystal used for this experiment was cadmium sulphide doped with antimony, supplied by Eagle Picher, Miami, Oklahoma.

The crystal was X-rayed to locate the c-axis and a 1 mm thick platlet was cut from it such that the c-axis lay in the plane of the platlet.

Room temperature resistivity measurements indicated that the sample had a resistivity of \( \approx 3.3 \) ohm cm. If a mobility of 100 cm\(^2\)/volt sec. is assumed, the carrier concentration should be \( \sim 2 \times 10^{16} \) per cc.

The sample used for these experiments had a volume of \( 2.5 \times 10^{-2} \) cc and had a signal to noise ratio of 10:1. Absolute sensitivity measurements for the spectrophotometer indicated that it was capable of detecting \( \sim 10^{12} \) spins/ gauss. This would then give a carrier concentration of \( \sim 10^{16} / \) cc for the sample used.
CHAPTER 4

Theory

The effective mass approximation can be used to describe an electron which is near a point of minimum energy in the conduction band.

For the case of a non-degenerate band the electronic g-value for a donor electron whose ionization energy is small with respect to the band gap, is given by (1):

\[ g_\# = 2 + \text{Im} \left[ \frac{\sum_{n \neq o} \langle 0 \uparrow | p_x | n \rangle \langle n | p_y | 0 \uparrow \rangle}{E_o - E_n} \right] \]

and

\[ g_\downarrow = 2 + \text{Im} \left[ \sum_{n \neq o} \frac{1}{E_o - E_n} \left\{ \langle 0 \uparrow | p_y | n \rangle \langle n | p_z | 0 \downarrow \rangle + \langle 0 \downarrow | p_y | n \rangle \langle n | p_z | 0 \uparrow \rangle \right\} \]

In these expressions \( |0\rangle \) refers to the band for which g is being calculated, \( |n\rangle \) refers to all other bands, and m is the mass of a free electron.

To apply these formulae to the conduction band of cadmium sulphide some knowledge of the position and structure of nearby bands is required. The extrema of the conduction and valence bands of CdS are at or very close to \( k = 0 \).
Figure 4.1 The band structure of $\mathbf{k} = 0$ in CdS. (Reynolds, Litton and Wheeler 1964) (a) and Ge (Cardona 1963a) (b). $\Gamma_7$ and $\Gamma_9$ are irreducible representations of the Wurtzite double group. $\Gamma_{15}$, $\Gamma_2'$, and $\Gamma_{25}$ are irreducible representations of the full cubic group (single group), and $\Gamma_{15c}$, $\Gamma_{1c}$ and $\Gamma_{15v}$ are the corresponding representations of the zincblende structure.
Figure 4.1 shows the bandstructure at this point. The band structure of germanium, the corresponding isoelectronic homopolar semiconductor, is also shown.

The conduction band minimum in CdS belongs to the irreducible representation $\Gamma_7$ of the wurtzite double group. It is separated by a gap of 3.58 ev from the uppermost of the three valence bands. These three spin degenerate bands are close together and belong to the $\Gamma_9$, $\Gamma_7$ and $\Gamma_7$ representations respectively. Another group of states with the same transformation properties is located 6.1 ev above the valence bands\(^{(9)}\).

The base-functions for the $\Gamma_7$ and $\Gamma_9$ representations are:

$$
\Gamma_7 : \begin{align*}
&\text{cs} \uparrow + \text{dz} \uparrow + \frac{1}{2}f(x + iy) \downarrow \\
&\text{cs} \downarrow + \text{dz} \downarrow + \frac{1}{2}f(-x + iy) \uparrow
\end{align*}
$$

$$
\Gamma_9 : \begin{align*}
&\frac{1}{\sqrt{2}} (x + iy) \uparrow \\
&\frac{1}{\sqrt{2}} (x - iy) \downarrow
\end{align*}
$$

where $x$, $y$, $z$ are p-orbitals; s an s-function; c, d, and f are constants; and $\uparrow$ and $\downarrow$ are the spin functions.

Some simplification of these base-functions can be effected since the conduction band is almost purely s-like and the $\Gamma_7$ valence bands are dominantly p-like\(^{(10)}\). This means that for the conduction band, $c = 1$ and $f = d = 0$, and for the valence bands, $c = 0$ as a first approximation. The case
of \( c \neq 0 \) for the valence bands will be considered in the discussion. The quasi-cubic model of Hopfield\(^{(5)}\) relates the remaining \( d' \)s and \( f' \)s to the observed valence band splittings. This model considers the wurtzite structure as a cubic crystal that has been uniaxially strained along a \((111)\)-direction. The valence band of a cubic semiconductor, with vanishing spin-orbit energy, consists of six states. Their rotation properties can be represented by the \( J = \frac{3}{2} \), and \( J = \frac{1}{2} \) states\(^{(11)}\):

\[
\begin{align*}
\{3/2,3/2\} &= \frac{1}{\sqrt{2}} (x + iy)\uparrow \\
\{3/2,1/2\} &= \frac{1}{\sqrt{6}} \left\{ 2z\uparrow + (x + iy)\downarrow \right\} \\
\{3/2,-1/2\} &= \frac{1}{\sqrt{6}} \left\{ 2z\downarrow - (x - iy)\uparrow \right\} \\
\{3/2,-3/2\} &= \frac{1}{\sqrt{2}} (x - iy)\downarrow \\
\{1/2,1/2\} &= \frac{1}{\sqrt{3}} \left\{ z\uparrow - (x + iy)\downarrow \right\} \\
\{1/2,-1/2\} &= \frac{1}{\sqrt{3}} \left\{ z\downarrow + (x - iy)\uparrow \right\} 
\end{align*}
\]

In this representation the spin orbit energy is diagonal, and the \( J = \frac{1}{2} \) and \( J = \frac{3}{2} \) states are split by an energy \( \delta \). The spin-orbit Hamiltonian matrix is given by:

\[
H_{S-\delta} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \delta & 0 \\
0 & 0 & 0 & 0 & 0 & \delta 
\end{pmatrix}
\]

\[4.4\]

\[4.5\]
The states to which the rows correspond have the same order as they have in eq. 4.4. If the crystal were cubic, with no hexagonal crystal field, $\delta$ would be the valence band splitting.

The application of a uniaxial strain in the z-direction will leave the $x^\uparrow$, $x^\downarrow$, $y^\uparrow$, and $y^\downarrow$ states unchanged but will shift the energy of the $z^\uparrow$ and $z^\downarrow$ states by an amount $\Delta$ with respect to them. If there were no spin-orbit coupling $\Delta$ would be the valence band splitting and in this representation the strain Hamiltonian would be:

$$H_{\text{strain}} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \Delta & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \Delta & 0 \\
\end{pmatrix}$$

The order of the rows of this matrix is $x^\uparrow$, $y^\uparrow$, $z^\downarrow$, $x^\downarrow$, $y^\downarrow$, $z^\uparrow$. $H_{s-o}$ and $H_{\text{strain}}$ may now be diagonalized to give the states and their energies relative to the $\Gamma_9$ level. The results are given in Table 4.1.

Since $E_1$ and $E_2$ are symmetric under interchange of $\Delta$ and $-\delta$, solving for $\delta$ and $\Delta$ in terms of $E_1$ and $E_2$ will give two sets of solutions:
\[ \delta = (E_1 + \frac{1}{2}E_2) \pm \frac{1}{2} \sqrt{(E_2 - E_1)^2 - 3E_1^2} \]

\[ \Delta = - (E_1 + \frac{1}{2}E_2) \pm \frac{1}{2} \sqrt{(E_2 - E_1)^2 - 3E_1^2} \]

These two solutions are referred to as the Hopfield model \( \delta > |\Delta| \) and the Birman model \( \delta < |\Delta| \).

Using the formulae 4.1 and 4.2 and the wave functions given in Table 4.1 it is possible to compute the valence band contribution to the \( g \)-shift at the bottom of the conduction band. The results of this calculation are:

\[ g_\| = 2 - 2 \frac{|I|^2}{m} \left\{ \frac{1}{E_g} - \frac{2 \lambda_2^2}{E_g + E_1} - \frac{2 \lambda_3^2}{E_g + E_1 + E_2} \right\} \]

\[ g_\perp = 2 + 2 \frac{|I|^2}{m} \left\{ \frac{2 \lambda_2^2}{E_g + E_1} \left( \frac{3E_1}{\delta} - 2 \right) + \frac{2 \lambda_3^2}{E_g + E_1 + E_2} \left( \frac{3(E_1 + E_2)}{\delta} - 2 \right) \right\} \]

where \( |I|^2 = \left| \langle \psi(\tilde{r}_i) | \tilde{p}^2 | \psi(\tilde{r}_i) \rangle \right|^2 \)
Table 4.1
The Valence Band States in Wurtzite

<table>
<thead>
<tr>
<th>Energy</th>
<th>Basis Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W = 0$</td>
<td>$\frac{1}{\sqrt{2}} (x + iy)^\uparrow \frac{1}{\sqrt{2}} (x - iy)^\downarrow$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$W = -E_1 = -\left{ \frac{\delta - \Delta}{2} - \sqrt{\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{\Delta}{3}} \right}$</td>
<td>$\lambda_2 \left{ \left(\frac{3E_1}{\delta} - 2\right) z \uparrow - (x + iy) \downarrow \right}$ $\lambda_2 \left{ \left(\frac{3E_1}{\delta} - 2\right) z \downarrow + (x - iy) \uparrow \right}$ $\lambda_2 = \left{ 2 + \left(\frac{3E_1}{\delta} - 2\right)^2 \right}^{-1/2}$</td>
</tr>
<tr>
<td>$W = -(E_1 + E_2) = -\left{ \frac{\delta - \Delta}{2} + \sqrt{\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{\Delta}{3}} \right}$</td>
<td>$\lambda_3 \left{ \left(\frac{3(E_1 + E_2)}{\delta} - 2\right) z \uparrow - (x + iy) \downarrow \right}$ $\lambda_3 \left{ \left(\frac{3(E_1 + E_2)}{\delta} - 2\right) z \downarrow + (x - iy) \uparrow \right}$ $\lambda_3 = \left{ 2 + \left(\frac{3(E_1 + E_2)}{\delta} - 2\right)^2 \right}^{-1/2}$</td>
</tr>
</tbody>
</table>
Experimental Results

The electron spin resonance spectrum of CdS:Sb at 1.1°K consists of a single line with no apparent hyperfine structure. The asymmetry of the line was found to decrease as the microwave power incident on the sample was reduced. Typical traces for various power levels are shown in Figure 4.2.

The g-value was measured as a function of the angle θ between the magnetic field and the c-axis. The results and their fit to

\[ g^2 = g_1^2 \sin^2 \theta + g_\|^2 \cos^2 \theta \]

are shown in Figure 4.3. The results are tabulated in Table 4.2 and are compared with the results of other workers.
Figure 4.2 Spin Resonance of CdS:Sb at 1.1°K
Figure 4.3  The g-value as a Function of the Angle between the Magnetic Field and the C-axis
Table 4.2

Results for the Conduction Band g-tensor in CdS

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>Width Between Inflection Points (gauss)</th>
<th>True Half Width (gauss)</th>
<th>Approximate Number of Spins</th>
<th>Conditions of Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS:Sb</td>
<td>1.788±.0005</td>
<td>1.770±.0005</td>
<td>15</td>
<td>≈ 20</td>
<td>≈ 10^{16}</td>
<td>1.1°K</td>
</tr>
<tr>
<td>a CdS:Br</td>
<td>1.789±.001</td>
<td>1.771±.001</td>
<td>≈ 34</td>
<td>≈ 50</td>
<td>≈ 3x10^{17}</td>
<td>1.7°K</td>
</tr>
<tr>
<td>a CdS:I</td>
<td>1.785±.001</td>
<td>1.767±.001</td>
<td>12</td>
<td>≈ 17</td>
<td>≈ 2x10^{17}</td>
<td>1.7°K</td>
</tr>
<tr>
<td>a CdS(10% zn):I</td>
<td>1.796±.001</td>
<td>1.780±.001</td>
<td>15</td>
<td>≈ 20</td>
<td>≈ 2x10^{16}</td>
<td>1.7°K</td>
</tr>
<tr>
<td>b CdS:Cl</td>
<td>1.79</td>
<td>1.78</td>
<td>5</td>
<td>8</td>
<td>≈ 10^{17}</td>
<td>4.2°K</td>
</tr>
<tr>
<td>c CdS(Ga &gt; Cu)</td>
<td>1.792</td>
<td>1.775</td>
<td>10</td>
<td></td>
<td></td>
<td>77°K</td>
</tr>
<tr>
<td>d CdS</td>
<td>1.78±.05</td>
<td>1.72±.10</td>
<td>exciton spectrum</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Slagsvold and Schwerdtfeger (1965) (17)
b) Lambe and Kikuchi (1958) (18)
c) Dieleman (1962) (19)
d) Hopfield and Thomas (1961) (20)
Discussion

Calculations in the hydrogen-like approximation show that the donor binding energy is given by (12):

$$E = 13.6 \frac{m^*}{m} \frac{1}{\kappa^2} \text{ (eV)}$$

where $\kappa$ is the static dielectric constant of the semiconductor. For the case of CdS $\frac{m^*}{m} \approx 0.2$ and $\kappa \approx 10$ giving a value of $\approx 0.028$ eV for the binding energy. This agrees with photoconductivity measurements (13), which indicate that the halogens give rise to localized levels 0.03 eV below the conduction band. Since the g-values measured for CdS:Sb are nearly the same as for CdS doped with halogens it is reasonable to assume that Sb also enters the CdS substitutionally as a shallow donor and will have nearly the same binding energy.

The wave functions of the donor states are composed of Bloch functions from the bottom of the conduction band with a hydrogen-like envelope function centred about the donor site. On this basis one would expect that the g-value of the donor level should be quite close to that of the conduction band. The difference would appear only in the replacing of $E_g$ with $E_g$ minus 0.028 eV, a typical shallow donor binding energy. The spin-orbit and crystal field parameters can be calculated from equations 4.7, using $E_1 = 0.016$ eV and $E_2 = 0.057$ eV (see Figure 4.1) to be:
\[ \Delta = -0.0294 \text{ eV} \quad \text{(Hopfield model)} \]
\[ \Delta = -0.0596 \text{ eV} \quad \text{(Birman model)} \]

The Birman model \((\xi < |\Delta|)\) would account for less than a quarter of the observed g-shifts when only the valence band contributions are considered. Observations by Sobolev(14) indicate that the shift in energies, upon deformation, for optical transitions between the two upper valence bands and the conduction band, in CdS and CdSe, are different. This led Sandomirskii(15) to conclude that the Hopfield model \((\xi > |\Delta|)\) is the preferable model. For these reasons our discussion of the g-shifts will be based upon the Hopfield model.

Cardona(4) has considered the effect of an anti-symmetric perturbation on the bandstructure of a homopolar semiconductor like germanium. The perturbed wave functions for such a system are:

\[ \Psi_p(\Gamma_{15c}) = a \Psi(\Gamma_{15}) - b \Psi(\Gamma_{25}) \quad 4.14 \]
\[ \Psi_p(\Gamma_{15v}) = b \Psi(\Gamma_{15}) + a \Psi(\Gamma_{25}) \quad 4.15 \]

where \(a\) and \(b\) are constants which may be expressed in terms of the "unperturbed" energies. This perturbation has negligible effect on the \(\Psi(\Gamma_{21})\) state. Hence:

\[ \Psi_p(\Gamma_{1c}) = \Psi(\Gamma_{21}) \quad 4.16 \]

The wave function for the polar material can be substituted into equation 4.10, using the information that the
transition \( \int_{2}^{15} \) is forbidden, to give:

\[
|I|^2 = a^2 \frac{|I_{\text{homopolar}}|^2}{\mathcal{m}}
\]  \hspace{1cm} 4.17

A good overall agreement between predicted and observed values for effective masses and g-values of wurtzite-type materials is obtained using \( p^2 = 21 \text{ eV} \), where \( p^2 \) is defined by:

\[
p^2 = 2 \frac{|I_{\text{homopolar}}|^2}{\mathcal{m}}
\]  \hspace{1cm} 4.18

The expression for 'a' (equation 4, ref. 4) can be used, with the known band splittings for Ge and CdS, to obtain \( a^2 = 0.75 \). Equations 4.17 and 4.18 then give for the transition to the valence bands:

\[
\frac{2 |I|^2}{\mathcal{m}} = 15.7 \text{ eV}
\]  \hspace{1cm} 4.19

The g-shifts computed for equations 4.8 and 4.9 are \( \Delta g_\parallel = -0.10 \) and \( \Delta g_\perp = -0.06 \). These values are less than half the observed g-shifts, and predict the wrong anisotropy.

Cadmium selenide, having a band gap of only 1.84 eV, should give a much better agreement if the discrepancies are due to improper consideration of the structure of the upper conduction bands. A comparison of the parameters of CdS and CdSe are shown in Table 4.3.
Table 4.3

Band Parameters for CdS

<table>
<thead>
<tr>
<th>c/a</th>
<th>$g'$</th>
<th>$g''$</th>
<th>$\delta$ (eV)</th>
<th>$\Delta$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$E_{g_c}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>1.623</td>
<td>1.785</td>
<td>1.767</td>
<td>0.0596</td>
<td>-0.0294</td>
<td>2.58$^a$</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.63</td>
<td>0.6$^{\pm}0.1^b$</td>
<td>0.51$^{\pm}0.05$</td>
<td>0.44$^c$</td>
<td>-0.04$^c$</td>
<td>1.84$^a$</td>
</tr>
</tbody>
</table>

a) Cardona (1963a)$^{(4)}$  
b) Sobolev (1964)$^{(14)}$  
c) Dimmock & Wheeler (1961)$^{(21)}$

$E_g$ is the energy separation between conduction bands.

The contribution to the g-shift from a group of states separated by an energy $E$, will be approximately proportional to $\frac{2|I|^2}{mE^2}$, where $|I|$ is the matrix element between the states and the band for which the g-shift is being calculated. The relative importance of the valence and conduction bands is given by

$$\frac{a^2}{1 - a^2} \cdot \frac{\delta}{\delta_c} \cdot \frac{E_g^2}{E_{g_c}^2} \quad 4.20$$

Although $\frac{\delta}{\delta_c}$ is not known, it should be of the order of unity. The expression (equation 4.20) has a value of 6 for CdS and
16 for CdSe. This gives a g-value of \( \approx 0.84 \) for CdSe. From equations 4.8 and 4.9 it is found that \( \Delta g_\kappa = -1.15 \) and \( \Delta g_\lambda = -1.06 \). This also has the incorrect anisotropy.

These results indicate that the quasi-cubic model is inadequate for calculations of the g-tensor. If all the constants in expressions 4.3 are allowed to be non-zero there will be additional terms in equations 4.8 and 4.9. Since these terms are difficult to estimate only a modification of the existing expressions will be considered here.

Hopfield \(^{15}\) has shown that the value of 'c' (equation 4.3) for the \( \Gamma_7 \) valence band should be at most of the order of \( \sqrt{A \over E_g} \). This then gives for the normalizing constants \( \lambda_2 \) and \( \lambda_3 \) (see Table 4.1), that:

\[
\lambda^2 = \frac{\lambda_2 g_c}{1 + \Delta \over E_g}
\]

4.21

The values of \( \Delta \over E_g \) for CdS and CdSe are \( \approx 0.01 \) and 0.02 respectively, indicating 1% and 2% lower values for \( \lambda \)'s.

Using the g-tensors of Table 4.3 and ignoring any possible contribution from the upper conduction bands, it is possible to estimate the amount of s-part admixture to the valence bands by treating \( \lambda_2 \) and \( \lambda_3 \) as parameters. The results, showing the expected order of magnitude admixtures, are given in Table 4.4.
Table 4.4
Comparison of λ's Obtained from Quasi-cubic Model
and from Fit of the g-tensor

<table>
<thead>
<tr>
<th></th>
<th>λ_2^2</th>
<th>λ_2^2</th>
<th>%</th>
<th>λ_3^2</th>
<th>λ_3^2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>quasi-cubic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reduction</td>
<td>1</td>
<td></td>
<td></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdS</td>
<td>0.292</td>
<td>0.289</td>
<td>1</td>
<td>0.208</td>
<td>0.200</td>
<td>4</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.1875</td>
<td>0.1875</td>
<td>0</td>
<td>0.321</td>
<td>0.289</td>
<td>10</td>
</tr>
</tbody>
</table>

It should be noted at this point that Hopfield and Thomas allowed a 15% s-part admixture to the valence states to account for the intensities of the exciton lines in CdS.

These considerations show that a generalization of the expression for cubic germanium-like semiconductors within the framework of the quasi-cubic model does not adequately explain the observed g-shift. Moreover, it gives the wrong sign for the anisotropy of the g-value for both CdS and CdSe. Allowing small s-part admixtures to the valence band states though, does make it possible to fit the observed g-tensors to the formulae. This suggests that more complete knowledge of the band structure is required to give a good correspondence between theory and experiment for the g-tensor in CdS and CdSe.
The Linewidth

Since the hyperfine structure due to the magnetic moments of the donor nuclei disappears in the impurity band region\(^{(2)}\), it is not unexpected that the observed lines show no structure.

If the resonance line for CdS:Sb is compared to those of CdS doped with halogens, then Table 4.5 would suggest that the linewidth for the antimony doped sample should be of the same order, or slightly greater than that of the iodine or bromine doped samples. This is in fact the case, although, because of the asymmetric lines the line shapes are not reliable enough to make a good comparison.
Table 4.5
Spins and Magnetic Moments of Donor Nuclei\(^{(a)}\)

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural Abundance</th>
<th>Spin</th>
<th>Magnetic Moment in Nuclear Bohr Magnetons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^{35})</td>
<td>75.4%</td>
<td>(\frac{3}{2})</td>
<td>0.82</td>
</tr>
<tr>
<td>Cl(^{37})</td>
<td>24.6%</td>
<td>(\frac{3}{2})</td>
<td>0.68</td>
</tr>
<tr>
<td>Br(^{79})</td>
<td>50.52%</td>
<td>(\frac{3}{2})</td>
<td>2.10</td>
</tr>
<tr>
<td>Br(^{81})</td>
<td>49.48%</td>
<td>(\frac{3}{2})</td>
<td>2.26</td>
</tr>
<tr>
<td>I(^{127})</td>
<td>100%</td>
<td>(\frac{5}{2})</td>
<td>2.79</td>
</tr>
<tr>
<td>Sb(^{121})</td>
<td>57.25%</td>
<td>(\frac{5}{2})</td>
<td>3.34</td>
</tr>
<tr>
<td>Sb(^{123})</td>
<td>42.75%</td>
<td>(\frac{7}{2})</td>
<td>2.53</td>
</tr>
</tbody>
</table>

Conclusions

A 3 cm microwave spectrometer employing straight crystal detection and 400 Hz field modulation has been assembled and shown to have a sufficient sensitivity to allow detection of various ESR signals in semiconductors such as silicon and cadmium sulphide. In particular, good signal to noise ratios were obtained at liquid He temperatures from an antimony-doped single crystal of CdS with a room temperature carrier concentration around $2 \times 10^{16}$ cm$^{-3}$. The single ESR line observed in this crystal is believed to be due to electrons in an impurity band about 0.03 eV below the bottom of the conduction band. The width of this line was about 3 times larger than that of a line reported seen in CdS:Cl. This is less than the ratio of the nuclear magnetic moments of the donor nuclei which is $\frac{\mu_s}{\mu_i} \approx 4$.

The $g$-value in CdS:Sb differs only slightly from those of CdS:Br and CdS:I, and like them exhibits a small anisotropy in the uniaxially symmetric $g$-tensor, with $g_\parallel - g_\perp = 0.018$.

It was found that knowledge of the bandstructure of CdS is insufficiently accurate to allow an unambiguous explanation of the $g$-tensor. Good agreement with experiment for CdSe and CdS can be obtained by considering only the
valence bands if small corrections are made to the quasi-
cubic model.

The reason for the highly asymmetric line is not
known at this stage but further work is planned on this
problem.
APPENDIX A

Calculation of the Valence Band States in Wurtzite

The total wave function of the valence band edge for a cubic semiconductor without inversion symmetry transforms as $\Gamma_7 + \Gamma_8$. The basis functions may be chosen as:

$\Gamma_8$: $\{3/2,3/2\} = \frac{1}{\sqrt{2}} (x + iy) \uparrow = |1\rangle$

$\{3/2,1/2\} = \frac{1}{\sqrt{6}} (2z \uparrow + (x + iy) \downarrow) = |2\rangle$

$\{3/2,-1/2\} = \frac{1}{\sqrt{6}} (2z \downarrow - (x - iy) \uparrow) = |3\rangle$

$\{3/2,-3/2\} = \frac{1}{\sqrt{2}} (x - iy) \downarrow = |4\rangle$

$\Gamma_7$: $\{1/2,1/2\} = \frac{1}{\sqrt{3}} (z \uparrow - (x + iy) \downarrow) = |5\rangle$

$\{1/2,-1/2\} = \frac{1}{\sqrt{3}} (z \downarrow + (x - iy) \uparrow) = |6\rangle$

The $\Gamma_7$ and $\Gamma_8$ states are split by an amount $\delta$ due to the spin-orbit interaction. The spin-orbit energy is diagonal in this representation and has the matrix:

$$H_{s-o} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \delta & 0 \\
0 & 0 & 0 & 0 & 0 & \delta
\end{pmatrix}$$
At this point it is convenient to transform to a representation with the basis $x^\uparrow, y^\uparrow, z^\downarrow, x^\downarrow, y^\downarrow, z^\uparrow$ since strain is diagonal in this representation. If the original basis is $u_n$, and the new basis is $v_n$, then we can write:

$$u_n = B_{in} v_i$$

where $B_{in}$ are elements of the unitary matrix $B$. This then gives the result:

$$H^u = B^\dagger H^v B$$

or

$$H^v = B H^u B^\dagger$$

Consideration of the basis functions gives:

$$B = \begin{pmatrix} 1/\sqrt{2} & 0 & -1/\sqrt{6} & 0 & 0 & 1/\sqrt{3} \\ i/\sqrt{2} & 0 & i/\sqrt{6} & 0 & 0 & -i/\sqrt{3} \\ 0 & 0 & 2/\sqrt{6} & 0 & 0 & 1/\sqrt{3} \\ 0 & 1/\sqrt{6} & 0 & 1/\sqrt{2} & -1/\sqrt{3} & 0 \\ 0 & i/\sqrt{6} & 0 & -i/\sqrt{2} & -i/\sqrt{3} & 0 \\ 0 & 2/\sqrt{6} & 0 & 0 & 1/\sqrt{3} & 0 \end{pmatrix}$$

as the transformation matrix. This can be applied to $H_{s-o}$ to give:

$$H_{\text{tran}} = B H_{s-o} B^\dagger$$

where,
The total Hamiltonian, neglecting admixtures, then becomes:

\[
H = \begin{pmatrix}
\gamma & i\gamma & \gamma & 0 & 0 & 0 \\
-i\gamma & \gamma & -i\gamma & 0 & 0 & 0 \\
\gamma & i\gamma & \gamma + \delta & 0 & 0 & 0 \\
0 & 0 & 0 & \gamma & -i\gamma & -\gamma \\
0 & 0 & 0 & i\gamma & \gamma & -i\gamma \\
0 & 0 & 0 & -\gamma & i\gamma & \gamma + \delta \\
\end{pmatrix}
\]

where \( \gamma = \frac{\delta}{3} \)

The eigenvalues of \( H \) may be found by solving the secular determinant \( |H_{ij} - \lambda I| = 0 \). The solutions are:

\[
W_{1,2} = 0 \\
W_{3,4} = \frac{\Delta + \delta}{2} + \sqrt{\left(\frac{\Delta - \delta}{2}\right)^2 + \frac{\delta \Delta}{3}} \\
W_{5,6} = \frac{\Delta + \delta}{2} - \sqrt{\left(\frac{\Delta - \delta}{2}\right)^2 + \frac{\delta \Delta}{3}}
\]
All of which are doubly degenerate as required by Kramer's theorem.

In the materials of interest $\delta$ is a positive quantity, so it is convenient to change its sign, to give:

$$W_{1,2} = 0$$

$$W_{3,4} = \frac{\Delta - \delta}{2} + \sqrt{\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{\delta \Delta}{3}}$$

$$W_{3,6} = \frac{\Delta - \delta}{2} - \sqrt{\left(\frac{\delta + \Delta}{2}\right)^2 - \frac{\delta \Delta}{3}}$$

To find the new basis functions it is necessary to solve the equation:

$$S (H - W I) = SW$$

This can be broken down into a number of sets of simultaneous equations:

$$S_{i1}H_{11} + S_{i2}H_{21} + S_{i3}H_{31} = W_{i}S_{i1}$$

$$S_{i1}H_{12} + S_{i2}H_{22} + S_{i3}H_{32} = W_{i}S_{i2} \quad i = 1, 3, 5.$$  

$$S_{i1}H_{13} + S_{i2}H_{23} + S_{i3}H_{33} = W_{i}S_{i3}$$

$$S_{i4}H_{44} + S_{i5}H_{54} + S_{i6}H_{64} = W_{i}S_{i4}$$

$$S_{i4}H_{45} + S_{i5}H_{55} + S_{i6}H_{65} = W_{i}S_{i5} \quad i = 2, 4, 6$$

$$S_{i4}H_{46} + S_{i5}H_{56} + S_{i6}H_{66} = W_{i}S_{i6}$$

which can be solved to give:
\[
S = \begin{pmatrix}
1/\sqrt{2} & -i/\sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1/\sqrt{2} & i/\sqrt{2} & 0 \\
-\lambda_2 & -i\lambda_2 & -(\frac{W_2}{\gamma^2}-2)\lambda_2 & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_2 & -i\lambda_2 & -(\frac{W_2}{\gamma^2}-2)\lambda_2 \\
\lambda_3 & i\lambda_3 & (\frac{W_3}{\gamma^2}-2)\lambda_3 & 0 & 0 & 0 \\
0 & 0 & 0 & -\lambda_3 & i\lambda_3 & (\frac{W_3}{\gamma^2}-2)\lambda_3
\end{pmatrix}
\]

where \( \lambda_i = (2 + (\frac{W_i}{\gamma^2} - 2)^2)^{-\frac{1}{2}} \)

The new basis functions can now be obtained through

\[
v_n = S_{in}\varphi_i
\]

\[
\varphi_i = S^{-1}_{np}v_n = (S^*)_{np}v_n = S^*_{pn}v_n
\]

where \( \varphi_i \) are the new basis functions. The final results of this calculation are given in Table 4.1.
APPENDIX B

Calculation of the Valence Band Contribution to the g-shift

The electronic g-value at a band edge is given by:\(^{(1)}\)

\[
g_n = 2 + \frac{4}{m} M
\]

where

\[
M = \text{Im} \sum_{n \neq 0} \frac{\langle 0 | p_x | n \rangle \langle n | p_y | 0 \rangle}{E_0 - E_n}
\]

\[
\text{Im} \sum_{n \neq 0} \frac{\langle 0 | p_x | n \rangle \langle 0 | p_y | n \rangle^*}{E_0 - E_n}
\]

The momentum operators are defined by:

\[
p_x | \Psi \rangle = -i \frac{\partial}{\partial x} | \Psi \rangle
\]

\[
p_y | \Psi \rangle = -i \frac{\partial}{\partial y} | \Psi \rangle
\]

The states to be considered are:

**Conduction band:** \[ s \uparrow + a_z \uparrow + \frac{1}{2} b \uparrow (x + iy) \downarrow = | 0 \rangle \]

**\( \Gamma_9 \) valence band:** \[-\sqrt{2} (x + iy) \uparrow = | 1 \rangle \]

\[
\sqrt{2} (x - iy) \downarrow = | 2 \rangle
\]

**Upper \( \Gamma_7 \) valence band:** \[ s_1 \uparrow + a_1 z \uparrow + \frac{1}{2} b_1 (x + iy) \downarrow = | 3 \rangle \]

**Lower \( \Gamma_7 \) valence band:** \[ s_2 \uparrow + a_2 z \uparrow + \frac{1}{2} b_2 (x + iy) \downarrow = | 5 \rangle \]

**Lower \( \Gamma_7 \) valence band:** \[ s_2 \downarrow + a_2 \downarrow + \frac{1}{2} b_2 (x - iy) \uparrow = | 6 \rangle \]
Applying the momentum operators to these states gives:

\[ p_x |1\rangle = \frac{1}{\sqrt{2}} \uparrow \quad p_y |1\rangle = -\frac{1}{\sqrt{2}} \uparrow \]
\[ p_x |2\rangle = -\frac{i}{\sqrt{2}} \downarrow \quad p_y |2\rangle = -\frac{1}{\sqrt{2}} \downarrow \]
\[ p_x |3\rangle = -iS_1 \left( \frac{x}{r} \right) \uparrow - \frac{i}{2}b_1 \downarrow \quad p_y |3\rangle = -iS_1 \left( \frac{y}{r} \right) \uparrow + \frac{1}{2}b_1 \downarrow \]
\[ p_x |4\rangle = -iS_1 \left( \frac{x}{r} \right) \downarrow + \frac{i}{2}b_1 \uparrow \quad p_y |4\rangle = -iS_1 \left( \frac{y}{r} \right) \downarrow + \frac{1}{2}b_1 \uparrow \]
\[ p_x |5\rangle = -iS_2 \left( \frac{x}{r} \right) \uparrow - \frac{i}{2}b_2 \downarrow \quad p_y |5\rangle = -iS_2 \left( \frac{y}{r} \right) \uparrow + \frac{1}{2}b_2 \downarrow \]
\[ p_x |6\rangle = -iS_2 \left( \frac{x}{r} \right) \downarrow + \frac{i}{2}b_2 \uparrow \quad p_y |6\rangle = -iS_2 \left( \frac{y}{r} \right) \downarrow + \frac{1}{2}b_2 \uparrow \]

If these are now used in the expression for \( M \), one gets

\[ M = \text{Im} \left\{ \frac{2}{E_g} \left[ \frac{1}{2} \int s^* d\tau \right] \left[ -\frac{1}{2} \int s d\tau \right] + \right. \]
\[ \left. \frac{1}{E_g + E_1} \left[ \frac{1}{2}b^*(-i) \int S_1 \left( \frac{x^2}{r} \right) d\tau + \frac{1}{2}b_1 \int s^* d\tau \right] \right. \]
\[ \left. - \frac{1}{2}b \int S_1^* \left( \frac{y^2}{r} \right) d\tau + \frac{1}{2}b_1 \int s d\tau \right] + \frac{1}{E_g + E_1 + E_2} \left[ \frac{1}{2}b^*(-i) \int S_2 \left( \frac{x^2}{r} \right) d\tau + \frac{1}{2}b_2 \int s^* d\tau \right] \]
\[ - \frac{1}{2}b \int S_2^* \left( \frac{y^2}{r} \right) d\tau + \frac{1}{2}b_2 \int s d\tau \right\} \]

Defining \( I_0 = \int s d\tau \), \( I_1 = \int S_1 \left( \frac{x^2}{r} \right) d\tau = \int S_1^* \left( \frac{y^2}{r} \right) d\tau \), \( I_2 = \int S_2 \left( \frac{x^2}{r} \right) d\tau = \int S_2^* \left( \frac{y^2}{r} \right) d\tau \), and substituting them into the equation for \( M \), one obtains:
\[
M = \frac{2}{E_g} \left( -\frac{1}{4} \right) \left| I_o \right|^2 + \frac{1}{E_g + E_1} \frac{1}{4} \left[ \left| b_1 \right|^2 \left| I_1 \right|^2 + \left| b_1 \right|^2 \left| I_o \right|^2 - 2 \text{Re} b^* b_1 I_o I_1 \right] + \frac{1}{E_g + E_1 + E_2} \frac{1}{4} \left[ \left| b_2 \right|^2 \left| I_2 \right|^2 + \left| b_2 \right|^2 \left| I_o \right|^2 - 2 \text{Re} b^* b_2 I_o I_2 \right]
\]

\[M = -\frac{1}{4} \left[ \left| I_o \right|^2 \left( \frac{2}{E_g} - \frac{\left| b_1 \right|^2}{E_g + E_1} - \frac{\left| b_2 \right|^2}{E_g + E_1 + E_2} \right) - \left| b \right|^2 \left( \frac{\left| I_1 \right|^2}{E_g + E_1} + \frac{\left| I_2 \right|^2}{E_g + E_1 + E_2} \right) - 2 \text{Re} \left( \frac{b^* b_1 I_o I_1}{E_g + E_1} + \frac{b^* b_2 I_o I_2}{E_g + E_1 + E_2} \right) \right]\]

If the conduction band is assumed to be a pure s-state, \(a=b=0\)

\[M = -\frac{1}{4} \left( \frac{\left| I_o \right|^2}{2} \left( \frac{1}{E_g} - \frac{\left| b_1 \right|^2}{E_g + E_1} - \frac{\left| b_2 \right|^2}{E_g + E_1 + E_2} \right) \right)\]

Comparison of the states \(|n\rangle\) with those in Table 4.1 gives:

\[\frac{1}{4} \left| b_1 \right|^2 = 2 \lambda_2^2 \quad \text{and} \quad \frac{1}{4} \left| b_2 \right|^2 = 2 \lambda_3^2\]

And hence:

\[g_n = 2 - \frac{2 \left| I_o \right|^2}{m} \left( \frac{1}{E_g} - \frac{2 \lambda_2^2}{E_g + E_1} - \frac{2 \lambda_3^2}{E_g + E_1 + E_2} \right)\]

A similar calculation can be done to give:

\[g_4 = 2 + \frac{2 \left| I_o \right|^2}{m} \left\{ \frac{2 \lambda_2^2}{E_g + E_1} \left( \frac{3E_1}{\delta} - 2 \right) + \frac{2 \lambda_3^2}{E_g + E_1 + E_2} \left( \frac{3(E_1 + E_2)}{\delta} - 2 \right) \right\}\]


