EPR STUDY OF CdIn$_2$S$_4$

by

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We accept this thesis as conforming to the

required standard

THE UNIVERSITY OF BRITISH COLUMBIA

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Department of Physics

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Date Nov. 25 / 1971
ABSTRACT

Properties of CdIn$_2$S$_4$ have been studied using EPR. The temperature dependence of the hyperfine interaction for Mn$^{2+}$ impurities has been measured over the range 1 K - 450 K. The results have been interpreted using both the localized vibration model and the interaction with the phonon continuum. The g-tensor for Co$^{2+}$ dopants has been determined, yielding $g_\perp = 4.07 \pm 0.15$, $g_\parallel = 6.00 \pm 0.05$ with the distortion axes along the four $\langle 111 \rangle$ directions. Both Mn$^{2+}$ and Co$^{2+}$ have a preference to substitute at a "B" site in the crystal. A 'conduction electron' signal that is dependent on the sulphur vacancy concentration has been observed with an isotropic $g = 1.68 \pm 0.005$. The $g$-value for a resonance ascribed to surface states was found to be 1.70. Strain experiments indicate that the band gap is most probably a direct one. Preliminary studies of production of sulphur vacancies by heat treatment and light excitation of electrons have been performed.
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CHAPTER 1 - INTRODUCTION

1.1 GENERAL INTRODUCTION

CdIn$_2$S$_4$ is a semiconductor that crystallizes in a cubic spinel form. Unlike most spinels it is neither ferri-, ferro- or antiferro-magnetic. It has a band gap of approximately 2 eV at room temperature. Optical properties such as photoluminescence and photoconductivity have been extensively studied but few EPR (electron paramagnetic resonance) experiments have been performed until the past year. Thus the substance is well suited for a general EPR study of its properties.

The unusual features of the material include a Landau-type second order phase transition at 403 °K and an inability of X-rays to determine the true crystal structure *. Other properties such as band structure and crystal field parameters are intrinsically interesting.

1.2 MOTIVATIONS

Owing to the nature of the study it is clarifying to present the purpose of the experiments in tabular form. The aims of the work are:

(i) to investigate the prediction of Czaja and Krausbauer (1969) that there exist discrete energy levels within the band gap inherent to the intrinsic crystal structure. It is possible that these levels could exhibit an EPR signal if they were occupied by electrons.

(ii) to elucidate the nature of the luminescent centers by the study of deep donors (transition ions) and shallow donors (in this case, sulphur vacancies).

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* This is because Cd$^{2+}$ and In$^{3+}$ have the same number of electrons around the positive nuclear core.
(iii) to undertake a general EPR study of the material with the ultimate aim of discussing the site assignment of impurities within the crystal.

(iv) to study the reported second order phase transition at 403 °K (Czaja, 1969) both by observing the Mn$^{2+}$ resonance as the crystal is heated through the transition temperature and by heat treating the samples prior to a low temperature EPR experiment.

(v) to observe the Mn$^{2+}$ spectrum, relate the temperature dependence to local or bulk properties of the crystal and establish a site assignment for the impurity.

(vi) to try to resolve the problem of the crystal structure which may be one of; a normal spinel, a partially inverted spinel, or a fully inverted spinel.

(vii) to observe an EPR signal from 'conduction electrons' so that the g-value may be related to band parameters and compared to other related materials.

(viii) to investigate the physical production of sulphur vacancies and the associated EPR signal.

(ix) to elucidate the nature of the band gap (direct or indirect) by applying uniaxial stress to a sample doped with sulphur vacancies.

(x) to make a preliminary study of the effect of illuminating the samples with white light.

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*For example the cations have two possible sites having tetrahedral and octahedral symmetries respectively.

**The difference between these is a rearrangement of Cd and In on the cation sites.

***In practice it is impossible to determine whether the electrons are in a donor band or in the conduction band, using EPR alone.
THESIS OUTLINE

Chapter 2 contains a description of the samples used in the experiments and a literature survey of CdIn$_2$S$_4$. Emphasis is also placed on the CdS - CdIn$_2$S$_4$ - In$_2$S$_3$ system.

Chapter 3 contains a brief description of the apparatus and a discussion of sensitivity.

Chapter 4 contains both experimental results and immediate conclusions for the transition ions Mn$^{2+}$ and Co$^{2+}$. An introduction to EPR, in general, and to crystal field theory, in particular, is presented.

Chapter 5 centers about the observed 'conduction electron' resonance along with additional studies of applied strain, light illumination, and the production of sulphur vacancies. A brief introduction to g-value theory for banded electrons is given.

Chapter 6 contains general conclusions and a list of additional experiments that could be performed.
CHAPTER 2 - LITERATURE SURVEY: SAMPLES

2.1 SAMPLES

CdIn$_2$S$_4$ is a semiconductor that may range in color and opacity from an almost-transparent deep red to an opaque black depending on the dopant and its concentration. All the crystals investigated were very brittle and chipped easily. CdIn$_2$S$_4$ has a melting point of 1105 °C and is conveniently synthesized by two main techniques;

(i) directly from the melt in closed quartz ampoules under excess sulphur vapor pressure *(Czaja and Krausbaier, 1969; Henning et al., 1969; Shand, 1969).

(ii) from the elemental vapors using chemical transport with iodine as the transporter (Beun and Nitsche, 1960; Boorman, 1970; Abdulaev et al., 1969).

The crystals for this thesis were obtained from sources utilizing both of these techniques (Appendix 1). Dr. W. Czaja generously supplied us with a large complement of samples grown using the first technique. Several other samples grown using the second method were obtained commercially from the New Brunswick Research and Productivity Council (NBRPC). These crystals were close to perfect octahedra with all faces being (111) planes. This facilitated the orientation of the samples and X-ray analysis proved unnecessary.

Dr. Czaja's samples had dislocation counts as low as 10$^4$ - 10$^5$ cm.$^{-2}$ for pure samples and the impurities had concentrations of 10$^{16}$ - 10$^{17}$ cm.$^{-3}$.

*Sometimes called the Stockbarger Technique (Shand, 1969).
The crystals supplied by NBRPC also had impurity counts of \(10^{16} - 10^{17}\) cm\(^{-3}\). No data is available on their dislocation counts but normally crystals grown from the vapor phase are relatively free of dislocations (Boormen, 1970).

### 2.2 Crystal Structure

\(\text{CdIn}_2S_4\) crystallizes in the spinel form having the same space group, \(O_h^7 (Fd\overline{3}m)\), as the diamond structure. The primitive rhombohedral unit cell contains two formula units. The face centered, cubic, compound cell contains eight formula units of \(\text{CdIn}_2S_4\) and has a lattice constant of 10.797 Å. Because of the complexity of the compound cell the problem is normally reduced to a consideration of the two cation sites in the substance (Figure 2.1).

These sites are generally referred to as "A" and "B" sites in the literature for all spinels. The notation is derived from antiferromagnetic spinels which have spins aligned on "A" and "B" superlattices.

If \(\text{CdIn}_2S_4\) were a normal spinel the "A" site would be occupied by a Cd atom and the "B" site by an In atom. However, it is very difficult--if not impossible--to distinguish between Cd\(^{2+}\) and In\(^{3+}\) ions by conventional X-ray techniques, since they are isoelectronic. It is only by indirect methods that one can determine the actual structure for this spinel (Suchow and Stemple, 1964). In the absence of any direct determination three possible structures have been suggested;

1. Normal spinel: \([\text{Cd}][\text{In}_2]S_4\)
2. Partially inverted spinel: \([\text{Cd}_{1/2}\text{In}_{1/2}][\text{Cd}_{1/2}\text{In}_{3/2}]S_4\)
3. Fully inverted spinel: \([\text{Cd}_{1/3}\text{In}_{2/3}][\text{ Cd}_{2/3}\text{In}_{4/3}]S_4\)

*where \{\} \equiv \text{tetrahedral, "A", site and [ ] \equiv \text{octahedral, "B", site.}
FIGURE 2.1 The normal cubic spinel structure for CdIn$_2$S$_4$. 
The essential difference between (ii) and (iii) is that in (ii) the Cd atoms are equally distributed on the "A" and "B" sites while in (iii) the Cd atoms are randomly distributed on the two sites.

2.3 PHASE TRANSITION

Czaja (1970) measured $C_p(T)$, the specific heat, and discovered an anomaly in $C_p$ at 403 °K that he attributed to a second order phase transition of the Landau type (order - disorder). This anomaly was approximately a 10% change in $C_p$ over a temperature range of ~5 °K. Very long times (~20 hours) were required for the establishment of internal equilibrium in the best crystals. However, when the samples were heat treated at 500 °C, sublimating sulphur from the samples to create sulphur vacancies, the relaxation times to establish internal equilibrium were lowered to a few hours.

A Landau type second order phase transition can only occur in this crystal if the structure is of type (ii), the partially inverted spinel, due to group theoretical arguments (Haas, 1965). The order - disorder transition is then due to a reordering of the Cd and In ions on the "A" sites. Above 403 °K they are distributed randomly on the sites, while below 403 °K they are arranged in a diamond type superlattice at these sites.
2.4 OPTICAL EXPERIMENTS

After the original synthesis and X-ray studies on CdIn$_2$S$_4$ powders by Hahn and Klinger (1950), most of the work reported in the literature has been optical in nature owing to the high photosensitivity of the compound.

The first experiments (performed at room temperature) measured the photoconductivity of CdIn$_2$S$_4$ (Bube and McCarroll, 1959; Beun and Nitsche, 1960; Koelmans and Grimmeiss, 1959). A peak in conductivity with optical excitation less than the band gap was observed. A dependence of intrinsic dark conductivity on sulphur vapor pressure above the crystal-forming melt was noted by Koelmans and Grimmeiss. Hall measurements of Beun and Nitsche indicated that all of their samples were n-type. Later experiments extended the photoconductivity measurements to 77 °K (Boltivets et al., 1969; Abdullaev et al., 1969). Abdullaev et al. demonstrated the significance of sulphur deficiency on the photoconductivity spectrum.

The next set of experiments were photoluminescence studies (Springford, 1963; Suchow and Stemple, 1964; Czaja and Krausbauer, 1969) performed from 6 °K up to 300 °K. Springford and Czaja both saw two maxima in the emission spectrum. Springford attributed the luminescent centers to "anion complexes in the region of cation vacancies". Czaja refined this model by using the partially inverted spinel structure to label the two sites as Cd ions at "B" sites and In ions at "A" sites, each in conjunction with a nearby sulphur vacancy. Heat treatment changed the spectra but no clear relationship could be established between the length of time the sample was treated and the intensity of the observed luminescence.
Electroluminescence was studied by Suchow and Stemple but no quantitative results were reported. Thermoluminescence experiments were carried out by Springford (1963).

Band gap energies were measured by several authors and may best be presented in tabular form:

<table>
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<th>$E_g$</th>
<th>Experimenter</th>
<th>Temperature</th>
<th>Method</th>
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<tr>
<td>2.18  eV</td>
<td>Bube et al., 1959</td>
<td>300 °K</td>
<td>Photoconductivity</td>
</tr>
<tr>
<td>2.2   eV</td>
<td>Koelmanns et al., 1959</td>
<td>300 °K</td>
<td>Optical absorption</td>
</tr>
<tr>
<td>2.35  eV</td>
<td>Springford, 1963</td>
<td>90 °K</td>
<td>Diffuse reflectivity</td>
</tr>
<tr>
<td>2.3   eV</td>
<td>Beun et al., 1960</td>
<td>300 °K</td>
<td>Optical absorption</td>
</tr>
<tr>
<td>2.3   eV</td>
<td>Abdullaev et al., 1969</td>
<td>77 °K</td>
<td>Optical absorption</td>
</tr>
<tr>
<td>2.37  eV</td>
<td>Czaja et al., 1969</td>
<td>77 °K</td>
<td>Optical absorption</td>
</tr>
<tr>
<td>2.22  eV</td>
<td>Czaja et al., 1969</td>
<td>300 °K</td>
<td>Optical absorption</td>
</tr>
</tbody>
</table>

TABLE 2.1 Experimental band gap values

2.5 EPR EXPERIMENTS

EPR in CdIn$_2$S$_4$ has a short history, the first report appearing two years ago. This work was that of Czaja and Krausbauer (1969) who did EPR on a Mn doped sample. They observed the characteristic six line hyperfine spectrum ($I = 5/2$) for the Mn$^{2+}$ ion and from the hyperfine splitting constant, $A$, deduced the amount of covalent bonding present in the host.*

Next, Henning et al (1969) published EPR data for Cr doped samples. They concluded from the properties of the spectra that they observed Cr$^{3+}$ at "B" sites. A distortion axis in the $\langle 111 \rangle$ directions was established and values of $g_u = 1.995 \pm .005$, $g_L = 2.000 \pm .005$ and $D = -(0.187 \pm .002)$ cm.$^{-1}$ were measured.

* for a discussion of the theory of this effect see Chapter 4.
Then, Brown et al. (1970a, 1970b) published papers on Er and Yb doped samples. Both were found to substitute as triply positive charged ions at "B" sites having distortion axes in the \langle111\rangle directions. For Yb\(^{3+}\) they found \(g_\| = 3.45 \pm 0.05\) and \(g_\perp = 2.00 \pm 0.05\) while for Er\(^{3+}\) the results were \(g_\| = 1.90 \pm 0.05\) and \(g_\perp = 9.0 \pm 2.0\). Optical data supported the site assignments. By analysing the crystal field splitting in terms of a point charge model they found that Czaja's model of a partially inverted spinel gave better agreement with experiment than either a normal, or a fully inverted spinel. However their results were far from conclusive.

It is interesting to note that in all work published where an impurity site is investigated the cation always sits at a "B" site regardless of its charge state.

2.6 BAND CALCULATIONS

Since the primitive cell of CdIn\(_2\)S\(_4\) contains two formula units and thus 64 valence electrons it is very difficult to carry out any worthwhile band structure calculations. The first person to attempt the problem was Rehwald (1967) who used the nearly free electron model. The main result was the identification of symmetry properties of the bands. Then he applied the model pseudopotential of Heine, Abarenkov and Animalu as a perturbation to the nearly free electron model (Figure 2.2), thus obtaining representative energy levels for high symmetry points in the Brillouin Zone. He also did a rough tight binding calculation (Figure 2.2). From this work no prediction as to whether the band gap is direct or indirect could be made.

The next attempt was by Meloni and Mula (1970) who used an empirical pseudopotential and a simplified model of the actual crystal structure in
FIGURE 2.2 Theoretical band structures of CdIn$_2$S$_4$
order to circumvent the problem of the large number of valence electrons in the unit cell (Figure 2.2). They chose a fictitious unit cell containing 1/4 of a formula unit. Their predictions include a valence band maxima essentially the same as Rehwald's, but they predict an indirect band gap of ~2.1 eV with the minima in the <111> directions. Czaja (1969) also predicted an indirect gap based on a simple argument. He reasoned that since In$_2$S$_3$ was known to have an indirect gap (Rehwald and Harbeke, 1965) and a continuous mixture between CdIn$_2$S$_4$ and In$_2$S$_3$ existed as single crystals, then CdIn$_2$S$_4$ was likely to have an indirect gap. As yet this prediction has not been verified directly by experiment.

2.7 THE CdS - CdIn$_2$S$_4$ - In$_2$S$_3$ SYSTEM

CdS is an extensively studied binary compound because of its photosensitivity and piezoelectric properties. It crystallizes in the Wurtzite structure which is non-cubic. The effect of heat treatment on both optical and EPR spectra has been thoroughly studied (Brailsford and Woods, 1968; Boer and Kennedy, 1967). Optical absorptions and EPR signals have been attributed to both Cd and S vacancies. The S vacancy was found to contribute an EPR line characteristic of a shallow donor and was also found to be sensitive to light illumination of the sample (Morigaki, 1964).

Until recently no single crystal intermediate mixtures of the CdS - CdIn$_2$S$_4$ system have been reported, however Boorman has privately communicated that he has succeeded in synthesizing single crystals of stoichiometric composition within the mixture by using vapor transport techniques for growth.

The other side of the system, CdIn$_2$S$_4$ - In$_2$S$_3$, is perhaps more
interesting because of the existence of continuous mixtures of the form \( \text{Cd}_{1-x}\text{In}_{2(1+x/3)}\text{S}_4 \). The mixed crystals, as well as the two end products, have a spinel structure. They have been studied optically by Czaja and Krausbauer (1969) and Suchow and Stemple (1964). Czaja found that the optical energy gaps of the crystals varied linearly with \( x \) in the mixture formula to an accuracy of \( 1\% \) at \( 77^\circ \text{K} \). Luminescence spectra were also observed as a function of \( x \).

Pure \( \text{In}_2\text{S}_3 \) crystallizes in two phases, \( \alpha \) and \( \beta \). There is an irreversible transition from \( \alpha \) to \( \beta \) at \( 330^\circ \text{C} \) (Hahn and Klinger, 1950), and thus from normal crystal growing techniques the resultant product is the \( \beta \) phase, which has a spinel structure with an ordered arrangement of sulphur vacancies. Microcrystals of the \( \alpha \) phase are created as a precipitate of a chemical reaction (Bube and McCarroll, 1959). The most comprehensive study of \( \beta-\text{In}_2\text{S}_3 \) is that of Rehwald and Harbeke (1965) who did an extensive study of conduction mechanisms. They also heat treated their samples to show that the concentration and sign of the charge carriers could be attributed to sulphur deficiencies. They deduced an indirect energy gap of 1.1 eV and a direct gap of 2.03 eV.

2.8 POINT FORM SUMMARY OF ESSENTIAL FEATURES

(i) There are two ways to grow \( \text{CdIn}_2\text{S}_4 \) crystals; directly from the melt and by chemical transport techniques. The crystals used in the experiments were grown using both methods.

*Hall coefficient, resistivity, optical absorption
(ii) The true crystal structure of \( \text{CdIn}_2\text{S}_4 \) is not directly established, except that it is a spinel which is normal or partially inverted or totally inverted.

(iii) Observation of a second order phase transition in \( \text{CdIn}_2\text{S}_4 \) led Czaja to propose that the true structure was a partially inverted spinel since second order transitions of the Landau type are possible only for this structure.

(iv) \( \text{CdIn}_2\text{S}_4 \) has been studied extensively by optical methods. Sulphur vacancies have been shown to play an important role in photoconductivity, luminescence and absorption spectra.

(v) EPR work has been confined to rare earths and transition elements. The results indicate that the cation impurity always substitutes at a "B" site regardless of its charge state. No shallow donor resonance has been reported.

(vi) There have been two attempts at band structure calculations, the latest predicting an indirect band gap.

(vii) The \( \text{CdS} - \text{CdIn}_2\text{S}_4 - \text{In}_2\text{S}_3 \) system is of interest because \( \text{CdIn}_2\text{S}_4 \) may be thought of as composed of \( \text{CdS} + \text{In}_2\text{S}_3 \). Also since both \( \text{CdIn}_2\text{S}_4 \) and \( \text{In}_2\text{S}_3 \) crystallize in spinel form there is a continuous single crystal mixture between the two. The single crystals on the other side of the system \( \text{(CdS} - \text{CdIn}_2\text{S}_4) \) crystallize in hexagonal and triclinic forms.
CHAPTER 3 - APPARATUS AND OPERATION

3.1 APPARATUS

For most of the experiments a standard EPR detection arrangement with a 'magic tee' and reflection cavity was used (Poole, 1967). However, for the later experiments a three port circulator was utilized (Figure 3.1). This configuration has the advantage of allowing the entire signal from the cavity to fall upon the crystal detector and thus the signal/noise ratio is improved by a factor of two over the standard 'magic tee' spectrometer.*

The static magnetic field, $H_0$, is monitored by an NMR (nuclear magnetic resonance) marginal oscillator spectrometer (Robinson, 1959), which is essentially the MHz equivalent of a GHz reflection cavity EPR spectrometer.

3.2 SENSITIVITY

Since many of the experiments were concerned with searching for EPR signals (which may have been weak) for various dopants in CdIn$_2$S$_4$, it was important to maintain the spectrometer at a high sensitivity.

The change in reflected power at resonance, $\delta P$, is proportional to the imaginary part of the susceptibility, $\chi''$, to first order in $1/Q$ (Appendix 2). Thus the requirements of optimum operation are two:

(i) maximum sensitivity to $\delta P$

(ii) detection of only the absorptive component

*If a magic tee is used the signal from the cavity splits equally between the detector arm and the klystron arm where it is dissipated in the ferrite isolator.
FIGURE 3.1 Experimental Arrangement
In order to ensure these, a bias voltage must be applied to the crystal detector (Appendix 3). If the bias is applied via a balance arm for the 'magic tee' spectrometer, the maximum sensitivity of the spectrometer occurs at critical coupling, independent of the bias power reflected to the crystal (Appendix 3). However, this is not feasible for two reasons (Wilmshurst, 1967):

(i) Near critical coupling, a phase change of 180° in the signal may occur when passing through resonance.

(ii) The phase of the bias voltage is critical in order to detect only the absorptive component.

Thus, in practice, the crystal detector was biased by undercoupling the cavity. Diode bias currents of 100 - 300 μamps were used.

Flicker noise (or 1/f noise; f = modulation frequency) is generated in the diode. This cannot be made minimal by using high frequencies because the modulation must penetrate the walls of the resonant cavity.

3.3 RESONANT CAVITIES

For most low temperature experiments a standard TE_{102} mode, brass cavity was used. For elevated temperature measurements a Varian (model E-453) cavity was used. Elevated temperatures were produced by the Varian air flow and heater system and were measured by a thermistor placed close to the sample.

For the low temperature measurements on CdIn_2S_4:Mn^{2+} a TE_{102} cavity with 0.005" thick stainless steel walls, electro-plated with copper on the inside was utilized. Modulation coils were constructed
and attached to the outside of the cavity for immersion directly in the He bath. This enabled the use of 100 KHz modulation field and hence reduced the effects of flicker noise in the diode detector. However, while higher frequency modulation should theoretically increase the signal/noise ratio by a significant factor the arrangement had several drawbacks. Eddy currents, induced in the cavity walls by the modulation were coupled to the strong static field, $\mathbf{H}_0$, and mechanical vibrations of the cavity were created. In the EPR spectrum this results in a noise component that increases as the static field is increased. Another much more serious problem is the production of the He bubbles arising from the heat dissipated both by the coils and the eddy currents in the cavity walls. This bubbling causes large fluctuations in the cavity coupling and thus the crystal current. To minimize these effects it is necessary to operate at low modulation power levels for very short periods of time.

For the CdIn$_2$S$_4$:Co$^{2+}$ experiments a brass TE$_{102}$ cavity was designed that enabled the sample to be rotated while in the He bath (Figure 3.2). The gear system was arranged so that one turn of the worm gear turned the sample holder through ~8°. There was slack of one turn of the worm gear within the gear train. This rotation coupled with the rotation of the magnetic field produced the necessary degrees of freedom to orient the crystal along its magnetic axis.

It is worth mentioning that the sample holder was made of lucite and the screws of teflon. Differential contraction between the lucite and the brass spur gear necessitated that the teflon set screw be inset into the brass gear to stop slipping at low temperatures.
STAINLESS STEEL TUBE
BRASS FLANGE
BRASS HOLDER FOR GEAR SYSTEM
- SOFT SOLDERED TO CAVITY
BRASS WAVE GUIDE SECTION
BRASS BOTTOM PLATE

FIGURE 3.2 $\text{TE}_{102}$ cavity with provision for rotating the sample holder

BRASS WORM GEAR
BRASS SPUR GEARS
5/16" LUCITE SAMPLE HOLDER - FIXED TO SPUR GEAR WITH AN OFF-SET TEFLOM SCREW
CHAPTER 4 - TRANSITION IONS

4.1 INTRODUCTION TO EPR THEORY

EPR is the resonant absorption of energy via magnetic dipole transitions between electronic energy levels. The energy level separation is directly dependent on the applied magnetic field, $\vec{H}_o$, and for a simple Kramer's doublet is given by $\delta E = g \beta H_o$, where the Bohr magneton, $\beta = (|e|\hbar/2m_e)$, and $g$ is the spectroscopic splitting factor or 'g-value'. The absorption also depends upon the excess number of electrons in the lower energy state compared to the higher one. This is determined by a Boltzmann factor $\exp(g \beta H_o/k_B T)$ and thus it is convenient to work at low temperatures and high magnetic fields. These properties are summarized in Figure 4.1.

![Diagram of EPR signal for a Kramer's doublet]

Figure 4.1 EPR signal for a Kramer's doublet
The finite line width of the absorption may be due to several causes in solids;

(i) spin - lattice interaction, interaction of the dipole moment with phonons.

(ii) spin - spin interaction, interaction between magnetic dipoles

(iii) unresolved fine or hyperfine structure, due to random strains or electric fields in the crystal.

A necessary condition for observation of EPR in solids is that the crystal exhibit a paramagnetic moment. This moment may be produced in four ways;

(i) free electrons or holes, as in metals or doped semiconductors*

(ii) atoms with an unfilled electron shell

(iii) free radicals, with an unpaired electron

(iv) an electron or hole trapped in a defect center.

### 4.2 INTRODUCTION TO CRYSTAL FIELD THEORY

Transition ion impurities exhibit magnetic dipole moments due to the filling of their electron shells in accordance with Hund's rules. In a solid an extra term must be added to the Hamiltonian for these electrons owing to the electrostatic interaction of the paramagnetic ion with its surrounding atoms.

\[ H = \sum_i \frac{p_i^2}{2m} - \sum_i Z e^2/r_i + \frac{1}{2} \sum_{ij} e^2/r_{ij} + \lambda \vec{L} \cdot \vec{S} + \vec{J} \cdot \vec{A} \cdot \vec{I} - \sum_i e \Phi(r_i) \]

The first three terms are the 'free ion' Hamiltonian and the last three are, in order; the spin - orbit coupling, the hyperfine interaction, and the crystal field interaction. They are applied as perturbations to the free ion ground state. The hyperfine interaction \( \vec{J} \cdot \vec{A} \cdot \vec{I} \) is the

*Loosely bound electrons or holes in shallow states are also placed in this category.
weakest and hence enters last in the perturbation formalism. If a point charge model for the neighboring atoms is assumed, the formalism may be categorized into three groups:

(i) **Weak Crystal Field** - the crystal field interaction, $\sum e\phi(r_i)$, is weaker than the spin - orbit coupling, $\lambda\mathbf{L}\cdot\mathbf{S}$. The crystal field lifts the $2J + 1$ degeneracy of the ionic ground state and since the energy differences are usually $\sim 10 - 100$ cm$^{-1}$, EPR is only observed in the lowest state if the selection rules for EPR ($\Delta J = \pm 1$) can be applied successfully. This case applies to the rare earth and actinide groups where the electrons in the shell contributing to the magnetic moment are shielded from the crystal field by outer electrons.

(ii) **Intermediate Crystal Field** - the crystal field interaction is stronger than the spin - orbit coupling. The $2L + 1$ orbital degeneracy is lifted by the Stark splitting due to the crystal field and since the splittings are $\sim 10^4$ cm$^{-1}$, EPR is observed only from the lowest orbital levels. If the lowest level is an orbital singlet, $\mathbf{L}$ is 'quenched' (Slichter, 1963) and the magnetic properties are due to spin transitions. Spin - orbit interaction and small distortions of the cubic field further split the ground state and cause anisotropic $g$-values. This case occurs for the 3d shell in the iron group.

(iii) **Strong Crystal Field** - the crystal field is strong enough to 'remove' electrons from the ion - i.e. high covalency in bonding. The same formalism as before may be used if one takes into account the fact that the coupling between electrons is broken down by the electric field of the ligands.* Ions of the platinum and palladium groups are of this type.

*Hund's rules and Russell - Saunders coupling are invalid.
Since the crystal field ultimately lifts the ground state degeneracy and separates the levels so that only the lower ones are populated, the magnetic properties may be described by a Hamiltonian containing an effective spin operator that acts only on the manifold formed by the lowest states. This general feature of all three cases is summarized by the so-called 'spin Hamiltonian'.

The theory stated so far, based upon a point charge model, assumes that the electric field produced by a neighboring nucleus, screened by a spherical cloud of electrons is the same as a charge centered at its nucleus. This is only true if the surrounding neighbor electron orbitals do not overlap with the impurity orbitals. Thus the theory does not apply quantitatively to crystals with appreciable covalent bonding. A better analysis of the problem using molecular orbital theory leads to several corrections for increasing covalency (Orton, 1968):

(i) The magnitude of the effective spin - orbit coupling parameter, \( \lambda \), is lowered. This also means that \( g \)-shifts are smaller.

(ii) The orbital contribution to the magnetic properties is reduced. In ions where \( \hat{L} \) isn't 'quenched' it becomes more so for increasing covalency.

(iii) The hyperfine interaction parameter, \( A \), is reduced. In fact the size of \( A \) for a fixed impurity may be used as a quantitative measure of covalent bonding (Kimmel, 1963).

(iv) Superhyperfine interaction occurs. Since the impurity electrons have a finite probability of being at the neighboring nuclei a superhyperfine contact interaction with the ligands may occur, exhibiting the EPR spectra characteristic of the nuclear spin of the ligands.
4.3a Introduction

In CdIn$_2$S$_4$ the two cations have charges of 2$^+$ and 3$^+$ respectively so that, assuming the impurities enter the lattice substitutionally, the EPR spectrum is expected to exhibit the properties of either Mn$^{2+}$ or Mn$^{3+}$. However Mn$^{3+}$ is a 3$d^4$ configuration that is strongly affected by a cubic crystal field to yield a spin Hamiltonian with $S = 2$ (Abragam and Bleaney, 1970) with a resultant zero field splitting and anisotropic spectrum. Because of relaxation effects the EPR of Mn$^{3+}$ is never observed at room temperature. The single isotropic spectrum, seen at room temperature and above, does not conform to this model and is therefore ascribed to Mn$^{2+}$ with fine structure unresolved due to weak coupling to the lattice. The spectrum has a large hyperfine interaction reflecting the nuclear spin of the Mn$^{55}$ nucleus ($I = 5/2$).

4.3b Mn$^{2+}$ - Crystal Field Interaction

Mn$^{2+}$ is a member of the iron group that has the electronic configuration 3$d^5$ and, according to Hund's rules, the ionic ground state is $^6S_{5/2}$. It is analysed using the intermediate crystal field approach. S - state ions are unusual because neither the cubic field nor the spin - orbit interaction, taken separately, to any order in perturbation theory give any splitting of the ground state. It is only when both are applied together that the degeneracy is lifted. This is expected to be small since the first contribution occurs in fifth order (Low, 1957).

*Notation: $(2S + 1)L^J$

#A good discussion of Hund's rules is found in Pake (1962, p. 11)
Because of the weak coupling to the lattice, the spin–lattice relaxation time, $T_1$, for Mn$^{2+}$ is fairly long and shows little temperature dependence, so that the resonance may be observed even at room temperature and above. Deviations from cubic symmetry cause the six-fold spin degenerate ground state to be split slightly. An effective spin Hamiltonian, for an axial distortion, may be written (Orton, 1968):

$$\mathcal{H}_s = g \mu_B H_0 \cdot S + D(S_z^2 - 1/3(S)(S + 1)) + (F/180)(35S_z^4 - 30S(S + 1)S_z^2$$

$$+ 25S_z^2 - 6S(S + 1) + 3S^2(S + 1)^2) + (a/6)(S_x^4 + S_y^4 + S_z^4 - (1/5)S$$

$$(S+1)(3S^2+3S-1))$$

where the $D$ and $F$ terms are due to the axial distortion and the $a$ term is caused by the cubic component of the crystal field. The $z$-axis is determined by the axial distortion in the crystal, not by the field, $H_0$.

In practice for many crystals the ligand field may be near-cubic and the fine structure may not be resolved, but may be the dominant factor in line width determination (Almeleh and Goldstein, 1962).

4.3c The Theory of the Hyperfine Interaction for Mn$^{2+}$

The Hamiltonian for the magnetic interaction of an electron with its nucleus may be written as (Abragam and Bleaney, 1970):

$$\mathcal{H}_{\text{hf}} = 2 \mu_n \hat{r} \cdot \hat{I} \cdot \left((1/r^3) - (\hat{s}/r^3) + 3\hat{r}(\hat{s},\hat{r})/r^5 + (8/3)\mu_0 S \hat{S}(\hat{r})\right)$$

where $\mu_n$ = the nuclear gyromagnetic ratio and $\hat{I}$ = nuclear spin. The first three terms are the classical interaction between magnetic dipoles while the last term is the contact term, which is usually dominant. For a general distribution of electrons about the nucleus the interaction is tensorial, $\hat{I} \cdot \hat{\mu} \cdot \hat{S}$, however for the spherical distribution of 3d$^5$ in a
cubic field it becomes isotropic and may be written: \( \mathcal{H}_{\text{hf}} = A \overline{\mathbf{r}} \cdot \mathbf{S} \) where \( A \) is a constant. If there is an axial distortion from cubic symmetry \( \mathcal{H}_{\text{hf}} \) must exhibit axial symmetry (Orton, 1968):

\[
\mathcal{H}_{\text{hf}} = A I_z S_z + A (I_x S_x + I_y S_y)
\]

It seems surprising that there should be a large hyperfine interaction for Mn\(^{2+}\) since the 3d electrons have no probability of being at the nucleus and the magnetic dipole interaction is far too weak to explain the observed \( A \)-values. The magnitude of the interaction has been explained by introducing core polarization (Watson and Freeman, 1957) which also accounts for the negative sign of \( A \) (Šimánek and Orbach, 1966). In addition, there is a 'configuration interaction' (Abragam and Bleaney, 1970) whereby the crystal field mixes in small amounts of excited state configurations with unpaired s-electrons which do have a significant probability of being at the nucleus and thus give rise to a contact hyperfine interaction. This mechanism results in a positive contribution to \( A \) and subtracts from the dominant mechanism of core polarization. Both mechanisms are responsible for the hyperfine interaction in the transition group.

4.3d The Temperature Dependence of \( A \)

A large temperature dependence of \( A \), over and above that explained by simple thermal expansion effects, was first observed for Mn\(^{2+}\) and V\(^{2+}\) in the cubic field of MgO by Walsh et al. (1965). The mechanism proposed was that the excited s-like configurations which give the contribution to \( A \) are mixed into the ground state by a phonon-induced dynamic crystal field (Šimánek and Orbach, 1966). By assuming a Debye spectrum for the phonons and a point charge model for the ligands, a
temperature dependence of the hyperfine coupling constant was determined:

\[ A(T) = A(0)(1 - C T^4 \sum_{x=0}^{\infty} \frac{x^3}{e^x - 1}) \]

\[ x = \frac{h \nu}{kT} \]

where \( \Theta \) is the Debye temperature for the solid and \( C \) is a constant that, in principle, can be calculated. Šimánek and Huang (1966) improved on this model and showed that covalency effects tend to increase the value of \( C \), previously calculated using the point charge approximation, although the form of the equation remained the same.

Žďánský (1968) pointed out that if the impurity has a mass or ionic radius differing appreciably from the host atom, local vibrational modes will be set up at the impurity site. The mechanism (mixing of excited states by a dynamic non-cubic crystal field) remains identical, except that the dynamic non-cubic field is induced by a localized phonon and not the continuum. The form of the dependence was derived as:

\[ A(T) = A(0)(1 - \sum_{i} C_i \exp(\frac{\hbar \omega_i}{kT}) - 1)^{-1} \]

where \( \omega_i \) is the resonant frequency of the \( i \)th localized mode and \( C_i \) is a constant. Žďánský and Kubec (1969) observed the temperature dependence of \( A \) for CdS:Mn\(^{2+} \) and found that the data could be explained with two local modes of vibration.

It should be noted that even for one local mode, the mechanism of Žďánský and Kubec has two adjustable parameters, while the mechanism of Šimánek and Orbach has only one.

*for CdIn\(_2\)S\(_4\) \( \Theta = 230 \degree K \) (Czaja and Krausbaruer, 1969).
4.3e Room Temperature Properties of the Spectra

The samples available were grown from both the melt and vapor phase techniques. The crystals with similar dopant concentrations exhibited a six line hyperfine spectrum with a rather large line width (Figure 4.2a), while samples with a larger concentration of dopants exhibited two superimposed six line spectra (Figure 4.2b), one with a line width the same as the weak dopant spectrum and the other having a much narrower line width. Analysis of the EPR spectra yielded:

TABLE 4.1 Experimental values for CdIn₂S₄:Mn²⁺

<table>
<thead>
<tr>
<th></th>
<th>Broad Lines</th>
<th>Narrow Lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-values</td>
<td>2.003 ± .002</td>
<td>2.004 ± .001</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>ΔH₁/₂</td>
<td>75 ± 2 G</td>
<td>6.5 ± .5 G</td>
</tr>
</tbody>
</table>

Where ΔH₁/₂ is the 'half width' between inflection points on the absorption spectrum. In the presence of second order effects there are corrections to g-value measurements and there is a correct technique for measuring A (Appendix 4).

For the broad line spectrum the measurements of A and ΔH₁/₂ were obtained by computer fitting a sum of overlapping Lorentzians to the experimental traces (Figure 4.2a). The line shape was best approximated by a Lorentzian curve although this was by no means perfect. Both spectra were found to be isotropic with respect to crystal orientation.
FIGURE 4.2 Experimental traces for CdIn$_2$S$_4$:Mn

(a) CdIn$_2$S$_4$ + .05 Mole% Mn

(b) CdIn$_2$S$_4$ + .1 Mole% Mn
4.3f The Temperature Dependence of the Spectra

The hyperfine coupling constant, $A$, was found to be temperature dependent for both the narrow and the broad line spectra (Kerr and Schwerdtfeger, 1971). The errors for the narrow line spectrum were much smaller, owing to the relatively small line width and thus this spectrum was extensively studied. The results are plotted in Figures 4.3 and 4.4 for a temperature range 1.1 °K - 450 °K. Temperatures above 300 °K were measured with a calibrated thermistor while the dry ice - acetone temperature of 197 °K was measured with a thermometer. At 1.1 °K and 4.2 °K both spectra were saturated at moderate microwave power levels and the power had to be decreased in order to observe EPR transitions*. Both $\Delta H_{1/2}$ and $g$ were independent of temperature, within experimental error.

*for no saturation $1 \gg \gamma H^2 T^2$ (Pake, 1962), where $T_1$ and $T_2$ are longitudinal and transverse relaxation times and $\gamma$ = gyromagnetic ratio.
**Figure 4.3** Experimental results for $\Gamma(T)$ fitted to the model of Kimel and Orbach

\[ \Gamma(T) = \Gamma(0) \left( 1 - CT^4 \right) \left( \int_0^{\Theta_B/T} \frac{x^2 dx}{e^x - 1} \right) \]

Errors = standard deviations

**HYPERFINE PARAMETER (IAI) IN CM\(^{-1}\) x 10\(^4\)**

**TEMPERATURE IN °K**
HYPERFINE PARAMETER \((1A_1)\) IN CM\(^{-1}\) x10

Errors \(\approx\) standard deviations

\[\frac{A(T)}{A(0)} - 1 - \frac{\text{EXP}(\nu_{ps}/kT)}{C}\]

FIGURE 4.4: Experimental results for \(A(T)\) fitted to the localized phonon model of density.
4.3g Comments and Discussion of Data

Because of the weak coupling of the 3d electrons of Mn$^{2+}$ to the lattice, their spectrum is insensitive to orientation and thus it is very difficult to ascribe the position of the impurity to either an "A" or a "B" site. However there are two indirect methods of labelling the spectra.

Since the linewidth is independent of temperature and saturation occurs at 4 °K it is likely that the linewidth source is inhomogeneous. One such source is unresolved fine structure 'smeared out' by random strains in the crystal. An observation that would conform to this picture is that the line shape is neither Lorentzian or Gaussian as it would be for a single line or a simple inhomogeneous broadening mechanism. If a postulate of cubic symmetry about each site is made, then it can be shown that to first order, the line width $\Delta H_{1/2}$ is proportional to the square of the cubic field strength (Stahl-Brada and Low, 1959).

In tetrahedral symmetry the crystal field strength is 4/9 of the crystal field strength in octahedral symmetry so that one would expect

$$\Delta H_{1/2}(\text{tetrahedral, "A", site}) \approx \frac{1}{5} \Delta H_{1/2}(\text{octahedral, "B", site}).$$

Thus the narrow line spectrum is ascribed to the "A" sites and the broad line spectrum to "B" sites. This discussion is at best qualitative since there is no way of ascertaining how much the cubic field is distorted at each site.

In all cases of paramagnetic impurities studied by EPR in which

* no D term in the spin Hamiltonian.
the site symmetry was determined it was found that the anion preferred the "B" site regardless of its charge state. Thus at low dopant concentrations Mn would populate "B" sites and for higher concentrations would start to occupy "A" sites.

The Debye theory of Šimánek and Orbach for the temperature dependence of A has been used to interpret the data in Figure 4.3. The curve is normalized at 411 °K and 1.1 °K. This yields a value for the constant C = (1.6±0.3) x 10^{-11}(°K)^{-4}.

From Šimánek and Orbach (1966) it is seen that a theoretical value for C, using the point charge model, is proportional to \( (V_C^2)/(\gamma c^5) \) where \( V_C \) is the crystal field strength, \( R \) is the anion – cation distance, \( \gamma \) is the density and \( c \) is the isotropic velocity of sound. Using an isotropic sound velocity for CdIn\(_2\)S\(_4\) calculated from the Debye model one finds \( C \approx 10^{-14} (°K)^{-4} \). Thus the theoretical value is three orders of magnitude too low. Better agreement may be attained if covalency effects are taken into account (Šimánek and Huang, 1966).

In Figure 4.4 the local vibration model has been used to interpret the data. The resulting fit is better than the previous theory due to the additional parameter in the formula. The vibration frequency was found to be \( 3.1 \times 10^{13} \) sec.\(^{-1} \) and the 'coupling' \( C \) was 0.0167.

The results should be comparable to CdS in a qualitative way since the nearest neighbor configuration is nearly the same*. Žďánský and Kubec, using the Debye model, found for CdS:Mn\(^{2+}\) that \( C = 2.58 \times 10^{-13}(°K)^{-4} \). Even better agreement with theory was obtained by assuming two local

\* \( R(\text{CdS}) = 2.52 \) Å, \( R(\text{CdIn}_2\text{S}_4) = 2.56 \) Å
modes of frequencies $\omega_1 = 4.25 \times 10^{14}$ and $\omega_2 = 1.11 \times 10^{12}$ with different 'couplings' $c_1' = 1.6 \times 10^{-3}$ and $c_2' = 7.4 \times 10^{-2}$.

If $|A|$ is used as a measure of covalency then, all other things being equal, $C$ should be larger for CdIn$_2$S$_4$ than for CdS since the former has more covalent bonding*. This effect may be the dominant one. The Debye temperatures are comparable; the crystal field is tetrahedral in both cases; the densities are of the same order and the dependence on $R$ is opposite to that observed.

The concept of a local vibration model for explaining the temperature dependence of $A$ is highly doubtful. The lower vibration frequency $\omega_1$ for CdS:Mn$^{2+}$ falls in the acoustic phonon band where no localized phonons should be present and the upper frequency $\omega_2$ is well above the predicted localized frequencies for CdS:Mn of 284 cm$^{-1}$ and 289 cm$^{-1}$ (Nusimovici et al., 1970). In CdIn$_2$S$_4$:Mn$^{2+}$ the mode frequency of $3.1 \times 10^{13}$ sec.$^{-1} = 990$ cm$^{-1}$ is too far away from the predicted values for CdS to be meaningful. Thus the localized vibration model is discarded as a tenable theory for $A(T)$ in both CdS:Mn$^{2+}$ and CdIn$_2$S$_4$:Mn$^{2+}$.

Also from the data, assuming the site assignments are valid, Mn$^{2+}$ has a strong preference to substitute into the "B" site. For a normal spinel this would require a charge compensation mechanism and thus an expenditure of energy by the crystal. For a partially (or fully) inverted spinel this is not necessary.

* $|A|$ at 300 °K for CdS:Mn$^{2+}$ is $65 \times 10^{-4}$ cm$^{-1}$ (Zdánský and Kubec, 1969)
A search for effects due to the phase transition at 130 °C (Czaja, 1970) was carried out but no quantitative results were obtained. A slight trend of increasing strength of the narrow line spectrum was seen but the expected line width increase due to fluctuations was not observed. In some ways this is not surprising since the effects of the transition were so small (10% change in C<sub>p</sub>) and the order-disorder takes place on "A" sites which for Mn would imply a third-nearest neighbor effect.

4.4 CdIn<sub>2</sub>S<sub>4</sub>:Co

4.4a Introduction

Assuming Co enters the crystal in a substitutional site there are four possible ways it can do so, without necessitating charge compensation. It can substitute at either an "A" or a "B" site as a triply or doubly charged anion. However, the Co<sup>3+</sup> ion is non-paramagnetic since, due to its larger charge, it always substitutes in a strong field configuration which is diamagnetic (Orton, 1968) and hence would exhibit no EPR signal. Co<sup>2+</sup> at an "A" site should have a spin Hamiltonian with g \( \approx 2 \) and \( S = \frac{3}{2} \) (Orton, 1968; Ham et al., 1960) because of the tetrahedral field. Co<sup>2+</sup> at a "B" site should have a spin Hamiltonian with an anisotropic \( g \approx 3 \rightarrow 7 \) and \( S = \frac{1}{2} \) (Orton, 1968; Abragam and Blenney, 1970) because of the octahedral field.

The features of the observed spectra conform to the latter assignment so that the resonance is attributed to Co<sup>2+</sup> at a "B" site. There is also an underlying background spectrum which is thought to be caused by Co<sup>2+</sup> at a "B" site surrounded by one or more sulphur
vacancies. The large number of possible sites for the vacancy around each impurity (6) plus the four inequivalent impurity sites in the crystal would lead to a random spectrum that exhibits properties very close to that of a powder (Appendix 5).

4.4b The Theory of Co$^{2+}$ in Octahedral Coordination

The cubic field splits the seven-fold degenerate ground state, $^4F$, of the 3d$^7$ configuration into two triplets and a singlet with a triplet lying lowest (Figure 4.5).

Following the notation of Abragam and Pryce (1951), the energy levels in the diagram are labelled by their wave functions.

Since an orbital triplet lies lowest in energy, 'quenching' does not occur in this case and the magnetic properties of the ground state reflect both the orbital and spin magnetic moments. The ultimate ground state is a Kramers doublet independent of the sign of $S$ (the trigonal splitting factor) and may be written as:

```
\begin{figure}
\centering
\includegraphics[width=\textwidth]{orbitals.png}
\caption{Orbital energy level diagram for Co$^{2+}$ in an octahedral field}
\end{figure}
```
\[ |1/2\rangle = a|1,3/2\rangle + b|0,1/2\rangle + c|1,-1/2\rangle \]
\[ |-1/2\rangle = a|1,-3/2\rangle + b|0,-1/2\rangle + c|-1,1/2\rangle \]

where \( a^2 + b^2 + c^2 = 1 \). The states on the right label the orbital angular momentum and the spin, respectively, of the lowest lying triplet, \( \phi' \), created by the crystal field. For a trigonal distortion this triplet may be written as:

\[
\begin{align*}
\phi'_x &= \xi \phi_x - \gamma T_x - \eta \psi_x \\
\phi'_y &= \xi \phi_y - \gamma T_y + \eta \psi_x \\
\phi'_z &= \xi \phi_z - \gamma T_z - \sigma \lambda
\end{align*}
\]

An effective orbital angular momentum \( l' \) operating on the manifold, \( \phi' \), yields effective Lande factors, \( -\alpha \) and \( -\alpha' \), along the symmetry axis and perpendicular to it (Abragam and Bleaney, 1970).

\[
\alpha = \gamma \xi - \sqrt{5} \xi \eta - \frac{1}{2} \xi \psi_x - \gamma \\
\alpha' = \gamma \xi + \frac{1}{2} \sqrt{5} \xi \eta + \frac{1}{2} \eta \psi_x - \gamma
\]

Since \( \xi \) has a value near 1, for a 'weak' field \( \alpha \approx 1.5 \) and no excited states are mixed into the ground state by the crystal field. For a strong field \( \alpha \approx 1 \) (Abragam and Pryce, 1951).

Griffith (1961) has presented a simplified version of the theory which includes the assumption \( \alpha \approx \alpha' \). A relation between \( g_\perp \) and \( g_\parallel \) in terms of a single parameter \( x \) can now be written;

\[
\begin{align*}
g_\parallel &= 2 + 4(\alpha+2)(3/x^2-4/(x+2)^2)/(1+6/x^2+8/(x+2)^2) \\
g_\perp &= 4(1+2\alpha/(x+2)+12/(x(x+2)^2))/(1+6/x^2+8/(x+2)^2)
\end{align*}
\]

where \( \alpha \) varies between 1 and 1.5. The trigonal splitting parameter, \( \delta \), may also be derived as; \( \delta = \alpha \lambda ((x+3)/2-3/x-4/(x+2)) \). This may be taken as a definition of the parameter \( x \). The spin–orbit coupling parameter, \( \lambda \), for the free Co\(^{2+}\) ion has a value \(-180 \text{ cm}^{-1}\) (Abragam and Pryce, 1951). For a pure cubic field, \( \delta = 0 \) (\( x = 2 \)), the expressions
reduce to \( g = g_u = g_\perp = 2/3(\alpha + 5) \), which leads to \( g \)-values of 4 - 4.3 for the expected range of \( \alpha \). In a distorted field the \( g \)-values may range as high as 9 or 10.

Second order effects are caused by the admixing of upper orbital levels through spin - orbit coupling (Appendix 6), and may be significant.

Covalency effects have been studied by Thornley et al. (1965). The effective spin - orbit coupling parameter and \( g \)-values are both reduced in magnitude as the covalency is increased.

4.4c Experimental Results

EPR signals were observed only at 4.2 °K and 1.1 °K owing to relaxation effects. There was no significant difference for the two temperatures and, thus, all data presented are for the lower temperature where the spectrometer has a higher sensitivity.

For an arbitrary orientation of the crystal the spectrum was too complicated to decipher since, assuming axial symmetry in \( \langle 11 \rangle \) directions, the "B" sites have four inequivalent \( \langle 11 \rangle \) directions and thus four spectra each containing 8 hyperfine lines. The procedure adopted was to orient the sample so that one of the simple crystallographic directions was parallel to \( \vec{H}_o \), where the spectra from different sites would coincide and simplify the EPR analysis. With a small rhombic distortion present the spectra from different sites would not coincide for any orientation.

A broad background line, relatively independent of orientation, was present in all of the spectra (Figure 4.6). The similarity of this line to a powder spectrum is evident. For this reason it was
ascribed to Co$^{2+}$ at "B" sites where one or more of the neighbors was a sulphur vacancy. The large number of possibilities for the relative position of the vacancy plus the four inequivalent sites would produce a spectrum that closely resembled a powder spectrum. As a check of this postulate, a sample was heat treated at 400 °C for 12 hrs. in order to produce more sulphur vacancies. The strength of the background line increased noticeably with respect to the 'normal' spectrum.

An experimental trace for $\vec{H}_0$ in a ⟨100⟩ direction is shown in Figure 4.6. All ⟨111⟩ directions are at the same angle, 54.74°, to a ⟨100⟩ direction. If the distortion axis is ⟨111⟩ the spectra should collapse into a simple eight-line pattern characteristic of the nuclear spin (I = 7/2) of the Co$^{59}$ nucleus. This collapse does occur partially; however, the inability to resolve the spectrum into eight lines suggests that there is a rhombic distortion in the crystal field. Further evidence for a small rhombic distortion is provided by the unresolved spectra at large angles to ⟨111⟩.

An experimental trace for $\vec{H}_0$ in a ⟨111⟩ direction is shown in Figure 4.6. The lower eight lines retained their internal structure and intensity when the crystal was rotated. For this reason this part of the spectrum was attributed to the one ⟨111⟩ direction parallel to $\vec{H}_0$. The measurement of $g_u$ directly from this spectrum is the most accurate experiment, since no summing from different sites occurs. The upper pattern was very sensitive in both internal structure and intensity to crystal orientation and is therefore attributed to the three ⟨111⟩ directions at 70.53° from $\vec{H}_0$. Quantitative measurements on these lines were not possible.
FIGURE 4.6 Experimental traces for CdIn$_2$S$_4$:Co$^{2+}$ at 1.1 °K
An experimental trace for $\mathbf{H}_0$ in a $\langle 110 \rangle$ direction is also shown in Figure 4.6. Both the lower and upper portions of the spectrum were sensitive to crystal orientation. This is expected since there are two $\langle 111 \rangle$ directions at $90^\circ$ and two at $35.26^\circ$ to $\mathbf{H}_0$. Using the conclusions of the previous experiments the lowest lines were attributed to the $\langle 111 \rangle$ directions at $35.26^\circ$ to $\mathbf{H}_0$. As before, no quantitative measurements were possible for the upper line pattern.

Using the experiments with $\mathbf{H}_0$ in these three simple directions the results are presented in tabular form:

<table>
<thead>
<tr>
<th>$\Theta$ (°)</th>
<th>$g(\Theta)$</th>
<th>$A(\Theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>6.00 ± .05</td>
<td>85.0 ± .05 G</td>
</tr>
<tr>
<td>35.26°</td>
<td>5.46 ± 1</td>
<td>87.0 ± 1.0 G</td>
</tr>
<tr>
<td>54.74°</td>
<td>4.58 or 4.92 ± 1</td>
<td>96.0 ± 1.0 G</td>
</tr>
</tbody>
</table>

**TABLE 4.2** Experimental values for CdIn$_2$S$_4$:Co$^{2+}$

$\Theta$ is the angle between $\mathbf{H}_0$ and the $\langle 111 \rangle$ axis in question. The two values are quoted for $g(54.74^\circ)$ because the spectrum is not unambiguously resolved. For a rhombic field the angles would also be slightly different but are still representative for the cases of non-zero $\Theta$. As $\Theta$ increases the rhombic field should cause the expected collapse of spectra to be less realizable. This behaviour is noted for $\Theta = 70.53^\circ$ and especially for $\Theta = 90^\circ$.

### 4.4d Analysis and Discussion of the Data

The background line described in the previous section has the general features of a powder spectrum (Appendix 5), although exhibiting a slight anisotropy. It has a correlation with sulphur vacancy concentration. For these two reasons it is ascribed to Co$^{2+}$ at a
"B" site surrounded by one or more sulphur vacancies.

The remaining spectra are attributed to Co\(^{2+}\) ions at regular "B" sites, surrounded by an octahedral array of S\(^{2-}\) ions that is distorted to form a rhombic crystal field at the impurity site. The data obtained from the three simplest crystallographic directions are not sufficient to determine the parameters in a spin Hamiltonian that reflects rhombic symmetry. Despite this shortcoming some useful information may still be derived.

Assuming that the rhombic distortion causes the two possible \(g(54.74^\circ)\) values, the first and last line in the (nine-line) spectrum should be half as intense as the rest. From Figure 4.6 it is seen that this is approximately true. Thus \(g_{\text{eff}}(54.74^\circ)\) is taken as an arithmetic mean of the two possible values so that analysis can be carried out for an axial spin Hamiltonian,

\[
\hat{H}_s = g \left( B^z \hat{S}_z + g_{z} \left( B^y \hat{S}_y + H S \right) \right). 
\]

This procedure is equivalent to defining \(g_{z} = \frac{1}{2} (g_x + g_y)\). Thus \(g_{\text{eff}}(54.74^\circ) = 4.75 \pm 1\). For the other angle, 35.26\(^\circ\), it is assumed that the rhombic field is not strong enough to resolve the spectra. Using this data a value \(g_{\perp} = 4.07 \pm 0.15\) is calculated while \(g_{\parallel}\) is measured directly as 6.00 \pm 0.05.

A graph of \(g_{\perp}\) vs. \(g_{\parallel}\) for the first order theory of Griffith is presented in Figure 4.7. It is seen that the experimental point for CdIn\(_2\)S\(_4\):Co\(^{2+}\) is well on the 'weak field' side of the curve. Other data points are taken from Orton (1968, p. 202). Second order corrections

\[
\hat{H}_s = g_z \hat{S}_z + g_x \hat{S}_x + g_y \hat{S}_y
\]

** the extreme weak field case is \(\alpha = 1.5\)
FIGURE 4.7 Plot of $g_\perp$ vs $g_\parallel$ for Co$^{2+}$ in an octahedral field

\[
\begin{align*}
g_\perp & = 2 + \frac{4}{X(X+2)} \left(\frac{X^2}{1+\frac{X^2}{X+2}}\right) \\
g_\parallel & = \frac{\left\{ 3 \left(\frac{X+2}{X^2} \right) \right\} - \frac{4}{X^2} \left(\frac{X+2}{X^2}\right)}{1+\frac{X^2}{X+2}} \left(\frac{X^2}{1+\frac{X^2}{X+2}}\right)
\end{align*}
\]
FIGURE 4.8 Plot of $g_n$ vs $x$ for Co$^{2+}$ in an octahedral field

\[ g_n = 2 + 4(\mathcal{C} + 2) \left( \frac{3X^2}{X^2 - (X+2)^2} \right) \left( \frac{g}{\mathcal{C}X^2 + (X+2)^2} \right) \]

\[ g_n = 2 + 4(\mathcal{C} + 2) \left( \frac{3X^2}{X^2 - (X+2)^2} \right) \left( \frac{g}{\mathcal{C}X^2 + (X+2)^2} \right) \]
give a better agreement the theoretical range of points \((g_u, g_\perp)\) and the experimental point (Appendix 6).

Using the extremal value for \(\alpha\) and the experimentally determined \(g_u\), a value for the parameter \(\lambda\) can be read from Figure 4.8 and \(\delta\), the trigonal splitting parameter, can be evaluated as a first order calculation. If the value of \(\lambda\) for a free ion \((-180 \text{ cm}^{-1})\) is used it is found that \(\delta = 446 \text{ cm}^{-1}\). Covalency would tend to reduce \(\delta\).

The hyperfine interaction tensor, \(\mathbf{A}\), should also exhibit the symmetry of the \(g\)-tensor, but for a small rhombic term may also be approximated by the axial case. The hyperfine interaction Hamiltonian takes the form:

\[
\mathcal{H} = A_u I_z S_z + A_{\perp} (I_x S_x + I_y S_y)
\]

The formula, \(g^2(\theta)A^2(\theta) = g_u^2 A_u^2 \sin^2 \theta + g_{\perp}^2 A_{\perp}^2 \cos^2 \theta\) (Abragam and Bleaney, 1970), is useful in interpreting the data. \(A_u\) is measured as \(85.0 \pm 0.5 \text{ G}\) while calculations yield \(A_\perp = 101 \pm 4 \text{ G}\).

4.5 CONCLUSIONS AND COMMENTS

The search for the effects of the second order phase transition at 403 °K was in vain, both for Mn and Co doped samples. A Co-doped sample was heated to \(-300 \text{ °C}\) for 5 hrs., quenched, and then placed in a microwave cavity at 1 °K and 4 °K. It was thought that the slow approach to internal equilibrium observed by Czaja (1970) would have allowed some changes to be 'frozen' in the crystal, however the effect

*the reduction of \(\delta\) occurs mainly because the effective spin – orbit coupling parameter is reduced with increasing covalency
was not observed.

Other transition elements that were studied were V, Cr, Fe and Cu. A resonance from Cr was observed that had features in common with the Cr$^{3+}$ spectrum in CdIn$_2$S$_4$ reported in the literature (Henning et al., 1969). No other useful EPR signals were seen. Samples doped with Ag, a member of the palladium (4d) group, were also examined in the spectrometer. The platinum (5d) group members Au and Hg were studied. The X-band spectrum of Eu, a rare earth (4f) group member, also yielded no signal.

The null results from these experiments could be due to several reasons. The ion may exist in a non-paramagnetic configuration in the crystal. The line width due to random strains in the crystal or a relaxation effect may be excessively wide. Or, the solubility of the impurity in CdIn$_2$S$_4$ may be low enough so that there is not a sufficient concentration of impurities to create a measurable EPR signal.

One connecting feature between the EPR spectra of Mn$^{2+}$ and Co$^{2+}$ in CdIn$_2$S$_4$ is that both exhibited a preference for the "B" site, even though their charge state would require compensation by the crystal if the structure were a normal spinel. This indicates that a partially or fully inverted spinel is more probable than the normal structure.
CHAPTER 5 'CONDUCTION ELECTRONS'

5.1 INTRODUCTION

In the previous chapter Mn$^{2+}$ and Co$^{2+}$ systems were discussed where the magnetic moment was produced by unpaired electrons localized about their parent nucleus. In this chapter a resonance is reported that is due to unlocalized electrons existing as a shallow donor impurity band or conduction electrons. Evidence for this explanation of the resonance is presented in sections 5.3 and 5.4.

The $g$-value is the measurable quantity of the most interest. Just as in the case of the crystal field interaction it is the spin - orbit coupling that ultimately causes the $g$-shift for conduction electrons. Under the assumption of interaction with only the nearest contributing band, relations between the $g$-shift, the effective mass tensor, the spin - orbit splitting of the nearest band and the energy separation to the band may be derived.

The linewidth of the EPR signal exhibited the properties of incomplete motional narrowing. This is the only mechanism that leads to an increase of line width with a temperature decrease.

*Since this thesis does not distinguish the observed resonance as either of these two cases the electrons will be referred to as 'conduction electrons' for convenience.
5.2 THE THEORY OF THE $g$-VALUE FOR BANDED ELECTRONS

If shallow donors are present in CdIn$_2$S$_4$, using the hydrogen-like approximation, their ground state energy will lie at a value,

$$ SE = 13.6 \, m^*/m^2 \text{ eV} $$

below a conduction band minimum. The dielectric constant, $\kappa$, has been measured as $12.7 \pm 4$ at $4.2 \, ^\circ K$ (Slagsvold, 1971). The effective mass $m^*$ is unknown at present. However, assuming $m^* \approx m$, we find $SE \approx 85 \, \text{meV}$. Since the band gap is $\approx 2.2 \, \text{eV}$ this means that the wave function of the donor ground state is almost entirely made up of conduction band wave functions and should thus exhibit properties of the conduction band.

Since the predicted band structure of CdIn$_2$S$_4$ has four minima at the Brillouin Zone edges in the $(111)$ directions (Meloni and Mula, 1970) it is of interest to study the $g$-value theory for Ge. This was developed by Roth (1960) under the assumption of validity of the effective mass approximation and using $\hbar \cdot \mathbf{p}$ perturbation theory for the nearest contributing level. The ultimate result is an isotropic $g$-value of the form;

$$ g = 2 - \delta(m/(3m_t) + 2m/(3m_l) - 1)/|E| $$

where $\delta$ is the spin-orbit splitting of the nearest contributing level, $|E|$ is the energy separation between the conduction band and this level, and $m_l$ and $m_t$ are the longitudinal and transverse effective masses, respectively, in each of the four valleys. In each valley the $g$-value exhibits an axial anisotropy given by:

$$ g_\parallel - 2 \approx - \delta(m/m_t - 1)/|E| \quad \text{and} \quad g_\perp - 2 \approx - \delta(m/m_l - 1)/|E| . $$

# most certainly an upper limit.
The observed $g$-value is isotropic since, for a cubic crystal, the singlet ground state is an isotropic average over the four valleys.\#\#\#\#\#\#

Another property of interest for Ge is that the inhomogeneous line broadening mechanism due to residual strains exhibits anisotropy, with the minimum line width occurring with $\mathbf{H}_o$ aligned in a $\langle 100 \rangle$ direction (Feher et al., 1959). This has been explained by Roth who uses the broadening mechanism of mixing of excited states into the ground state by the random strains. The effect due to shear strains vanishes for $\mathbf{H}_o$ parallel to $\langle 100 \rangle$.

If, however, the band gap should be a direct one, for a cubic crystal the Roth relations reduce to $g = 2 - \frac{\Delta}{E}(m/m^* - 1)$, where $m^*$ is the isotropic effective mass.

The line shape and width of a conduction electron resonance is not an easy subject to discuss quantitatively. The quasi-continuous series of levels that participate in the EPR experiment need not all have the same magnetic field splittings since the levels observed have a range of $k$-values (i.e., they have slightly different $g$-values) when coupled with the density of states curve this effect may result in wide asymmetric resonances. There also may be an asymmetric inhomogeneous broadening mechanism. Another factor that may cause asymmetry in CdIn$_2$S$_4$ is that it is suspected to be slightly non-cubic.

\#\#\#\#\#\#

The isotropic average is given by $g = \frac{1}{3}g_u + \frac{2}{3}g_d$.\#
(Boorman, 1971) so that the cubic averaging process for an isotropic
$g$-value is no longer valid.

5.3 PROPERTIES OF THE SPECTRA

Resonances that are tentatively attributed to conduction electrons
have been observed in several samples and also have been created in the
laboratory by heat treatment. The evidence for labelling the resonance
as produced by conduction electrons (or banded electrons) is four-fold:

(i) The samples that showed a resonance also affected the quality
factor of the microwave cavity. This indicates that 'free' carriers
have been produced to increase the sample conductivity and make it
'lossy'. Intrinsic samples had no noticeable effect on the cavity $Q$.

(ii) The fact that the line width is a decreasing function of
temperature means that the resonance is incompletely motionally narrowed.
This is the only mechanism that satisfactorily explains the behaviour.
The increasing 'freedom' of electrons at higher temperatures suggests
that they are present either in an impurity band or in the conduction
band.

(iii) In a solid, a single isotropic line having a $g$-value radically
different from and less than a free electron value can only arise from a
conduction electron state. Hole states are not 'visible' to EPR because
of random strains interacting with the degeneracy at the valence band maximum.

(iv) The signals have been produced in the lab by heat treating the
samples. This is known to create sulphur vacancies (Koelmans and
Grimeiss, 1959) which for CdS produce a shallow donor and thus a
characteristic shallow donor EPR signal (Brailsford and Woods, 1968).

The appearance of a typical spectrum is shown in Figure 5.1. The line is isotropic but varies slightly in width (a few Gauss) and g-value ($t \sim 0.002$) for different samples. The variation in $g$ with temperature may or may not be significant because it is not clear where to measure $g$-values for such an asymmetric line. The choice made for these experiments was to measure $g$ at the cross over point of the baseline.
FIGURE 5.1 'Conduction electron' resonance experimental traces
The spectra appear to have Dysonian line shapes (Dyson, 1955) but a room temperature resistivity measurement yielded a resistivity, \( \rho \approx 250 \ \Omega \cdot \text{cm.} \), which is much too high to account for a skin depth effect (Slagsvold, 1966).

Another resonance that should exhibit some properties of the conduction band is that due to the surface states. They arise from the finite boundary conditions imposed by a surface and are most noticeable in powders. The spectrum of a sample before and after it was ground into a powder is shown in Figure 5.2. Another powder sample that was provided by Dr. I. Shepherd also exhibited a resonance with \( g \approx 1.76 \) and a large line width of \( \approx 70 \) G. This resonance was only observed at 77 °K. The sample did not exhibit a resonance characteristic of sulphur vacancies.

5.4 SULPHUR VACANCIES AND HEAT TREATMENT TECHNIQUES

The conduction electron resonance was originally observed in one of Dr. Czaja's samples that had been heated until the vapor pressure of the sublimated sulphur was one atmosphere. This resonance has also been reproduced by heat treatment of intrinsic samples in evacuated closed quartz ampoules.

A simple, open, cylindrical, two-element oven capable of attaining temperatures of \( \sim 650 \) °C was used for all the experiments.

*This measurement was difficult to perform because of the problem of attaching leads to the sample. A four point probe could not be used and even a silver print contact method yielded slightly non-ohmic results. The value of \( \rho \) quoted was the slope of the I - V curve at low currents. The resistivity of intrinsic samples was too high to measure using available techniques in our laboratory.
FIGURE 5.2 Surface state resonances
It is obvious that sulphur vacancies are created, even for modest oven temperatures, since after quenching a deposit of sulphur on the side of the quartz tube is noted.

However, the mechanism of producing the vacancy responsible for the observed resonance is not a simple one. Samples heated under a continuous vacuum had no EPR signals even though they strongly affected the cavity Q. On the other hand, equivalent samples heated under identical conditions in closed quartz ampoules had widely different signal strengths.

One parameter in the technique that, despite the irreproducibility, affects the signal to a sufficient degree to enable one to make at least a qualitative comparison is the sulphur vapor pressure over the heated sample. Four identical intrinsic samples were placed in evacuated quartz ampoules having sealed volume ratios of 1:2:3:4. The unit of volume was $\sim 1.3 \text{ cm}^3$ and each sample weighed $\sim 0.08 \text{ gm}$. Each sample was heated for 2 hrs. at 500 °C, quenched in water and then immediately placed in the EPR X-band spectrometer. The results for the first three samples are shown in Figure 5.3. The fourth sample had no resolvable signal. As far as possible all the parameters of the spectrometer were kept constant, however the most unreliable experiments are those at 1 °K since the helium pump introduces noise that is difficult to maintain at a constant level from one experiment to the next.

The fact that the signal is enhanced for the smaller volumes (higher sulphur vapor pressure) does not imply that these volumes lead to the production of more sulphur vacancies, since the production of
FIGURE 5.3 Qualitative effects of sulphur vapor pressure on the 'conduction electron' EPR signal
more charge carriers also degrades the Q of the microwave cavity and reduces the resulting signal/noise ratio.

A study of the effect of the time of heat treatment, with other things constant, was inconclusive. However there was some evidence that the vacancies 'relaxed' out of the specimen as a function of time.

5.5 STRAIN EFFECTS*

The application of uniaxial stress on a sample may resolve the question of whether or not the band gap is direct or indirect.

For an indirect band gap the resulting strain produces two effects (Wilson and Feher, 1961). First, the valleys are shifted to different energy levels, depending on their orientation with respect to the strain axis, and thus are not equally populated. The resulting g-value is no longer isotropic. Secondly, the g-values within each valley are changed since the applied strain changes the symmetry of the crystal and may admix bands that in the absence of strain would not contribute in the g-shift calculation. Normally if $g_{\perp}$ and $g_{\parallel}$ in each valley are significantly different the application of strain will cause a relatively large g-shift, which is predominantly due to valley repopulation (Feher and Wilson, 1960).

If, however, the band gap is direct, strain causes a relatively small g-shift since the second mechanism is the only active one (Slagsvold, 1966).

*The apparatus used for this experiment was borrowed from Pieter Cullis who will describe its operation in detail in his future thesis.
A rectangular sample was cut for the experiments. Uniaxial compressional stress was applied in two random directions at right angles to each other, of sufficient force to ultimately crush the sample. The resulting change in g-value was found to be less than 0.001.

5.6 **LIGHT EXCITATION**

An attempt was made to observe an effect on the EPR signal due to photo-created electrons. The relaxation time of the photo-created electrons is expected to be much larger for an indirect band gap than for a direct gap. This is because the relaxation from an indirect band gap necessitates the emission of a phonon while the other case has a direct process. However, even if the number of photo-created electrons is large; for the equipment used, relaxation times in the order of $10^{-2}$ sec. would be needed in order to see an effect. No effect was observed.

5.7 **DISCUSSION AND COMMENTS**

Because of the sample's increased conductivity, the incomplete motional narrowing of the EPR line and the $g$-shift from the free electron value the observed resonance in CdIn$_2$S$_4$ is attributed to either conduction electrons or to electrons in a donor band. Furthermore, since sulphur vacancies are easily created by heat treatment and are known to produce a shallow donor level in CdS it is most probable that the resonance is due to sulphur vacancy defect states in CdIn$_2$S$_4$.

*A 250 W. projector bulb was the light source; a flexible fiber optics light guide directed light to the cavity, and a quartz light pipe was used as a sample holder.*
It is impossible to derive any quantitative results from the \( g \)-value measurements because both the spin - orbit splitting, \( \delta \), and the effective mass tensor, \( \bar{m}_e \), are unknown. However it is noteworthy to compare the results to those of CdS (Slagsvold, 1966).

### Table 5.1 Comparison of donor electrons in CdS and CdIn\(_2\)S\(_4\)

<table>
<thead>
<tr>
<th></th>
<th>( g )</th>
<th>( \Delta H_{1/2} )</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS:I</td>
<td>1.77-1.79</td>
<td>12 G</td>
<td>1.7 °K</td>
</tr>
<tr>
<td>CdIn(_2)S(_4)</td>
<td>1.68</td>
<td>19 G</td>
<td>1.1 °K</td>
</tr>
<tr>
<td>CdIn(_2)S(_4)</td>
<td>1.68</td>
<td>13 G</td>
<td>4.2 °K</td>
</tr>
</tbody>
</table>

The \( g \)-tensor is not isotropic for CdS because the crystal structure is non-cubic. The line widths are measured as the field between inflection points of the absorption. The larger \( g \)-shift for CdIn\(_2\)S\(_4\) cannot be explained simply by the change in band gap energy.# The \( g \)-value for conduction electrons has not been measured in any other spinels.

The incomplete motional narrowing of the resonance is not unusual for conduction electrons. For example it has also been observed in Ge:P (Feher et al., 1959) and may be present in Si:P (Quirt, 1971).

The laboratory preparation of samples exhibiting a conduction resonance appears to be very complex, and is only studied qualitatively in this thesis. Sulphur vapor pressure was shown to be a contributing factor while other suspected parameters in the treatment process are; furnace temperature, time of heat treatment, shape of sample##, quenching

---

# \( E_o(CdS) = 2.58 \text{ eV} \) while \( E_o(CdIn\(_2\)S\(_4\)) = 2.3 \text{ eV} \)

## If surface effects were important the sample shape would be a parameter.
technique and time lapse between heating and the EPR experiment. A study of time of heat treatment was inconclusive.

From the surface state resonance it is also difficult to derive any quantitative results. One interesting feature, however, is that the intrinsic powder sample did not exhibit surface EPR lines at low temperatures. This indicates that electrons produced by the sulphur vacancies occupy the surface states of the powder or indeed, that the surface states themselves are sulphur vacancies whose states are modified by the nature of the surface. The surface EPR line is not likely to be caused by an adsorbed gas radical on the surface since the g-value is relatively close to the value for conduction electrons.
CHAPTER 6 CONCLUSIONS

6.1 GENERAL CONCLUSIONS

The significant results of this thesis are;

(i) the observation of the temperature dependence of the hyperfine interaction parameter, $A$, for CdIn$_2$S$_4$:Mn$^{2+}$ and the indirect correlation of the Mn$^{2+}$ with particular sites in the crystal.

(ii) the observation of the $g$-tensor for CdIn$_2$S$_4$:Co$^{2+}$ and the direct correlation of the Co$^{2+}$ with "B" sites.

(iii) the observation of an EPR signal whose $g$-value is attributed to conduction electrons, the correlation of the signal to sulphur vacancy concentration, and the interpretation of the uniaxial strain experiments.

These three results may be applied to the original motivations of the thesis (Section 1.2) in order to derive several general conclusions.

The fact that there were no EPR signals in the intrinsic samples implies that the discrete luminescent levels within the band gap (Czaja and Krausbauer, 1969) either were not occupied with enough unpaired electrons or they had an EPR resonance that was very broad.* These levels were not conducting since the material behaved like a good insulator.

The luminescent centers were attributed to sulphur vacancy complexes in the literature. Czaja and Krausbauer, as part of their model for the centers, required that the crystal structure be a partially inverted spinel. Experiments have shown that sulphur vacancies are

*The sensitivity of the spectrometer is $\sim 10^{13}$ spins/Gauss line width.
present, even in crystals that are good insulators (CdIn$_2$S$_4$:Co$^{2+}$ broad background line). The vacancies are also easily created by heat treatment. Since all ions studied by EPR that can be assigned to specific sites have a strong preference for the "B" site in the crystal, regardless of their charge state, it is more probable that the crystal structure is partially or fully inverted because a mechanism of charge compensation need not be invoked.

It is not surprising that the effects of the second order phase transition at 403 °K were not noted on either the EPR spectrum of CdIn$_2$S$_4$:Mn$^{2+}$ (observed continuously through the transition) or the EPR spectrum of CdIn$_2$S$_4$:Co$^{2+}$ (observed at 1.1 °K after the sample had been heated above 403 K and quickly quenched) since the effect is, at best, a rearrangement of second – nearest neighbours.

The temperature dependence of A for CdIn$_2$S$_4$:Mn$^{2+}$ is best interpreted using the Debye model of Šimánek and Orbach. The localized phonon model is not tenable since the predicted frequency of the local mode is too far away from the values for CdS:Mn which has essentially the same nearest neighbour configuration.

The sulphur vacancy resonance is attributed to a donor level that may or may not be merged with the conduction band. Quantitative conclusions from the g-value measurement may only be made when; the nature of the band gap is established, a measurement of the spin - orbit splitting of the valence band is made, or the effective mass tensor in the conduction band is measured. Qualitatively, the g-value is useful in order to predict the g-value of conduction electrons in In$_2$S$_3$ within
the CdS - CdIn$_2$S$_4$ - In$_2$S$_3$ system. Assuming the same linear relation between CdS - CdIn$_2$S$_4$ as is between CdIn$_2$S$_4$ - In$_2$S$_3$, the conduction electrons in In$_2$S$_3$ should have $g \approx 1.6$.

The nature of the band gap is illuminated by the effects of strain on the conduction electron resonance. The null results indicate that either the band gap is direct or that $g_u - g_l$ in each valley is small. The former is the more probable of the two.

6.2 POSSIBLE ADDITIONAL EXPERIMENTS

An almost inevitable consequence of research leading to a thesis is that some experiments are only partially completed or never attempted. This study has suggested several possibilities that may best be enumerated.

(i) Cyclotron resonance - this may be a difficult experiment to perform since the electrons must remain in their cyclotron orbits for a relatively long time before they are scattered. Attempts on the available intrinsic samples grown from the melt were unsuccessful. Intrinsic samples grown from the vapor phase using a transport gas would probably offer a better chance of success.

(ii) Optical absorption - a close look at the band gap absorption tail may resolve the question of whether or not the band gap is direct. If possible, it would also be of interest to determine the spin - orbit splitting at the valence band maximum.

(iii) Hall measurements - it would be interesting to determine whether any of the samples are predominantly p-type so that devices such as diodes and electroluminescent crystals may be developed.
(iv) Faraday rotation - one of the easiest methods, in principle, to get a value for $m^*$. The experiment could be performed at room temperature in the ordinary geometry and the Voigt geometry with the ratio of the two angular rotations of the plane of polarization giving $m^*$ directly (Lax, 1962).

(v) Infrared studies - a study of the 'shallow donor' excited states may be feasible. Also the excited states of the Mn$^{2+}$ ion could be observed and the site symmetry deduced.

(vi) Transport properties - may shed some light on the nature of the charge carriers and the band structure, however the difficulties with good electrical contacts make the experiments hard to do.

(vii) Additional studies of heat treatment techniques - because of irreproducibility these experiments may be difficult, however they would still be interesting.

(viii) Studies of the CdS - CdIn$_2$S$_4$ - In$_2$S$_3$ system - CdS has been extensively studied, but little is known about In$_2$S$_3$ or the intermediate compounds on either side of CdIn$_2$S$_4$. For example, it would be interesting to study the shallow donor sulphur vacancy resonance throughout the system.#

(ix) Additional optical excitation experiments - the experiment performed was only a preliminary one with a weak light source.##

---

# It would seem that In$_2$S$_3$ might be a good starting place since preliminary experiments indicated that sulphur vacancies are easily produced.

## Experiments in this laboratory are presently being contemplated that will monitor EPR transitions by looking at the polarization of emitted light.
BIBLIOGRAPHY


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Slagsvold, B., private communication (1971).


**APPENDIX 1 SAMPLES**

Table A1.1 Available samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>Doping</th>
<th>EPR Signal?</th>
<th>Comments</th>
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<td>Intrinsic</td>
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</tr>
</tbody>
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*C = Dr. Czaja, R.C.A. Labs, Zurich, Switzerland  
NBRPC = New Brunswick Research and Productivity Council  
B = Bongers et al., Phillips Research Lab, Holland  
S = Dr. I. Shepherd*
APPENDIX 2 THE MEASUREMENT OF $\chi''$

The EPR signal that is observed in a normal experiment is the change in power reflected to the crystal detector due to the power absorption of the sample at resonance. It can be shown that this signal is proportional to $\chi''$, the imaginary part of the susceptibility.

An equivalent circuit for a cavity of an EPR spectrometer is shown in Figure A2.1

\[
L = L_0 (1 + 4 \pi \eta \chi), \quad \text{where} \quad L_0 = \text{cavity inductance away from resonance}, \quad \eta = \text{filling factor} = \frac{\text{volume of sample}}{\text{volume of cavity}}, \quad \text{and} \quad \chi = \text{complex susceptibility of sample} = \chi' - i \chi'' \quad \text{where} \quad \chi' \text{ and } \chi'' \quad \text{are real functions of } \omega.
\]

The impedance $Z = R + i(\omega L + 1/(\omega C))$, $R = R_0 + R'$.

The change in $\text{Re}\{Z\}$ due to resonant sample is $\delta R = 4\pi \omega L_0 \eta \chi''$. The change in $\text{Im}\{Z\}$ due to resonant sample is $\delta L = 4\pi \eta L_0 \chi''$.

Defining $\omega_0 = (1/(L_0 C))^{1/2}$, it can be seen that the sample also causes a
shift of the frequency at resonance given by $\delta \omega = -1/2(\omega_0/L_0)\delta L$.

Now, away from resonance $Q_o = \omega_0 L_o / R = 2\pi(\text{energy stored})/(\text{energy dissipated})$ per cycle. The quantity measured by the spectrometer is the change in power reflected by the cavity at resonance which is proportional to $\delta Q$, the change in the cavity quality factor due to a resonating sample.

$$
\delta Q = \omega_0 S_L / R + \delta \omega L_o / R - \omega_0 S_R / R^2
$$

$$
= 2\pi \eta Q_o \chi' - 4\pi \eta Q_o^2 \chi''
$$

The first term is the dispersive part due to the change in resonant frequency of the cavity. For $\chi' \sim \chi''$ this is a factor $1/Q_o^* \lessgtr$ less than the second term and is therefore usually neglected.

Thus $\delta Q \simeq -4\pi \eta Q_o^2 \chi''$ and the quantity measured is proportional to $\chi''$.

$^{*}\frac{1}{Q_o} \sim 1/8000$ for a typical $X$-band cavity.
APPENDIX 3 MAXIMUM SENSITIVITY OF A MICROWAVE BRIDGE AND DETECTOR

The sensitivity of an EPR spectrometer depends on the coupling of the cavity, the operation point of the diode detector on its I-V curve, and how bias is applied to attain this operation point. Interrelations between these three conditions yield an optimum condition for the microwave bridge.

A schematic diagram of a magic tee reflection spectrometer is shown in Figure A3.1.

The reflection coefficient $\Gamma = \text{complex ratio of reflected/incident } E$ at any specific point. $\Gamma_0 = \text{reflection coefficient at the cavity coupler iris away from resonance}; \quad \Gamma_r = \text{reflection coefficient at the cavity iris at resonance}; \quad \text{and } \Gamma_b = \text{reflection coefficient at the tuner in the balance arm of the bridge.}$

Using the equivalent circuit of Figure A2.1 it is calculated that $\Gamma_0 = (R - R_e)/(R + R_e)$ and $\Gamma_r = (R + \delta R - R_e)/(R + \delta R + R_e)$ where $\delta R$ is a small quantity. One defines $\delta R = (\Gamma_r - \Gamma_0) = 2R_e\delta R/\delta R + R_e)^2 = \frac{\delta R}{R+R_e} \left(1 - \frac{\Gamma_r^2}{\Gamma_0^2}\right)$.

The power incident on the detector is $P_c = \frac{1}{4} |\Gamma_r - \Gamma_b|^2 P_i \text{ where } P_i \text{ is the power incident on the tee. At resonance the crystal power becomes}$
\[ P_{cr} = \frac{1}{4}|\Gamma_0 - \Gamma_b|^2 P_i. \] The change in crystal power may be defined as,
\[ \Delta P = P_{cr} - P_c = \frac{1}{4}(2\Re\left\{\Delta \Gamma (\Gamma_0 - \Gamma_b)\right\} + |\Delta \Gamma|^2)P_i. \]

Now, \((\Gamma_0 - \Gamma_b)\) can be made real by adjusting the phase on the balance arm tuner so that for small \(\Delta \Gamma\), \(\Delta P \propto \frac{1}{2} P_i \Delta \Gamma (\Gamma_0 - \Gamma_b)\).

It is desirable, for two reasons, to be in the linear portion of the I-V curve of the diode detector;

(i) for a given change in voltage, \(\Delta V\), the detector has a maximum response, \(\Delta I\), in the linear region.

(ii) in order to have the signal, \(\Delta I\), proportional to \(X^n\),
\[ \Delta I = \frac{dI}{dP_c} \Delta P \] must be proportional to \(\Delta P\). This is true only for \(I \gg \Delta I\), or in the linear region.

Thus, the EPR signal is a small change in current, \(\Delta I\), on a large background current, \(I\). For the linear region of crystal bias
\[ \frac{dI}{dP_c} \propto P_c^{-1/2} \] (i.e., \(I \propto V\) and \(\Delta I \propto \Delta P/P_c^{1/2} = \frac{1}{2} P_i \Delta \Gamma (\Gamma_0 - \Gamma_b) = P_i^{1/2} \Delta \Gamma\).

or, more simply, \(\Delta I \propto (1 - \Gamma_0^2)\).

This has a maximum for \(\Gamma_0 = 0\) independent of \(\Gamma_b\). Thus for maximum sensitivity the cavity should be critically coupled. The bias current for the detector can be attained by introducing reflections in the balance arm, not affecting the sensitivity.
APPENDIX 4 MEASUREMENT OF $g$ AND $A$ IN THE PRESENCE OF AN HYPERFINE INTERACTION

The Hamiltonian for a simple spin system is $\mathcal{H} = g \vec{\mathbf{H}} \cdot \vec{S} + A \vec{I} \cdot \vec{S}$ where $\vec{S}$ is the spin of the electrons and $\vec{I}$ is the nuclear spin.

Considering the second term as a perturbation, first order theory yields the energy levels $E_1 = g \mu_B H M + A m$ where $M$ and $m$ are the electronic and magnetic quantum numbers respectively. The EPR selection rules, $\Delta M = \pm 1$ and $\Delta m = 0$, are used to derive an expression for the resonant frequency; $\hbar \nu = g \mu_B H + A m$. For $I = 5/2$ ($\text{Mn}^{2+}$) this gives a spectrum of six equally spaced lines when sweeping $H$ at constant $\hbar \nu$.

To second order the energy levels are given by (Van Wieringen, 1955);

$$E_2 = g \mu_B H M + A m m - \frac{A^2}{4 \hbar \nu} (2mS(S + 1) - 2MI(I + 1) - 2Mm(M - m)).$$

Applying the EPR selection rules yields the resonant condition;

$$\hbar \nu = \frac{1}{2} \left( g \mu_B H + A m + ((g \mu_B H + A m)^2 + 2A^2 (I(I + 1) - m^2))^{1/2} \right).$$

For the case of $I = 5/2$ this leads to a pattern of lines slightly shifted from the first order case. This is represented schematically in Figure A4.1.

![Figure A4.1 Representation of an \(I=5/2\) hyperfine spectrum to second order](image)

Thus, the entire spectrum is shifted to a lower $H_0$ value, so that an experimental measurement of $g$ would be in error by an amount $\delta g$;

\*The calculation will be carried out for CdIn$_2$S$_4$ where $S=1/2$ and $I=5/2$.\*
\[ \delta g = \frac{h \nu}{2} \frac{\delta \Delta}{\Delta} = \frac{5}{4} - \frac{A^2}{g(\epsilon g^2) \Delta}. \]

For \( A \sim 100 \text{ G} \) and \( H_0 \sim 3 \times 10^3 \text{ G} \) one finds \( \delta g \sim 10^{-3} \) which is experimentally measurable.

To second order, the hyperfine pattern is shifted toward the low field value, independent of the sign of \( A \) but the width of the entire pattern is still 5A, and therefore the best method of determining \( A \) is to measure the field difference between the two extreme lines.
Consider a spin system described by a Hamiltonian for a single crystal, \( \mathcal{H} = g_n (\mathbf{H} \cdot \mathbf{S}) + g_\perp (\mathbf{H} \cdot \mathbf{S} \perp) \). For a fixed klystron frequency, \( \nu \), the resonant field for a single spin is given by:

\[
H = \frac{h \nu}{g(\Theta)} = \frac{h \nu}{\left( g_n \cos \Theta + g_\perp \sin \Theta \right)^{1/2}}.
\]

In a powder the spins are randomly oriented, with the fraction of spins having an angle in the range \( \Theta \) to \( \Theta + d\Theta \) being \( 1/2 \sin \Theta d\Theta \). If \( dN \) is the fraction of spins in any \( d\Theta \) having resonant fields in the interval \( dH \), then

\[
dN = A(H)dH = 1/2 \sin \Theta d\Theta = 1/2 \sin \Theta \frac{d\Theta}{dH} dH
\]

where the shape function \( A(H) = 1/2 \frac{H^2}{g^2_n} (g_n^2 - g_\perp^2)^{-1/2} \left( \frac{H}{g_n} \right)^{-1/2} \).

**FIGURE A5.1** Single line powder spectrum for anisotropic \( g \)-values
If there is an hyperfine interaction present, also exhibiting axial symmetry, the resonant field for one spin is, to first order;

\[
H = \frac{\hbar \omega}{g(\Theta) \phi} - \frac{A(\Theta) M}{g(\Theta) \phi}
\]

where \(M\) is the nuclear magnetic quantum number.

The resultant shape function \(A(H)\) is a superposition of shape functions for each hyperfine line (Gersmann and Swalen, 1962)

\[A(H)\]

\[\text{FIGURE A5.2 Three line powder spectrum for anisotropic } g\text{-values}\]

It can be seen that for a large line width the spectrum reduces to a case similar to the finite line width case previously described. For a rhombic \(g\) and \(A\) even more 'smearing out' of the hyperfine structure in the powder spectra occurs (Kneubuhl, 1960). The experimental trace of a \(\text{Co}^{2+}\) doped \(\text{CdIn}_2\text{S}_4\) powder closely approaches the spectrum of a single spin randomly distributed.
APPENDIX 6 SECOND ORDER g-VALUE CORRECTIONS FOR Co$^{2+}$

The second order corrections to $g_{\perp}$ and $g_\parallel$ for Co$^{2+}$ due to admixing of upper levels may be written (Abragam and Pryce, 1970);

\[ g_{\parallel}^{(2)} = (3a^2 - c^2)\nu_1 + b^2\nu_\parallel + (6^{1/2}ab - 8^{1/2}bc)\nu_5 \]

\[ g_{\perp}^{(2)} = b^2\nu_5 + c^2\nu_\parallel + 3^{1/2}ac\nu_6 + 2^{1/2}bc\nu_7 \]

where the parameters $a$, $b$, and $c$ are related to $x$ by; $a:b:c = \frac{6^{1/2}}{x} : -\frac{8^{1/2}}{x+2}$ and $a^2 + b^2 + c^2 = 1$ (see section 4.4b).

Assuming $x \approx 1$ and considering only the next nearest orbital level, $\Psi$ (see Figure 4.5), we calculate $a = -0.870$, $b = +0.356$ and $c = -0.336$. For a trigonal field the coefficients, $\nu_i^t$, may be written as;

$\nu_1^t = 5/2y$, $\nu_2^t = 10y$, $\nu_3^t = 15/2y$, $\nu_4^t = 5y$, $\nu_5^t = 5y$, and $\nu_6^t = \nu_7^t = 0$,

where $y \equiv -\sqrt{SE}$ and $SE$ is the energy separation between the ground state and $\Psi$.

If we further assume $SE \approx 3000$ cm.$^{-1}$ and $\lambda = -180$ cm.$^{-1}$, then $y = 0.06$ and the $g$-value corrections are;

$g_\parallel^{(2)} = 0.210$

$g_{\perp}^{(2)} = 0.072$ .

Thus, to second order, the theoretical curve for $g_\parallel$ vs. $g_{\perp}$ will be shifted to higher $g$-values.

*The second assumption is certainly a good one (the free ion value) while the other one uses a representative value for $SE$ taken from Abragam and Pryce's paper.