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AN INVESTIGATION OF THE SEMICONDUCTOR-TO-METAL TRANSITION IN CHLORINE DOPED CADMIUM SULFIDE USING NUCLEAR MAGNETIC RESONANCE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

by

Frank D. Adams, B.S., M.A.

*****

The Ohio State University
1971

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CHAPTER I

INTRODUCTION

The purpose of this research was to study the semiconductor-to-metal transition in chlorine doped cadmium sulfide using nuclear magnetic resonance (NMR) as the primary experimental tool. Cadmium sulfide and other II-VI chemical compounds are being studied by the Air Force Aerospace Research Laboratories because of their usefulness in solar batteries, radiation detectors, photosensitive devices and for other semiconductor applications. Although basic knowledge about these compounds has increased immensely in the past few years, much remains to be learned, especially with respect to their electronic band structure.

Because nuclear magnetic moments interact with the electronic system via the hyperfine interaction, NMR experiments can be used to study such problems. However, before presenting a detailed discussion concerning this investigation, it is appropriate to review some of the historical developments which led to the use of NMR as an experimental research tool.
In 1924, Pauli\(^1\) postulated the existence of nuclear angular momentum and a nuclear magnetic moment in order to account for the hyperfine structure observed in atomic spectra. Although this laid a foundation for nuclear magnetic resonance, the development of NMR into a useful experimental tool did not come about for some two decades. Some early experiments to measure nuclear moments were performed in 1933 by Estermann and Stern\(^2\) and by Frish and Stern\(^3\). They extended the atomic beam deflection method of Gerlach and Stern\(^4,5\). The first NMR experiments are attributed to Rabi and his colleagues\(^6\) who in 1939 further modified the beam deflection method to include an electro-magnetic radiation field at a frequency which would induce transitions between the quantized nuclear Zeeman levels. The beam arrangement in the magnetic field was such that only those molecules which suffered no

\(^1\)W. Pauli, Naturwissenschaften 12, 741 (1924).
\(^4\)O. Stern, Z. Phys. 7, 249 (1921).
change of energy would be deflected into a detector. At
the resonance frequency, the number of molecules reaching
the detector was sharply reduced.

Although these early NMR experiments provided rather
accurate measurements of the nuclear magnetic moment, the
full potential of NMR was not realized until it was
detected in bulk matter. Unsuccessful attempts to do
such experiments are reported by Gorter\textsuperscript{7} in 1936 and by
Gorter and Broer\textsuperscript{8} in 1942. The first successful experi­
ments which detected NMR in bulk matter were carried out
independently by Purcell, Torrey and Pound\textsuperscript{9} and by Bloch,
Hansen and Packard\textsuperscript{10} in 1945.

Purcell and his colleagues measured the power loss
caused by NMR absorption in a tuned electrical circuit
which was driven by a radio-frequency generator. Since
this loss was exceedingly small, the tuned circuit was
placed in one arm of a balanced radio-frequency bridge.
Their first success was to detect the proton resonance
in solid paraffin.

\textsuperscript{8}C. J. Gorter and L. F. J. Broer, \textit{Physica}, 9, 591
(1942).
\textsuperscript{9}E. M. Purcell, H. C. Torrey, and R. V. Pound,
\textsuperscript{10}F. Bloch, W. W. Hansen, and M. E. Packard,
Bloch and his colleagues found the proton resonance in water using a different experimental approach. They detected the feeble electromotive force due to the in-phase precession of nuclear moments at the resonance condition. They used two tuned circuits with the coils in mutually perpendicular positions to prevent coupling. One circuit provided a resonant E.M. field while the second detected the "nuclear induction" signal. Although experimentally different than the approach used by the Purcell group, this method of NMR detection is based on the same fundamental principles.

At this point in time a rich new field of research was opened. In the past twenty-five years, thousands of papers have been published to document research performed using NMR as an experimental tool. NMR signals have been detected in gases, liquids and solids. Measurements of the resonance frequency, the line width or structure, the signal strength, the relaxation time, and many other parameters provide basic data which can be used to check the validity of a proposed theoretical model or in some cases will suggest a new one. It should be emphasized that although NMR measurements provide precise data on certain aspects of the nuclear state, NMR parameters are also strongly affected by interactions of the nucleus with electrons and other nuclei.
A study of these effects most often reveals information about atomic or even macroscopic properties in bulk matter. In particular, nuclear magnetic moments can interact strongly with the conduction electrons of metals and semiconducting crystals. Thus, it is possible to study the electronic band structure using NMR.

The electrical properties of semiconducting materials are routinely manipulated by controlling the number and types of impurities. The conductivity of an n-type semiconductor can be easily increased by the addition of small amounts of a donor impurity. If the addition of impurities is carried to excess, it is possible for the resulting material to exhibit metallic properties. In a series of theories set forth by Mott\textsuperscript{11,12} and by Matsubara and Toyozawa\textsuperscript{13}, it is predicted that the transition to a metal takes place in two rather sudden steps. First, with increasing impurity concentration, an impurity band can form; the material then exhibits some metallic character, but is still not a true metal. With a further increase


in impurity concentration the impurity band merges with the crystal conduction band and all metallic properties are observed.

Impurity band conduction and the semiconductor-to-metal transition have been theoretically and experimentally investigated by many researchers. The work done by Conwell\textsuperscript{14} is typical. The electrical properties (conductivity, Hall coefficient, etc.) were examined as a function of temperature and impurity concentration. Most of the efforts have been directed towards the Group IV semiconductors (germanium and silicon) and a few of the III–V compounds. These include some recent investigations in which NMR methods have been employed\textsuperscript{15,16,17,18}.

Some investigations of impurity conduction in II–VI semiconductors have been reported, particularly involving

\begin{itemize}
  \item \textsuperscript{17}N. M. Alexander, \textit{Phys. Rev.} 172, 331 (1968).
  \item \textsuperscript{18}D. Jerome, \textit{Rev. Mod. Phys.} 40, 830 (1968).
\end{itemize}
cadmium oxide$^{19,20,21}$ and cadmium sulfide$^{22,23,24}$. NMR methods have been utilized by Look and by students working

\begin{enumerate}
\end{enumerate}
Their most recent studies were directed towards studying the semiconductor-to-metal transition in crystalline cadmium oxide. It was Dr. Look who suggested that an NMR investigation of the metallic transition in cadmium sulfide might be fruitful. The only other experimental NMR work reported on cadmium sulfide was pertaining to very pure crystals.


In Chapter II the theoretical basis of NMR methods is reviewed along with certain pertinent parts of semiconductor theory. The experimental apparatus and procedures used are described in Chapter III. Results are reported and discussed in Chapter IV. A brief summary and recommendations are set forth in Chapter V.
CHAPTER IX

REVIEW OF THEORY

In this chapter existing theory of NMR and semiconductor-to-metal transitions will be reviewed for the sake of completeness.

1. Nuclear Magnetic Resonance

Consider first an isolated nuclear spin possessing a total angular momentum \( \mathbf{J} \) and a magnetic moment \( \mu \). These two properties are related by the equation

\[
\mu = \gamma \mathbf{J}
\]  

(1)

where \( \gamma \) is the gyromagnetic ratio. A dimensionless spin angular momentum vector \( \mathbf{I} \) is defined by

\[
\mathbf{J} = \hbar \mathbf{I}
\]  

(2)

where \( \hbar \) is Planck's constant divided by \( 2\pi \). The spin angular momentum has a magnitude \( \sqrt{I(I+1)} \) where \( I \) is either an integer or a half-integer value. In a magnetic field \( \mathbf{H} \), the Hamiltonian may be written

\[
\mathcal{H} = -\mu \cdot \mathbf{H}
\]  

(3)
If the magnetic field has a constant magnitude $H_0$ and is parallel to the $z$ axis, then

$$ H = -\vec{\mu} \cdot \vec{e}_z H_0 $$

(4)

where $\vec{e}_z$ is the $z$ axis unit vector. By using (1) and (2),

$$ H = -\gamma \hbar H_0 I_z $$

(5)

The eigenvalues $m$ of $I_z$ may take on any of $2I+1$ values: $I, I-1, ..., -I$. In particular, the Cd$^{113}$ nuclei have spin $\frac{1}{2}$ so that a matrix representation of the Hamiltonian is

$$ H = -\frac{\gamma \hbar H_0}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} $$

(6)

Note that (6) is written explicitly in terms of the $z$ component of the Pauli spin matrix.

The above Hamiltonian shows a nuclear Zeeman splitting of the energy levels by an amount $\Delta E = \gamma \hbar H_0$. Quanta of radiation energy, which are absorbed or emitted when transitions between energy levels take place, will have an angular frequency $\omega_0$ given by

$$ \omega_0 = \gamma H_0 $$

(7)

---

A pertinent question now concerns how to cause transitions between the Zeeman energy levels. It will be shown next that a small time-dependent variation of the magnetic field can be, under certain conditions, highly effective in stimulating such transitions.

Consider next a small time-dependent perturbation of the magnetic field such that

$$H(t) = H_0 \bar{e}_z + H_1(t)$$

where

$$|H_1(t)| \ll H_0.$$  

The perturbation term $H_1(t)$ can always be decomposed into Fourier components along each of the coordinate axes, i.e.,

$$H_1(t) = \sum_{j=1}^{3} \bar{e}_j \int_0^\infty A_j(\omega) \exp(-i\omega t) d\omega$$

where $A_j(\omega)$ is the Fourier amplitude and $\bar{e}_1$, $\bar{e}_2$, and $\bar{e}_3$ correspond to the $x$, $y$, $z$ directional unit vectors respectively. Since the time-dependent factors have the same form for all Fourier components, it is useful to make a perturbation calculation with the angular frequency $\omega$ as a parameter.

If the stationary eigenfunctions of the unperturbed system are denoted by $|1\rangle$ for $E_1 = -\gamma \hbar \omega / 2$ and by $|2\rangle$ for
\[ E_2 = \frac{\gamma \hbar H_0}{2}, \text{ then a time-dependent state equation can be written as} \]

\[ |\psi(t)\rangle = \sum_{k=1}^{2} C_k(t) |k\rangle \exp(iE_k t) \quad (10) \]

The time-dependent coefficients \( C_k(t) \) are given by

\[
C_k(t) = C_k(0) + \frac{1}{4\pi} \sum_{\ell=1}^{2} \int_0^t \, dt \, <k|H_p|\ell> \, C_{\ell}(t) \exp[i(E_k - E_\ell) t] \quad (11)
\]

where \( H_p \) is the perturbing term of the Hamiltonian. For a first order calculation, the coefficients \( C_{\ell}(t) \) inside the integral are set equal to their initial (t=0) values.

General Fourier components for \( H_p \) along the x, y, z coordinates are

\[
H_{px}(\omega) = -\frac{\gamma \hbar A_x(\omega)}{2} \exp(-i \omega t) \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}
\]

\[
H_{py}(\omega) = -\frac{\gamma \hbar A_y(\omega)}{2} \exp(-i \omega t) \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}
\]

and

\[
H_{pz}(\omega) = -\frac{\gamma \hbar A_z(\omega)}{2} \exp(-i \omega t) \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (12)
\]

---

For calculational purposes, let \( C_1(o) = 1 \) and \( C_2(o) = 0 \). Using (11) through (12), the probability amplitudes have components of the forms:

\[
C_{2x}(\omega, t) = \frac{\gamma A_x(\omega)}{2} \exp\left[\frac{i(\omega - \omega_0) t}{\omega_0 - \omega}\right] -1
\]

(13)

\[
C_{2y}(\omega, t) = \frac{i \gamma A_y(\omega)}{2} \exp\left[\frac{i(\omega - \omega_0) t}{\omega_0 - \omega}\right] -1
\]

(14)

and

\[
C_{2z}(\omega, t) = \frac{\gamma A_z(\omega)}{2} \exp\left[\frac{i \omega t}{\omega}\right] -1
\]

(15)

where \( \omega_0 = \gamma \hbar H_0 \).

The total probability amplitude involves a summation over both \( \omega \) and the spatial components, i.e.,

\[
C_2(t) = \sum_{\xi=1}^{3} \int_{-\alpha}^{\alpha} d\omega \ C_{2\xi}(\omega, t)
\]

(16)

The probability of stimulating a transition is

\[ P(t) = C_2(t) C_2(t)^* \]

This last calculation cannot be done without specifying the Fourier coefficients. Fortunately, the conditions for NMR are revealed in the component equations for the probability amplitude.

Equation (15) can be disposed of first since this component is negligible except for very slow changes in the \( z \) component of the magnetic field (\( \omega \) near zero).

This is uninteresting in terms of a resonance condition.
Now (13) and (14) are essentially the same. This might be anticipated from the cylindrical symmetry of the problem. The probability amplitudes are small except near \( \omega = \omega_0 \). This defines the nuclear magnetic resonance condition. It should be noted at this point that the calculation for a transition from state \( |2\rangle \) to \( |1\rangle \) is almost identical to the above calculation and yields the same physical result. That is, transitions between the Zeeman levels may be stimulated by electromagnetic radiation of angular frequency \( \omega = \omega_0 \) with the magnetic vector in the \( x-y \) plane.

If the \( H_1 \) field has only one Fourier component near the resonance frequency, the major contribution to the transition probability can be calculated using (13) through (16). The transition probability is \( P(t) = C_2 \cdot C_2^* \) or,

\[
P(t) \approx \gamma^2 s^2 \frac{\sin^2 \left[ \frac{\omega (\omega_0 - \omega)}{2} t \right]}{(\omega_0 - \omega)^2},
\]

where \( s^2 = a_x a_x^* + i a_x a_y^* + a_y a_y^* \). The terms \( a_x \) and \( a_y \) are the appropriate Fourier amplitude coefficients along the \( x \) and \( y \) axes. Note that \( a_z \) does not enter into the equation.
The method employed here to investigate the nuclear magnetic resonance condition is just one of several that may be used. It was selected because of the insight that is obtained as one proceeds from a simple static magnetic field to a field having time-dependent components. It should be pointed out, however, that for certain specified time-dependent magnetic fields, the calculation can be carried out exactly. This is done in Abragam\textsuperscript{34} for an $H_1$ rotating in the x-y plane at an angular frequency $\omega$. The procedure involves integration of the Heisenberg equation of motion. For this particular $H_1$ there is shift in the resonance frequency. To a first approximation, the resonance occurs at

$$\omega = \omega_0 \left[ 1 + \left( \frac{H_1}{2H_0} \right)^2 \right]. \quad (18)$$

Since, in general, $H_1$ is small compared to $H_0$, the shift can usually be neglected. The transition probability derived from this calculation has the same form as that obtained using the time-dependent perturbation approach. In fact, for a rotating field of magnitude $H_1$, the appropriate components associated with (17) are $a_x = ia_y = H_1/2$, thus,

$P(t) \approx \gamma^2 H_1^2 \frac{\sin^2 \left[ \frac{\hbar}{\omega_0 - \omega} t \right]}{(\omega_0 - \omega)^2}$  \hspace{1cm} (19)

Additional insight into the NMR phenomenon is obtained from a semi-classical view-point. Suppose a magnetic dipole $\mu$ is in a steady magnetic field $H_0$ as shown in Figure 1. The dipole will precess about the field vector with an angular frequency given by the Larmor equation (see Eq. (7)). When another small magnetic field $H_1$ is applied perpendicular to $H_0$ and is made to rotate about it, the dipole will experience a couple tending to change the angle $\theta$. If the frequency of rotation is different from $\omega$ or in the opposite sense, the couple will vary and produces only small oscillatory perturbations in the precessional motion. When the rotational frequency is $\omega_0$, however, the couple will effect a net change in the angle $\theta$. This corresponds to an exchange of energy between the rotating field $H_1$ and the rest of the system.

The classical model explicitly brings out the rotational character of NMR. In particular, it shows what type of time-dependent field in the x-y plane is most effective for stimulating transitions between energy levels. In the previous quantum mechanical treatment, the time-dependence of $H_1$ was broken into components with
Figure 1. Classical Precession of a Magnetic Dipole
sinusoidal variations of the amplitude along stationary basis vectors. A particular component can be further decomposed into two vectors which are rotating in opposite directions in any plane containing the original basis vector. The amplitude of each rotating vector is just one half the maximum unidirectional amplitude. Thus a linear oscillating magnetic field, which is perpendicular to \( \mathbf{H}_0 \), always has one component rotating in the same direction as the nuclear precession.

In general, nuclear spins in bulk matter cannot be treated as free particles. Magnetic coupling between nuclei and interactions between the spin system and other particles in matter cause a spread in the Zeeman energy levels. This results in a corresponding distribution of resonance frequencies. As with all spectra from physical matter, the NMR line has a non-zero width and may even have a complex structure.

These interactions present a difficulty in relation to the previous probabilities calculations. Using (19), the probability at resonance \( (\omega = \omega_0) \) is \( P = \frac{k \gamma^2}{2} H_1^2 t^2 \). This result does not agree with experiments when a collection of nuclear spins are involved. To reconcile this it is only necessary to introduce the idea of a line shape function \( f(\omega_0) \) and then to integrate over \( \omega_0 \). The equation for the probability is then
\[ P(t) = \gamma^2 H_1^2 \int \frac{\sin^2 \left[ \frac{1}{2} (\omega_0 - \omega) t \right]}{(\omega_0 - \omega)^2} f(\omega_0) \, d\omega_0 \quad . \] (20)

For small values of \( t \), a realistic line shape function will be practically constant over a range of values of \( \omega_0 \) which contribute significantly to the integral and can, therefore, be taken out of the integral. This yields

\[ P(t) \approx \frac{1}{4\pi} \gamma^2 H_1^2 f(\omega) \, t \quad . \] (21)

This equation will be used in the next section.
2. **Spin-Lattice Relaxation Time**

In the previous section it was shown that NMR is a selective process which differentiates between nuclei according to their magnetic moment \( \mu \). In general, the term "spin" will denote the type of nucleus being studied by NMR. The term "lattice" will refer to the material in which the spin system is embedded. Consideration will now be given to how interactions between the spin system and the lattice affect NMR parameters.

For the following development, it is assumed that the spin-spin coupling is small enough so that when \( H_0 \) is more than a few hundred gauss, the energy levels for each spin are, to a first approximation, the same as those for an isolated nucleus. The coupling is not entirely neglected, however, since the spin system is considered to be in internal thermal equilibrium.

In diamagnetic solids, the spin-lattice interaction, although much smaller than the spin-spin coupling, tends to bring the entire assembly into thermal equilibrium. In general, the final equilibrium temperature will be almost the same as the lattice temperature since the heat capacity of the spin system is negligible compared to that of the lattice (except for very low temperature).

Now suppose that an appropriate material resides in a steady magnetic field \( H_0 \). Let the spin number \( I \) for the
nuclear spins in question be $\frac{1}{2}$. There are then two possible energy levels separated by a gap $2\mu H_0$. It will be assumed that the entire assembly is in thermal equilibrium, that is there is no net exchange of energy between the spin system and the lattice. In this equilibrium condition, the total probability of an upward transition by absorption will equal the total probability for a downward transition by emission. If $N_1$ represents the number of nuclei in the upper energy state ($m = -\frac{1}{2}$) and $N_2$ is the number in the lower energy state ($m = +\frac{1}{2}$) then the total probability

$$W_2 N_2 = W_1 N_1,$$

(22)

where $W_1$ is the probability per nucleus in the upper energy state that a downward transition will occur and $W_2$ is the probability per nucleus in the lower energy state for an upward transition. Since the spin system is in internal equilibrium the population ratio $N_2/N_1$ is determined by the Boltzmann factor $\exp(2\mu H_0/kT_s)$ where $k$ is the Boltzmann constant; $T_s$ is the spin system temperature. The Boltzmann factor can be expanded in a Maclaurin's
series and all except the first two terms may be neglected, so that,35

\[
\frac{N_2}{N_1} = \exp \left( \frac{2\mu H_0}{kT_s} \right) = 1 + \frac{2\mu H_0}{kT_s} .
\] (23)

It should be noted that \(2\mu H_0/kT_s\) is usually a very small number compared to one, and that the population of the lower energy state exceeds that of the upper state by a small but finite amount. Of course, it is this excess population which makes possible nuclear magnetic resonance absorption.

By using (22) and (23) and remembering that in equilibrium the spin temperature \(T_s\) equals the lattice temperature \(T\), it is possible to write expressions for \(W_1\) and \(W_2\) in terms of a mean probability \(W = (W_1 + W_2)/2\).

\[
W_1 = W(1 + \mu H_0/kT) \quad (24)
\]

and

\[
W_2 = W(1 - \mu H_0/kT). \quad (25)
\]

As one might expect, the probability for a downward transition exceeds that for an upward transition so that the system can remain in equilibrium.

\[\text{35This is a very good approximation; except at very low temperatures, each term after the first is in the order } 10^6 \text{ times smaller than the preceding term.}\]
Now suppose the assembly is not in thermal equilibrium; in particular, let the spin temperature be greater than that of the lattice. The excess population in the lower energy state will now be less than before (equation (23)); the transition probabilities, however, will be the same (equations (24) and (25)). As a result the total probability for a downward transition exceeds that for an upward transition; the population for the lower energy state will therefore increase. This tends to bring the entire system into thermal equilibrium. If \( n \) represents the number of excess spins \( (N_2 - N_1) \) in the lower energy state, then the time rate of change of \( n \) (\( n \) changes by two for each transition) is given by

\[
\frac{dn}{dt} = 2(N_1 \omega_1 - N_2 \omega_2)
\]

\[
= (N - n) \omega_1 - (N + n) \omega_2,
\]  \hspace{1cm} (26)

where \( N \) is the total number of spins \( (N_1 + N_2) \). Upon substituting (24) and (25) into (26), one obtains

\[
\frac{dn}{dt} = 2W (N \mu H_0 / kT - n).
\]  \hspace{1cm} (27)

If \( n \ll N \), which is true for all practical cases, then the term \( N \mu H_0 / kT \) is a very good approximation of the number of excess spins \( n_0 \) when the system is in thermal equilibrium;
\[ n_0 = N_H_0/kT. \quad (28) \]

The differential equation is then

\[ \frac{dn}{dt} = 2W (n_0 - n). \quad (29) \]

After integrating (29) one obtains

\[ n = n_0 - (n_0 - n_1) e^{-2Wt}, \quad (30) \]

where \( n_1 \) is the value of \( n \) when \( t \) is zero. Equation (30) has the familiar form of the capacitor charging equation and has a characteristic time constant of \((1/2W)\). This time constant is defined as the "spin-lattice relaxation time" \( T_1 \);

\[ T_1 = 1/2W. \quad (31) \]

Suppose now that a small magnetic field \( H_1 \) is made to rotate in a plane perpendicular to the steady field \( H_0 \). If the rotational frequency is the same as the Larmor precessional frequency, transitions will be stimulated between the two energy levels. The probability per nucleus in the lower energy state that a stimulated upward transition will occur is equal to the probability per nucleus in the upper energy state for a stimulated downward transition. Since the population in the lower energy state exceeds that in the upper state, there will be a greater
number of upward transitions. This corresponds to a net absorption of energy by the spin system from the rotating field $H_1$.

The larger number of transitions in the upward direction will tend to decrease the excess population in the lower energy level. The spin temperature, therefore, will increase since the population ratio may still be described by equation (23). One may think of the spin system as being subjected to a process of radiofrequency heating.

If the coupling between the spin system and lattice did not exist, the spin temperature would increase without bounds. The spin-lattice interaction, however, will cause the spin system to approach a finite temperature which is a function of the magnitude of $H_1$ and the amount of coupling. This approach can be described by adding another term to the right side of the differential equation (29),

$$\frac{dn}{dt} = \frac{1}{T_1} (n_0 - n) - 2 \dot{P},$$

where $\dot{P}$ is the probability per second per excess nucleus for a stimulated transition.

The term $\dot{P}$ is calculated by differentiating (21) with respect to $t$ and is found to be a function of several parameters of the system, namely $\gamma$, $H_1$ and the amount of
spin-spin interaction. Up until now the spin-spin interaction has only been mentioned as such and will now be discussed in more detail before the present trend of thought is continued.

When a sample of bulk matter is immersed in a steady magnetic field $\overrightarrow{H_0}$, each separate spin is subjected to a field $\overrightarrow{H_0} + \overrightarrow{\Delta H}$, where $\overrightarrow{\Delta H}$ is the vector summation of the fields contributed by each of the neighboring magnetic nuclei. The magnitude and direction of $\overrightarrow{\Delta H}$ will vary from one nucleus to another so that, in general, each spin will be in a slightly different field. As a result there will be a distribution of the Larmor precessional frequencies. The resonance condition, therefore, will not be perfectly sharp but broadened over a finite range of frequencies.

This is not the only mechanism that causes broadening. A magnetic nuclear spin precessing at the Larmor frequency produces a rotating magnetic field that can induce a transition in a neighboring spin. There is, in fact, a mutual exchange of energy between the spins. The amount of broadening resulting from this spin energy exchange process is of the same order of magnitude as that caused by the local field $\overrightarrow{\Delta H}$.

The total amount of broadening depends largely on the type of matter and the state in which it exists. Liquids,
in general, have resonance lines as narrow as 0.001 gauss while solids may have line widths of 10 gauss or more\textsuperscript{36}. 

In the previous section the spectral line shape of the resonance condition was described by a normalized function \( g(\omega) \), where

\[
\int_{-\infty}^{\infty} g(\omega) \, d\omega = 1. \tag{33}
\]

The quantity \( 1/g(\omega)_{\text{max}} \) is a rough guide to the resonance line width and in connection with this, a new quantity \( T_2 \) (an inverse measure of line width) is defined.

\[
T_2 = \tau g(\omega)_{\text{max}}. \tag{34}
\]

\( T_2 \) has the units of time and is called the spin-spin interaction time. It is characteristic of the time it takes the spin system to approach internal equilibrium.

If the frequency \( \omega \) is at the center of the resonance line, then

\[
p = \frac{1}{2} g^2 H_1^2 T_2. \tag{35}
\]

When (35) is substituted into (32), the steady state solution can be found by letting \( dn/dt = 0 \) from which

\textsuperscript{36}The high frequency random motion of liquid particles tends to average the local field \( \Delta H \) to nearly zero in a short period of time.
\[
\frac{n_s}{n_0} = \frac{1}{1 + \gamma^2 H_1^2 T_1 T_2} = z,
\]

where \(n_s\) is the number of excess nuclei in the lower energy state when a steady state is reached. The quantity \(n_s/n_0\) is called the saturation factor \(z\). By using (32), the differential equation (32) is now

\[
\frac{dn}{dt} = \frac{n_s - n}{ZT_1}.
\]

Upon integrating (37), one obtains

\[
n = n_s - (n_s - n_a) e^{-t/ZT_1},
\]

where \(n_a\) is the initial value of \(n\). The characteristic time constant associated with the approach to a steady state in the presence of a rotating field \(H_1\) is, therefore, \(ZT_1\).
3. **Bloch's Equations**

In order to observe NMR and make measurements of some of the NMR parameters such as $T_1$, it is necessary to relate equations developed in the last two sections to macroscopic properties of bulk matter. This was elegantly done by Bloch using semi-classical arguments\(^\text{37}\).

Because of the relationship between the magnetic moment $\vec{\mu}$ and the angular momentum $\vec{J}$ given by (1), the equation of motion for a nuclear magnet is

$$\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{H} \quad .$$

Note that (39) easily reveals much of the phenomena already explored in Section 1 of this chapter. If $\vec{H} = H_0 \vec{e}_z$ in a constant field, $\vec{\mu}$ precesses about $\vec{H}$ at the Larmor angular frequency $\omega_0 = \gamma H_0$. The value of $\mu_z$ is a constant of the motion. If the magnetic field has a small rotating component $H_1$ in the x-y plane, the expression for $d\mu_z/dt$ remains small unless the rotational frequency $\omega$ approaches the Larmor frequency $\omega_0$. This exposes the resonance condition.

Consider next a collection of weakly interacting nuclear spins. The magnetization $\vec{M}$ is a vector sum over

\(^{37}\text{F. Bloch, Phys. Rev. 70, 460 (1946).}\)
all nuclear magnetic moments in a unit volume. It follows from (39) that

\[ \frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H} \]  

(40)

The above equation is not complete with regard to a spin system embedded in a lattice. The right-hand side gives only the interaction of \( \vec{M} \) with the external magnetic field \( \vec{H} \). This is not the only mechanism which can cause \( \vec{M} \) to change. Both spin-spin and spin-lattice relaxation mechanisms can affect the time-dependence of \( \vec{M} \).

The spin-lattice interaction can be added to (40) in a remarkably simple fashion. It was previously shown that, in a steady magnetic field, the excess number of spin \( \eta \) in the lower energy level will approach an equilibrium value according to (30) with a characteristic time \( T_1 \). Since \( M_z \) is proportional to \( \eta \) the z component of (40) is not zero when \( \vec{H} \) is constant, but rather,

\[ \frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \]  

(41)

Bloch argued that the z component of (40) should have an additive term which is the right-hand side of (41).

The transverse components \( M_x \) and \( M_y \) are zero if the spin system is in thermal equilibrium when \( \vec{H} \) is a constant. This physically means that there is no phase coherence in
the spin system as each nuclear moment precesses at the Larmor frequency. If by some means a phase coherence did exist, local irregularities in the magnetic field will cause individual spins to get out of phase with each other in a time of the order of the spin-spin interaction time \( T_2 \). For simplicity, Bloch assumed that \( M_x \) and \( M_y \) would approach zero exponentially with a characteristic time \( T_2^* \). Thus the \( x \) and \( y \) components of (40) require additive terms of the form \(-M_x/T_2\) and \(-M_y/T_2\) respectively. The differential equations can then be written:

\[
\frac{dM_x}{dt} = \gamma (M_y H_z - M_z H_y) - \frac{M_x}{T_2} , \tag{42}
\]

\[
\frac{dM_y}{dt} = \gamma (M_z H_x - M_x H_z) - \frac{M_y}{T_2} , \tag{43}
\]

and

\[
\frac{dM_z}{dt} = \gamma (M_x H_y - M_y H_x) + \frac{M_0 - M_z}{T_1} . \tag{44}
\]

This set of differential equations can be solved for fields with a component rotating in the \( x-y \) plane, that is,

\[
H_x = H_1 \cos \omega t, \tag{45}
\]

\[
H_y = -H_1 \sin \omega t, \tag{46}
\]

and

\[
H_z = H_0 . \tag{47}
\]
A steady state solution derived in Andrew\textsuperscript{38} is

\begin{align*}
M_X &= \frac{1}{2} \chi_0 \omega T_2 \left[ \frac{(2H_1 \cos \omega t) \Delta \omega T_2 + 2H_1 \sin \omega t}{1 + (\Delta \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right], \\
M_Y &= \frac{1}{2} \chi_0 \omega T_2 \left[ \frac{2H_1 \cos \omega t - (2H_1 \sin \omega t) \Delta \omega T_2}{1 + (\Delta \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right],
\end{align*}

and

\begin{align*}
M_Z &= \chi_0 H_0 \left[ \frac{1 + (\Delta \omega)^2 T_2^2}{1 + (\Delta \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right],
\end{align*}

where \( \Delta \omega = \omega_0 - \omega \) and \( \chi_0 \) is the static susceptibility defined by \( M_0 = \chi_0 H_0 \). In actual experiments the rotating field is usually one of the rotating components of a linearly polarized field \( H_x = 2H_1 \cos \omega t \). It is, therefore, convenient to define the transverse susceptibilities using complex notation. Let transverse components be defined by

\begin{align*}
H_T &= H_X + iH_Y, \\
M_T &= M_X + iM_Y, \\
X_T &= X' - iX'', \\
\end{align*}

and

\begin{align*}
M_T &= X_T H_T.
\end{align*}

\textsuperscript{38}E. R. Andrew, \textit{loc. cit.}
This yields
\[ \chi' = \frac{1}{2} \chi_0 \omega_0 T_2 \left[ \frac{(\Delta \omega) T_2}{1 + (\Delta \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right] \] (55)

and
\[ \chi'' = \frac{1}{2} \chi_0 \omega_0 T_2 \left[ \frac{1}{1 + (\Delta \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right] . \] (56)

A physical interpretation of (55) and (56) is obtained by the following argument. The time-dependent component of \( H \) is ordinarily produced by a sinusoidal current in an inductor. If a coil of inductance \( L_0 \) is filled with a material of magnetic susceptibility \( \chi(\omega) \), then the inductance becomes
\[ L = L_0 \{ 1 + 4\pi \chi(\omega) \} . \] (57)

Using (53) and the fact that the impedance \( Z_{RL} = R_0 + i\omega L \), where \( R_0 \) is the coil resistance, the following expression is obtained:
\[ Z_{RL} = R_0 + 4\pi L_0 \omega \chi'' + iL_0 \omega (1 + 4\pi \chi') . \] (58)

Thus \( \chi'' \) increases the resistance and is a measure of NMR absorption, whereas \( \chi' \) changes the inductance and is a measure of NMR dispersion. A sketch of \( \chi' \) and \( \chi'' \) is shown in Figure 2.
The preceding discussion is intended to show that there are two macroscopic effects, rather closely related, that are accessible to an experimenter who wishes to measure parameters associated with NMR. These effects are the dynamic changes in magnetic susceptibility and magnetization associated with NMR. As referenced in Chapter I, Pound and Bloch used these effects respectively to first detect the NMR phenomenon in bulk matter.

Transient solutions of Bloch's equations depend on how the resonance condition is approached. A variety of phenomena are encountered which depend to a large degree on the time taken to pass through the resonance line as compared to such NMR parameters as $T_1$, $T_2$, $(\gamma H_1)^{-1}$ and
Even a summary treatment of all the possible transient effects would require considerable development and is not appropriate here. Rather, a qualitative discussion will be presented on those aspects of transient behavior which are relevant to the experimental work reported in subsequent chapters.

The steady state equations (48), (49), and (50) are appropriate for what Bloch called "slow passage". This means that the time spent in passing through the resonance line is very long compared to all of the characteristic time parameters $T_1$, $T_2$, $(\gamma H_1)^{-1}$ and $(\gamma H_0)^{-1}$. Bloch also derived solutions for what he termed "rapid passage" which are valid when the transit time $\delta t$ is short compared to $T_1$ and $T_2$, but long with respect to $(\gamma H_1)^{-1}$. "Slow passage" and "rapid passage" conditions bracket the regime of interest but neither one is entirely applicable to the experimental work to be discussed. For this work, the appropriate conditions are $T_1 \gg \delta t \gg T_2$ and $(\gamma H_1)^{-1}$. Under these restrictions the spin system is in thermal equilibrium with itself, but not necessarily at the lattice temperature. If the spin temperature is different from the lattice temperature and $\omega \neq \omega_0$, then the spin temperature will approach the lattice temperature in a characteristic

\[39\] F. Bloch, loc. cit.
time \( T_1 \). This means that the \( M_z \) magnetization will approach its steady state value at the same rate. If the magnetization is measured by NMR during a passage where \( T_1 >> \delta t >> T_2 \) and \((\gamma H_1)^{-1}\), its value will be essentially constant during the transit\(^40\). This provides a method for sampling the magnetization during its approach to spin-lattice equilibrium and, therefore, is a technique for measuring the parameter \( T_1 \). The actual experimental procedure will be discussed in Chapter III.

In view of the simplicity used in his assumptions, Bloch's equations are amazingly accurate in describing NMR phenomena for small values of \( H_1 \). When the magnitude of \( H_1 \) approaches the line width, however, deviations from experimental results are noted. This is particularly true in solids. For example, the resonance line width is modified from that predicted by Bloch's equations. Also the saturation phenomena are different\(^41\). Bloch's equations predict that \( \chi' \) and \( \chi'' \) will saturate at the same rate (see the term \( \gamma^2 H_1^2 T_1 T_2 \) in equations (55) and (56)).

\(^40\)This is not strictly true. Once transit of the resonance line begins, the characteristic time constant is \( ZT_1 \) according to (38). For \( M_z \) to remain constant, it is required that \( ZT_1 >> \delta t \). However, if this last condition is not met, the peak value of \( M_z \) measured during the transit is found to be proportional to the value that \( M_z \) had just prior to entering the resonance line.

\(^41\)A. C. Redfield, Phys. Rev. 98, 1787 (1955).
Experimentally the $x'$ component saturates more slowly than does $x''$.

For larger values of $H_1$ in solid materials, the assumption that the spin-spin and spin-lattice interaction terms are simply additive is no longer valid. In fact, the spin system is substantially modified by a large $H_1$. Near resonance the total magnetization vector tends to "lock on" to the rotating field and precess coherently with it. These effects have been accounted for in a theory developed by Redfield$^{42}$.

In the Redfield theory, a coordinate transformation to a rotating frame of reference, which is synchronized with the $H_1$ rotational field, is made. From this viewpoint, the z component of $\vec{H}$ is reduced by $\omega/\gamma$ and is, therefore, zero at resonance. Also the time-dependence of the transverse field is eliminated thus simplifying the equations of motion for $\vec{M}$. A good discussion of the effects caused by a large $H_1$ is given in Abragam$^{43}$. There are important differences between Redfield's theory and Bloch's phenomenological equations. However, with one exception, they are incidental to the experimental work reported here. This one exception concerns the fact

$^{42}$Ibid.

$^{43}$A. Abragam, loc. cit. Chapter XII.
that the dispersion component of the susceptibility $\chi'$ is not saturated by a large $H_1$ as easily as predicted by Bloch's equations. This effect was used to advantage and is discussed in Chapter III.
4. Spin-Lattice Relaxation Mechanisms

In the previous discussions, considerable attention was given to determining conditions for stimulating transitions between nuclear Zeeman levels. It was shown that radiation at the Larmor frequency, with a magnetic component in the x-y plane, is the cardinal factor for such transitions. Since the spin system and lattice are coupled, time dependent terms in the interaction can cause fluctuations in the magnetic field. Fourier components at the Larmor frequency are likely to stimulate spin transitions.

There is a subtle difference in the spin transitions stimulated by an externally produced rotating field as compared to those caused by the spin-lattice interaction. The coherent field produced by a R.F. generator is, in effect, an infinite temperature heat reservoir coupled to the spin system. The quantum states of interest in the magnetic field are by definition equally populated. This is the reason why the probability per nucleus for an upward transition is equal to that for a downward transition. A net exchange of energy between the field and the spin system is totally dependent on the excess population in one of the nuclear Zeeman levels. On the other hand, the lattice is at a finite temperature and can act as either a heat reservoir or heat sink. The probability per nucleus that a lattice stimulated transition will take
place is not the same for upward and downward transitions. A lattice stimulated spin transition implies that there are quantum levels in the lattice which are spaced by $\Delta E = 2\mu H_0$, and these states are populated in accordance with a Boltzmann distribution. This increases the probability per nucleus of the lattice stimulating a downward transition as compared to an upward transition. Hence the spin system and the lattice can approach a common equilibrium temperature when no externally generated $H_1$ field is present.

There are many mechanisms by which the lattice can relax the nuclear spin system. Which of these are dominant depends on such basic parameters as type and phase of material, density, temperature, NMR frequency and impurity content. Only relaxation mechanisms which are important in cadmium sulfide (CdS) will be discussed here.

An appropriate spin-lattice interaction Hamiltonian for CdS is primarily concerned with the magnetic interactions between nuclear spins and electrons in the lattice. The terms in the Hamiltonian naturally fall into one of three categories. First, there are terms of the form $\mathbf{I} \cdot \mathbf{L}/r^3$ which couple the nuclear spin and the electron orbital angular momentum. In diamagnetic solids, the orbital angular momentum is quenched so that these terms
may be neglected. Next, there are terms of the form \[ (I \cdot \vec{S}/r^3 - 3(I \cdot \vec{r})(\vec{S} \cdot \vec{r})/r^5) \]. This is a classical dipole-dipole coupling of the spin \( I \) with the electron spin \( \vec{S} \). In the last category there are terms of the form \( I \cdot \vec{S} \delta(\vec{r}) \) where \( \delta(\vec{r}) \) is the Dirac delta function. This is a scalar-contact interaction and is required for \( S \) state electrons which have non-zero wavefunctions at the nuclear spin site.

Spin-lattice relaxation by non-degenerate electrons will be considered first. CdS is normally a semiconductor. Electrons must be thermally excited to the conduction band and are, therefore, non-degenerate. In this sense Maxwell-Boltzmann statistics may be used to describe the conduction electron population.

In CdS the conduction electrons have mainly \( S \) state character. An appropriate Hamiltonian takes the form

\[
H = -\frac{8\pi}{3} \gamma_e \gamma_n n^2 (I \cdot \vec{S}) \delta(\vec{r})
\]

(59)

where \( \gamma_e \) = electronic gyromagnetic ratio,
and \( \gamma_n \) = nuclear gyromagnetic ratio.

The dipole-dipole coupling is neglected since it is small

\[^{44}\text{A magnetic field can slightly unquench the orbital angular momentum. This will cause small "chemical shifts" in the NMR frequency, but is still negligible in terms of spin-lattice relaxation.}\]
compared to the scalar-contact interaction. From (31), \( \frac{1}{T_1} = 2W \); thus the spin-lattice relaxation time can be determined by finding the transition probability. A perturbation calculation using (59) is carried out in Abragam and yields

\[
\frac{1}{T_1} = \frac{32}{9} \gamma_e^2 \gamma n^2 nV^2 \left| \langle \psi_e(o) \rangle \right|^2 \frac{2}{[2\pi (m^*)^3 kT]^4}, \tag{60}
\]

where
- \( n \) = conduction electron density
- \( V \) = sample volume
- \( m^* \) = effective mass of conduction electron
- \( k \) = Boltzmann's constant
- \( T \) = temperature

\( \langle |\psi_e(o)|^2 \rangle \) = electronic probability density at the nucleus averaged over all energy states (normalized on sample volume \( V \)).

This indicates that if the dominant spin-lattice relaxation mechanism is due to non-degenerate conduction electrons, the \( T_1 \) will be independent of the magnetic field \( H_0 \) and proportional to \( n^{-1} T^{-4/3} \).

Spin-lattice relaxation by degenerate electrons will be considered next. When CdS is highly doped with an impurity such as chlorine, it will exhibit metallic

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\(^{45}\) Abragam, loc. cit. (page 355).

\(^{46}\) Ibid, (page 389).
properties. Particular details are discussed later in this chapter, but of importance here is the fact that the Fermi level is in the conduction band. Even at room temperature the electrons are degenerate with an energy distribution in the conduction band in accordance with Fermi statistics.

The interaction Hamiltonian is again given by (59); however, for this case only electrons with energies on the Fermi surface can cause spin transition. A detailed calculation is carried out in Abragam and yields

\[
\frac{1}{T_1} = \frac{64}{9} \pi^3 \gamma e^2 \gamma n^2 \hbar^3 <\phi_f(o)\phi_f(o)> 2p^2(E_f)kT , \quad (61)
\]

where \( \rho(E_f) \) = electron density of states at Fermi level \( E_f \),

and \( <\phi_f(o)\phi_f(o)> \) = electronic density at nucleus averaged over states on the Fermi surface (normalized on sample volume).

For free electrons

\[
\rho(E_f) = \frac{(3n/8\pi^2)^{1/3}}{\hbar^2} m^* V \quad (62)
\]

where \( V \) is the sample volume.

Thus, the \( T_1 \) for relaxation by degenerate electrons is independent of \( H_0 \) and proportional to \( n^{-2/3} T^{-1} \).

\[47\] Ibid, (page 358).
Spin-lattice relaxation by paramagnetic impurities is the third and final mechanism to be discussed. Although CdS is a diamagnetic solid, it is possible to have paramagnetic sites scattered throughout the lattice due to impurities or dislocations. The interaction is a dipole-dipole coupling between the nuclear spin and the unpaired electron of a paramagnetic ion. From a general point of view, there are several possible processes in which a paramagnetic impurity causes nuclear transitions. These are discussed in considerable detail in Abragam.

In a material such as CdS, the predominant paramagnetic relaxation process involves a nuclear spin flip unaccompanied by a mutual electron flip. This is possible because the electronic levels are broadened more than the nuclear splitting. Although there are no "exchange flips" between the electron and the nuclear spin, the electron is flipping due to "electron spin-lattice relaxation". Changes in $S_z$ cause magnetic fluctuations at the nuclear site and those Fourier components at the Larmor frequency induce nuclear transitions. A transition probability $W$ is given by

$$W = \frac{1}{5} \left( \gamma_n \gamma_e \right)^2 \frac{S(S+1)}{r^6} \frac{1}{1+(\omega r)^2}$$

48Ibid, (Chapters VIII and IX).

where $\tau = $ longitudinal electron relaxation time\textsuperscript{50}. The angular dependence has been averaged in (63).

The $r^{-6}$ factor in (63) makes the direct relaxation process extremely sensitive to range. It would appear that those nuclei very close to the paramagnetic site are most easily relaxed. Although this is true, the close in nuclei are also subjected to a large static magnetic field from the paramagnetic ion and this shifts their resonance frequency by a considerable amount. As a result these spins are essentially isolated from the rest of the spin system. Only those nuclei beyond a critical range $r = b$ can communicate with each other via the spin-spin interaction. For this reason $b$ is called the "spin diffusion barrier radius".

The process of spin diffusion can be described by a diffusion equation of the form

$$\frac{\partial \theta}{\partial t} = D \Delta \theta \tag{64}$$

where $\theta$ is the spin temperature at a point. $D$ is a diffusion constant given by\textsuperscript{51}

$$D = \frac{a^2}{50T_2} \tag{65}$$

\textsuperscript{50}If the electron spin-spin interaction is strong, $\tau$ may be the transverse relaxation time.

where $a$ is the lattice spacing.

Now when the diffusion barrier radius $b$ is small, a region just beyond $b$ will be strongly relaxed by the paramagnetic center. The remainder of the spin system will tend to equilibrium via the spin diffusion process. Blumberg\textsuperscript{52} has calculated $T_1$ for this case and found

$$\frac{1}{T_1} = 8.5 N_p (CD^3)^{1/2} \quad (66)$$

where $C = \frac{1}{5} (\gamma_n \gamma_e h)^2 S(S+1) \frac{1}{1+(\omega t)^2}$, and $N_p$ = density of paramagnetic impurity sites. He denoted this as diffusion limited relaxation.

When $b$ is large, the direct relaxation process is weaker and the entire spin system (outside radius $b$) can remain in self thermal equilibrium. Blumberg called this the "rapid diffusion" case and found

$$\frac{1}{T_1} = \frac{4\pi}{3} N_p C b^{-3} \quad (67)$$

This equation is valid for $b \gg (C/D)^{1/2}$. If $b \ll (C/D)^{1/2}$ then (66) may be used\textsuperscript{53}.

\textsuperscript{52}W. E. Blumberg, loc. cit.

For both diffusion limited and rapid diffusion relaxation the $T_1$ is frequency dependent if $\omega \tau$ is of the order one or larger. The temperature dependence of $T_1$ enters via the electron spin-lattice relaxation time $\tau$. In general $1/\tau$ is an increasing function of the temperature. A plot of $T_1$ versus $T$ is usually characterized by a minimum in $T_1$ at a temperature where $\omega \tau \approx 1$. At lower temperatures, $T_1$ is frequency dependent whereas at higher temperatures the frequency dependence is quenched.

For some descriptive details concerning spin-lattice relaxation from paramagnetic ions, the reader is referred to a paper by Fukushima and Vehling\textsuperscript{54}.

5. **Knight Shift**

In bulk matter, the observed NMR frequency is often shifted from the value calculated using (7). The amount of shift is, in general, peculiar to the material being studied. The two most common frequency shifts are "chemical shift" and "Knight shift". A chemical shift arises from a slight unquenching of the orbital angular momentum when a magnetic field is present. In CdS it is about 0.08 percent of the field $H_0$. Chemical shifts are incidental to the research being reported herein, and will not be discussed further.

The Knight shift is named after Professor Walter Knight. He was the first to observe that the nuclear magnetic resonance of Cu$^{63}$ in metallic copper occurs at a 0.23 percent lower field than in diamagnetic CuCl$^{55}$. Townes$^{56,57}$ suggested that this shift is due to a magnetic interaction with conduction electrons and is primarily a phenomenon associated with metals. The Knight shift is always downfield for a fixed $\omega$ and increases with atomic number.

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$^{56}$Ibid.

The interaction between a nuclear spin and conduction electrons was discussed in the preceding section. The appropriate Hamiltonian is given by (59). Except at very high temperatures, the conduction electrons in most metals are degenerate; thus the interaction concerns only those electrons at the top of the Fermi distribution (electron states on the Fermi surface). Essentially, these electrons are polarized by the magnetic field and, therefore, add to it at the nuclear site.

The Knight shift $K$ is obtained by a first order perturbation calculation on (59) and yields\(^{58}\)

$$K \equiv \frac{\Delta H}{H_0} = \frac{8\pi}{3} \langle |\psi_f(0)|^2 \rangle V \chi_e$$ \hspace{1cm} (68)

where $\langle |\psi_f(0)|^2 \rangle$ is the electronic probability density at the nucleus averaged over the Fermi surface and normalized to the sample volume $V$. $\chi_e$ is the electronic susceptibility which for a free electron gas is

$$\chi_e = \frac{3\hbar^2 \chi_e n}{8E_F^2}$$ \hspace{1cm} (69)

where $E_f$ is the Fermi energy. Combining (68) and (69) together with $E_f = (\hbar^2/2m) \cdot (3\pi^2n)^{2/3}$, the Knight shift is

$$K = \left(\frac{8}{9\pi}\right)^{1/3} \frac{\gamma_e^2 m^* V}{4\pi k} |\langle \phi_f(0) \rangle|^{2} n^{1/3}.$$ 

(70)

The Knight shift is independent of temperature and magnetic field and is proportional to the cube root of the electron concentration\(^{59}\).

Since conduction electrons are also responsible for spin-lattice relaxation, there should be a relationship between the Knight shift and $T_1$. This was recognized by Korringa\(^{60}\) who showed that

$$T_1 T K^2 = \hbar \gamma_e^2 / 4\pi k \gamma_n^2 .$$

(71)

This equation is simply derived by combining (61), (62) and (70). The product $T_1 T K^2$ is called the Korringa product and is a constant of the material. It is valid when the conduction electrons are degenerate.

In semiconductors and in a few metals, the conduction electrons may be non-degenerate. The Hamiltonian is again

\(^{59}\)A second order correction to (70) shows that the Knight shift is slightly dependent on field and temperature. This arises from the Fermi energy dependence on these parameters.

\(^{60}\)J. Korringa, Physica, 16, 601 (1950).
given by (59); however, now Boltzmann statistics must be used. This changes the physical situation as compared to that for degenerate electrons in two ways. First, the energy distribution in the conduction band is highly dependent on temperature. Second, all of the conduction electrons now contribute to the shift.

Zhogolev\textsuperscript{61} has derived the Knight shift for non-degenerate conduction electrons. He found that

\[ K = \frac{\pi n^2 V e^2 < |\phi_e(0)|^2 > n}{3kT} \]

where \( < |\phi_e(0)|^2 > \) is again the electron probability density at the nucleus averaged over all states (normalized to the sample volume \( V \)). The Knight shift is proportional to \( n/T \). At room temperature, with \( n = 10^{19} \text{cm}^{-3} \), the Knight shift is more than an order of magnitude larger in a metal (degenerate) than in a semiconductor (non-degenerate). The difference becomes greater for a decrease in electron concentration.

A Korringa product can also be obtained for non-degenerate conduction electrons; however, it is not a constant. By combining (60) and (72), the Korringa product is

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\textsuperscript{61}D. A. Zhogolev, Soviet Physics-Solid State, Vol. 9, 42 (1967).
At room temperature, with $n = 10^{19} \text{cm}^{-3}$, the Korringa product is more than an order of magnitude larger in a metal (degenerate) than in a semiconductor (non-degenerate).

The preceding discussion shows that the Knight shift and Korringa product are sensitive indicators on whether the conduction electrons are degenerate or non-degenerate. A semiconductor-to-metal transition should be accompanied by a marked change in these parameters.

\[
T_1TK^2 = \frac{\pi 2\hbar^4}{32\sqrt{2\pi}m^3k^5} \left( \frac{\gamma_e}{\gamma_n} \right)^2 \left( \frac{n}{T^{3/2}} \right).
\]  
(73)
6. **CdS in the Solid State**

In the solid state, cadmium sulfide is a dimorphous compound which crystallizes in both the hexagonal-wurtzite and the cubic-zincblende structures. Both are loosely packed arrays which transform to close-packed phases at high temperature. The hexagonal form is stable below 900°C. The cubic form is stable below 100°C; it reverts to the hexagonal type above this temperature. The hexagonal form is found naturally as Greenockite. Cubic crystals are found in nature, although rarely. The natural cubic form is called Hawleyite. Only the hexagonal-wurtzite form of CdS was investigated by this author.

The chemical bonding forces in CdS are about seventy percent ionic with the remainder being covalent. The band gap between the valence band and the conduction band is about 2.5 eV. Ultra pure CdS is an insulator in the dark, but is photoconductive for illumination with wavelengths less than 0.5 microns.

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63M. Neuberger, *Cadmium Sulfide Data Sheet DS-124/2E*, Wright-Patterson Air Force Base, Ohio; Air Force Materials Laboratory (March 1967).
In less pure form, CdS is almost always an n-type semiconductor. Some common dopants which provide donor electrons are aluminum, bromine, chlorine, indium, iodine and cobalt. Sulfur vacancies or cadmium interstitials in the lattice are also donors.

In particular, chlorine atoms will go into the CdS lattice as a sulfur substitution. As a donor, it will provide one electron per chlorine atom. In lightly doped CdS:Cl crystals, the ground state of the extra electron is very shallow. It lies just 0.03 eV below the bottom of conduction band. At room temperature (kT = 0.026 eV), many of the donor electrons are excited to the conduction band; this significantly reduces the resistivity as compared to pure CdS.

At lower temperatures, most of the donor electrons will be trapped in their ground states. This is marked by

64Ibid.

65Acceptor impurities such as copper, silver and gold have limited solubility in CdS. In addition, during the crystal growth process, there is a tendency for acceptors to be compensated by sulfur vacancies (donors) in the lattice.

66S. Toyotomi and K. Morigaki, loc. cit.
an increase in resistivity since the electrons are not in the conduction band. It should be noted that although the donor electron in its ground state is trapped or localized near the chlorine impurity site, its orbit has a range of many lattice spacings. This is because the electron does not participate in the chemical bonding process and is "screened" from the chlorine nuclear charge by the lattice. An estimate of the orbital range and binding energy for the donor electron in its ground state can be obtained by using the Bohr theory of the hydrogen atom with a slight modification. The electronic mass $m$ is replaced by the effective mass $m^*$ and the charge $e$ is replaced by $e/\sqrt{\varepsilon}$ where $\varepsilon$ is the dielectric constant. The appropriate equations for the binding energy $E_n$ and Bohr radius $r_n$ are

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

(74)

and

\[ r_n = \frac{\varepsilon n^2 \hbar^2}{e^2 m^*} \]  

(75)

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For CdS the effective mass $m^* = 0.19 m$; the dielectric constant $\varepsilon$ has a value of 9.3 so that in the ground state ($n = 1$), the binding energy is .03 eV. The corresponding Bohr radius is $26 \text{Å}$. Nearest neighbor spacing in CdS is about $2.5 \text{Å}$.

7. **Semiconductor-to-Metal Transition**

It is helpful to picture mentally what happens to the electronic band system as the chlorine impurity concentration is increased. At low concentrations, the donor ground states are degenerate and spatially localized within a few tens of angstroms of their respective impurity sites. These electrons contribute to the electrical conduction process only if they are thermally excited to the conduction band. Electrical properties are basically those of a semiconductor.

As the impurity concentration is increased, the average spacing between impurity sites will be reduced. At moderate concentrations, the ground state wave functions of adjacent impurity sites will begin to overlap. This lifts the degeneracy on the donor levels and allows the formation of an impurity band. When the wave function overlap is significant, an impurity conduction band is

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$^{68}$S. Toyotomi and K. Morigaki, **loc. cit.**
formed. Even at very low temperature, the electrons are relatively free to move from one impurity site to another. At this stage the Cl-doped CdS crystal has some metal-like properties, but cannot be considered a true metal. At low temperature, the electrical properties are determined by the nature of the impurity conduction band and should be rather metal-like. At room temperature, the donor electrons are excited to the CdS conduction band and the material should behave like a high conductivity semiconductor.

As the impurity concentration is further increased, the impurity conduction band will spread in both energy and spatial extent. Finally at a rather high concentration, one would expect the impurity conduction band and the CdS conduction band to overlap and merge. When the zero temperature Fermi level is in the conduction band, the material will have truly metallic properties. The number of conduction electrons will be independent of temperature and have free access to all parts of the crystal volume via the conduction band. Figure 3 is a sketch of the band structure for low, moderate and high impurity concentrations.

The above description concerning the formation of an impurity conduction band in moderately doped CdS:Cl is somewhat vague. This was done intentionally in order to
FIGURE 3

Band Structure for Different Impurity Concentrations
MODERATELY DOPED

CONDUCTION BAND

--

IMPURITY BAND

VALENCE BAND

HEAVILY DOPED

CONDUCTION BAND

MERGES WITH
IMPURITY BAND

VALENCE BAND
first present the "overall picture". This regime must now be looked at more carefully.

It should be noted from the outset that "impurity bands" are poorly understood. Only fragmented information is available at this writing. This much is known. At a moderate-to-low doping concentration the degeneracy of the impurity level is lifted. At low temperature, where thermal excitation of donor electrons to the crystal conduction band is improbable, some "impurity conduction" is observed; however, an "activation energy" is required. As the impurity concentration increases, the activation energy decreases and goes to zero at a critical concentration \( N_c \). At this point the electrons are "free" carriers and there exists an impurity conduction band. This phenomenon was predicted and investigated by Mott. He showed (for a monovalent system) that as the interdonor spacing is reduced, free carriers will appear at a critical impurity concentration

\[
N_c = (0.25/a_i)^3
\]  

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\( ^{69} \) M. Alexander and D. Holcomb, loc. cit.

\( ^{70} \) N. F. Mott, loc. cit.

\( ^{71} \) N. F. Mott and W. D. Twose, loc. cit.
where $a_i$ is the atomic radius of the impurity atom\textsuperscript{72}. A reasonable estimate of $a_i$ is obtained by using (75) the Bohr radius. For CdS:Cl the value of $N_c$ is about $9 \times 10^{17} \text{cm}^{-3}$.

Matsubara and Toyozawa\textsuperscript{73} investigated the merging of the impurity conduction band with the crystal conduction band. They predicted that this occurs at a somewhat higher concentration $N_{cb}$ given by

$$N_{cb} \approx \frac{1}{4\pi} a_i^{-3} . \quad (77)$$

For CdS:Cl the value of $N_{cb}$ is $4.5 \times 10^{18} \text{cm}^{-3}$.

It must be emphasized that the theories set forth by Mott and by Matsubara and Toyozawa are approximate in nature and that numerical values calculated using (76) and (77) must be used with caution. This is particularly true when the value of $a_i$ is estimated from simple Bohr theory.

\textsuperscript{72}It is assumed that the number of donor electrons available for conduction is equal to the number of impurity atoms. This is valid if the number of acceptor impurities relative to the number of donors is small so that compensation can be neglected.

\textsuperscript{73}T. Matsubara and T. Toyozawa, \textit{loc. cit.}
8. **The Hall Effect**

The final subject to be reviewed is the Hall effect. This is appropriate since it relates the number of conduction electrons to measurable electrical properties of a material. For a detailed treatment of the Hall effect, the reader is referred to a text by Putley\(^7^4\). Much of the material reviewed here is discussed in Putley and in any good text on solid state physics such as Kittel\(^7^5\) or Dekker\(^7^6\).

The idea of a Hall effect can be obtained first from some rather simple arguments. Consider a block of conducting material residing in a steady magnetic field \(\mathbf{H} = (0,0,H_z)\). If an electrical current is made to flow parallel to the \(x\) axis, the charge carriers will, at first, be deflected along the \(y\) axis by the Lorentz force \(q(\mathbf{v} \times \mathbf{H})/c\) where \(q\) is the charge and \(\mathbf{v} = (v_x,0,0)\) is the velocity of charge carriers. If no current path is provided for the \(y\) direction, then the deflected charges produce a gradient in the charge density. The resulting electric field \(E_y\) opposes and balances the Lorentz force so that in a steady state the \(y\) component of the current

\(\ldots\)


\(^{7^5}\)Charles Kittel, *loc. cit.*

is zero. The potential associated with \( E_y \) produces a "Hall voltage" across the \( y \) dimension of the material. For simplicity, assume that all charge carriers have the same velocity so that the current \( \bar{J} \) is

\[
\bar{J} = nqv
\]  

(78)

where \( n \) is the density of charge carriers. The balance equation is

\[
\overline{E} + \frac{1}{c} (v \times \overline{H}) = 0,
\]  

(79)

or

\[
\overline{E} + \frac{1}{nqc} (\bar{J} \times \overline{H}) = 0
\]  

(80)

In terms of the components defined above,

\[
E_y = \frac{J_x H_z}{nqc}
\]  

(81)

For this geometry, the Hall coefficient is defined by

\[
R_H = \frac{E_y}{J_x H_z}
\]  

(82)

The Hall coefficient is purposely defined in terms of measurable parameters. From (81) it can be deduced that \( E_y \) is proportional to \( J_x \) and \( H_z \) so that \( R_H \) depends only on the charge \( q \) and density of charge \( n \). For the simple case presented here,

\[
R_H = \frac{1}{nqc}
\]  

(83)
Note that the sign of the Hall coefficient is indicative of the sign of the charge so that for electrons $R_H$ is negative. Of equal importance is the fact a measurement of $R_H$ as defined by (82) allows a determination of the charge density $n$ via (83), at least within the framework of the simple model assumed here.

Before enlarging on this concept of the Hall effect, it is appropriate to mention a few words about the electrical conductivity $\sigma$. Under the assumption that Ohm's law is valid,

$$J_x = \sigma E_x \quad .$$

(84)

By using (78), the above yields

$$\sigma = n q c v_x / E_x \quad .$$

(85)

The mobility $\mu$ is defined as the average drift velocity per unit electric field so that

$$\sigma = n |q| c \mu \quad ,$$

(86)

as related by (86), $\mu$ is the "conductivity" mobility.

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77In this document, the symbol $\mu$ is used for both magnetic moment and mobility. Within context there should be no confusion since these two entities are not discussed together.
A glance at (83) suggests that the mobility can be defined by

\[ \mu \equiv \sigma | R_H | \]  \hspace{1cm} (87)

As defined by (87) \( \mu \) is called the Hall mobility. In the simple model used here conductivity and Hall mobilities are identical. This is not true in general; (83) will require some modifications for more sophisticated models. However, (82) and (87) will be used to define the Hall coefficient and the Hall mobility respectively.

The non-physical part of the simple model used above is that individual electrons in a conduction band do not travel at a fixed velocity which depends only on \( \sigma \) and \( \bar{E} \). In fact, under normal circumstances, the energy imparted to an electron by an electric field is small compared to its total kinetic energy. A more valid model, therefore, involves a transport calculation which accounts for the velocity distribution of electrons in the conduction band.

The general equations for charge transport in the presence of a magnetic field are developed in great detail by Putley\(^{78}\). Of particular interest here are two of his results: first, for non-degenerate electrons in a semiconductor,

\(^{78}\text{E.H. Putley, loc. cit. (Chapter 3).}\)
second, for degenerate electrons in a metal,

\[ R_H = -\frac{3\pi}{8} \cdot \frac{1}{ne^2} \]  \hspace{1cm} (88)

where \( e \) is the magnitude of the electronic charge\(^7^9\). Note that for a metal, the Hall coefficient is identical to that obtained using the "simple" model. Even the numerical factor \( 3\pi/8 \) which appears in (88) is within 20 percent of unity. This is, in fact, indicative of the general case where only one type of charge carrier is involved. For almost any realistic electron scattering mechanism, the numerical factor in the equation for \( R_H \) is always close to unity, usually within 20 or 30 percent.

From (88) and (89), it is obvious that the temperature dependence of \( R_H \) is subordinate mainly to how the electron concentration varies with temperature. The type of electron scattering mechanism can change with temperature; however, this affects only the numerical factor which is always close to unity.

For metals at room temperature and below, the conduction electrons are usually degenerate. The Fermi level is

\(^7^9\)In both (88) and (89) it is assumed that the electrons are scattered by lattice vibrations.
in the conduction band, and thus the electron concentration is independent of temperature.

In a semiconductor, the situation is more complicated. Electrons gain the conduction band via thermal or optical photons excitation. As a result, the conduction electron concentration is temperature dependent.

Let \( N_d \) denote the concentration of donor impurities, and let \( E_d \) be the impurity ionization potential. If \( kT \gg E_d \), then most of the impurity atoms will be ionized and the electron concentration should approach \( n = N_d \).

At lower temperatures, \( n \) is found by calculating the number of impurity atoms that are ionized. Let the zero energy level (\( E = 0 \)) be at the bottom of the conduction band. The impurity level is then \( E = -E_d \). The Fermi-Dirac distribution function is

\[
   f_e(E) = \frac{1}{1 + \exp \beta (E - E_F)}
\]

where \( \beta = 1/kT \), and \( E_F \) is the Fermi energy. The concentration of unionized impurity atoms \( N_d^0 \) is given by

\[
   N_d^0 = \frac{N_d}{1 + \exp \beta (-E_d - E_F)}
\]

\( ^{80} \)There are two sources for these electrons. These are ionization of impurity atoms (impurity conduction) and excitation of valence electrons (intrinsic conduction). The latter is only important in ultra pure CdS and is neglected here.
The concentration of ionized impurity atoms \( N_d^+ = (N_d - N_d^0) \) is also the concentration of conduction electrons if compensation is neglected. Thus

\[
n = \frac{N_d}{1 + \exp \frac{\beta (E_d + E_F)}{kT}}.
\]

(92)

In order to use (92), an expression for the Fermi energy must be obtained.

The conduction electron concentration is also given by the general expression

\[
n = \int_{-\infty}^\infty \rho(E) f_E(E) \, dE
\]

(93)

where \( \rho(E) \) is the density of states, and as before \( E \) is the energy measured from the bottom of the conduction band.

If \( kT \ll (E-E_F) \), then

\[
f_E(E) \approx \exp \beta (E_F-E)
\]

(94)

The density of states is

\[
\rho(E) = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} E^{1/2}
\]

(95)

81Charles Kittel, loc. cit. (Chapter 7).
By using (94) and (95), the electron concentration is obtained from (93) and is

$$ n = n_0 \exp (\beta E_f) $$

(96)

where $n_0 = 2(m_e kT/2\pi \hbar^2)^{3/2}$. By equating (92) and (96) and considering a low temperature limit, an explicit expression for $\exp (\beta E_f)$ can be obtained. Thus (96) becomes

$$ n = (2N_d)^{1/2}(m_e kT/2\pi \hbar^2)^{3/4}\exp(-\frac{1}{2} E_d/kT) $$

(97)

A plot of $\ln(n)$ versus $1/T$ has a slope which approaches $-E_d/2k$ for low temperatures. This is one method of determining the impurity ionization potential $E_d$.

It must be remembered that compensation was neglected in obtaining (97). If at low temperatures there are fewer conduction electrons than there are acceptor impurity atoms, an appreciable fraction of the ionized donor atoms are being compensated by these acceptors. This tends to pin down the Fermi level near $E_f = -E_d$. For this case Putley\textsuperscript{82} shows that

$$ n \approx (n_0 N_d/2N_A) \exp(-E_d/kT) $$

(98)

\textsuperscript{82}E.H. Putley, loc. cit. (Chapter 4).
where \( N_a \) is the number of acceptor impurities and is small compared to \( N_d \). At very low temperatures the slope of a \( \ln(n) \) versus \( T \) plot is \( -E_d/k \) in (98) as compared to \( -E_d/2k \) in (97).

Thus far the temperature dependence of \( R_H \) has been discussed for a large \( N_d \) (heavily doped - metal) and a small \( N_d \) (lightly doped - semiconductor). In a moderately doped crystal, an impurity conduction band may be present. The number of conduction electrons will, therefore, be independent of temperature; however, the fraction of electrons in the impurity conduction band itself will be highly dependent on temperature. Since the mobility of electrons in the impurity band will most likely differ from the mobility of electrons in the crystal conduction band, \( R_H \) may have some temperature dependence. Conwell\(^{83}\) showed that \( R_H \) should have a maximum value when \( n_i \mu_i = n \mu \), where \( n_i \) and \( \mu_i \) are associated with the impurity conduction band and the unsubscripted symbols refer to the crystal conduction band. A broad maximum in appropriate \( R_H \) versus \( T \) data has been experimentally observed by Conwell\(^{84}\), Mott and Twose\(^{85}\), and others.

\(^{83}\)E. M. Conwell, loc. cit.

\(^{84}\)ibid.

\(^{85}\)N. F. Mott and W. D. Twose, loc. cit.
9. Summary of Important Relationships

It is appropriate to list in summary form some of the more important relationships discussed in the previous eight sections of this chapter.

A. The nuclear magnetic resonance frequency is given to first order by the Larmor equation:

\[ \omega_0 = \gamma_n H_0 \]  \hspace{1cm} (99)

B. The number of excess spin in the lower Zeeman level approaches equilibrium according to:

\[ n = n_0 - (n_0 - n_1) e^{-t/T_1} \]  \hspace{1cm} (100)

The Bloch susceptibilities \( X' \) and \( X'' \) are directly proportional to \( n \).

C. If the spin-lattice relaxation mechanism is due to non-degenerate conduction electrons, then

\[ \frac{1}{T_1} \propto n^{1/2} \]  \hspace{1cm} (101)

If the spin-lattice relaxation mechanism is due to degenerate conduction electrons, then

\[ \frac{1}{T_1} \propto n^{2/3} \]  \hspace{1cm} (102)

If the spin-lattice relaxation mechanism is due to paramagnetic impurities, then \( T_1 \) is almost always proportional
to $N_p^{-1}$ and may have a minimum when the temperature is such that $\omega t \approx 1$. $T_1$ will usually be frequency dependent at lower temperatures.

D. The Knight shift in metals (degenerate electrons) is independent of temperature with

$$K = n^{1/3} \quad (103)$$

The Korringa product $T_1TK^2$ is a constant of the material. The Knight shift in semiconductors (non-degenerate electrons) is much smaller than in metals having the same value of $n$. It also depends on temperature. The corresponding Korringa product is much smaller in a semiconductor as compared to a metal. It is not a constant of the material but depends on both $n$ and $T$.

E. As the amount of donor impurity is increased in CdS:Cl, it will exhibit a semiconductor to metal transition. This is predicted to occur in two steps: first, an impurity conduction band is formed at a critical impurity concentration $N_C$; second, the impurity conduction band merges with the crystal conduction band at a slightly higher impurity concentration $N_{C_1}$. In CdS:Cl this is predicted to occur for an impurity concentration of the order of $10^{18} \text{cm}^{-3}$. 
F. The Hall coefficient is defined by:

\[ R_H = -\frac{E_Y}{J_x H_z} \]  \hspace{1cm} (104)

The conduction electron concentration \( n \) is related to \( R_H \) by

\[ R_H = -\frac{1}{\text{enc}} \] \hspace{1cm} (degenerate electrons) \hspace{1cm} (105)

\[ R_H = -\frac{3\pi/8}{\text{enc}} \] \hspace{1cm} (non-degenerate electrons). \hspace{1cm} (106)

The Hall coefficient is independent of temperature for a metal but is a decreasing function of temperature for a semiconductor.

This concludes a review of existing theory appropriate to an NMR investigation of the semiconductor-to-metal transition in CdS:Cl. It was not intended that this be a complete treatise of the subject; but rather, an attempt was made to lay a foundation for discussing specific experiments and their results. These experiments are the topic of the next chapter.
CHAPTER III
THE EXPERIMENT

In this chapter, the apparatus used to conduct an NMR investigation is briefly described. This is followed by a discussion of the experimental methods which were employed. Finally, the techniques used to reduce and analyze experimental data are described. In this last section, a few experimental results are presented in preliminary form. This is necessary to adequately describe and justify certain data reduction procedures.

1. Apparatus

The large steady magnetic field $H_0$ required to do NMR experiments was provided by a Varian model V4012A electromagnet. The configuration employed for all experiments used two 12 inch pole pieces with a 2-9/16 inch gap. Static fields up to 11 kilogauss with a uniformity of ±1.0 gauss could be produced over approximately three-quarter of the volume between the pole pieces.

The V4012A has two options for selecting and stabilizing the magnetic field. The first is a self-contained current regulator with feedback. The second option allows
external control and stabilization and was the option used for all experiments reported herein. External control was accomplished with a Varian Fieldial Regulator Mark II (trade name). This device employs a Hall effect probe which senses the magnetic field strength (between pole pieces) in terms of a Hall voltage. The driving current to the Hall probe is highly regulated and the probe itself is embedded in a constant temperature oven. Fluctuations in the Hall voltage are, therefore, indicative of changes in the magnetic field and are used to stabilize this field by means of a sophisticated feedback network.

The Varian Fieldial provides for selecting the magnetic field strength via a digital switch-dial system. In the 5-10 kilogauss range the dial settings are within 0.2% of the actual field. The short term field stability (random noise) is rated at one part per million rms or 2 milligauss rms, whichever is greater. The long term stability is ten parts per million or 5 milligauss, whichever is greater.

The Varian Fieldial also has a built-in "field sweep" mechanism. This device can increase or decrease the field in either a single sweep or in one of two continuous sweep patterns: sawtooth and triangular. The "sweep range" is adjustable from 250 milligauss up to full field. Eight "sweep times" are available from 0.5 to 100 minutes.
A Varian Wide-Line NMR Spectrometer, model V4200B, was used to induce and detect NMR signals. This apparatus can be subdivided into six major components: a transmitter, a modulator, a V4230B probe, a receiver, a signal processor, and a recorder. Figure 4 is a functional block diagram of these components.

The transmitter is a radio frequency (RF) generator. It has a variable frequency oscillator (VFO) which can operate from 2 to 16 MHz in three bands: 2-4 MHz, 4-8 MHz, and 8-16 MHz. The VFO is enclosed in a constant temperature oven for frequency stability. Additional frequency stability may be achieved by synchronization of the VFO with an external crystal controlled oscillator. The VFO signal is amplified and then fed through a variable attenuator. This allows the transmitter output level to be varied from zero up to about one watt. The RF output is fed to a transmitter coil in the V4230B probe and is used to generate the oscillating field $H_1$.

The modulator is an audio frequency (AF) oscillator and variable gain power amplifier system. It can provide up to 50 watts of AF power at five set frequencies: 20, 40, 80, 200 and 400 Hz. The amplifier input also has provisions for an external input signal if VFO operation is desired. The output of this unit is fed to modulation-sweep coils in the V4230B probe.
FIGURE 4

Functional Block Diagram of NMR Spectrometer
The heart of the spectrometer is the V4230B probe. This unit is constructed to fit between the pole pieces of the magnet with its longitudinal axis perpendicular to the field. A simplified drawing and an electrical schematic diagram\(^8\) are shown in Figures 5 and 6. The probe performs several functions. First, it is a sample holder. Second, it houses the transmitter coil mentioned above. This is a modified Helmholz coil tuned to the transmitter frequency. It is positioned to produce a linear oscillating magnetic field \(2H_1\) parallel to the longitudinal axis and throughout the volume occupied by the sample\(^8\). The probe also houses a receiver coil. This is a solenoid encircling the sample volume; however, it is positioned with its axis in the vertical direction which is perpendicular to both the transmitter coil axis and the steady magnetic field \(H_0\). This orthogonal configuration tends to completely decouple the transmitter and receiver coil. As discussed in Chapter II, the \(H_1\) field (transmitter coil) causes the nuclear magnetization to precess coherently with it when a resonance condition exists. The rotating magnetization induces a feeble emf in the

\(^8\)Figures 5 and 6 were obtained from the Varian Equipment Manual.

\(^8\)The linear oscillating field \(2H_1\) is equivalent to two counter-rotating fields of magnitude \(H_1\).
Figure 6. Electrical Diagram for V420B Probe

- Twin Connector
- Red Coax Connector
- Green Coax Connector
- Receiver Coil
- Sweep Coil
- Transmitter Coil
- U-Mode Paddle (Blue)
- V-Mode Paddle (Red)
receiver coil. The induced component which is in-phase with the \( H_1 \) field is proportional to the \( \chi' \) susceptibility, whereas the out-of-phase component is proportional to \( \chi'' \).  

In order to separate the \( \chi' \) and \( \chi'' \) components, the probe has two sets of flux steering paddles. Each set consists of a fine and a coarse tuning paddle. The \( u \)-mode paddles are resistive coils which can cause a small amount of leakage between the transmitter and receiver coil. The leakage is in-phase with the \( H_1 \) field because of the construction of these \( u \)-mode paddles. The \( v \)-mode paddles are low resistance coils and can induce an out-of-phase leakage in the receiver coil. In either case, the leakage and NMR signals are superimposed. In normal operation the leakage signal is made much larger than the NMR signal, but it is kept as small as possible within this limitation. Now if the leakage is in-phase with \( H_1 \), then changes in the \( \chi' \) component will appear as amplitude modulation on the total signal. Changes in the \( \chi'' \) component will appear as phase modulation. This is called \( u \)-mode operation. If the leakage is out-of-phase, the \( \chi'' \)

\(^{88}\text{Note in equation (58) that the in-phase component is proportional to } \chi''. \text{ This is, of course, due to nuclear induction in the transmitter coil. The receiver coil is orthogonal to the transmitter coil and thus a } \pi/2 \text{ phase shift is observed in the nuclear induction.}\)
component will appear as amplitude modulation, whereas the \( \chi' \) component will cause modulation of the phase. This is called \( v \)-mode operation. Since the receiver, which will be discussed next, incorporates an amplitude modulation (AM) detector, the \( u \)-mode and \( v \)-mode paddles provide a means of separating the \( \chi' \) dispersion and \( \chi'' \) absorption components of the NMR signal respectively. The V4230B probe houses two additional inductors which serve as modulation-sweep coils. These are Helmholtz coils wound parallel to the magnetic pole faces. They may be used to increase, decrease, sweep or modulate the \( H_0 \) magnetic field at the sample position. When used in a field modulation application, these coils are powered by the 50 watt AF amplifier previously described. It is advantageous to sine-wave modulate the main \( H_0 \) magnetic field at an audio frequency because it allows the NMR signal to be processed by narrow bandpass amplifiers and phase sensitive detection apparatus which improve the signal-to-noise ratio.

Before proceeding, it is appropriate to discuss field modulation in a little more detail since it affects the operation of much of the equipment to be described later. For many applications, the main field is modulated by an amount which is small compared to the linewidth of the NMR signal being observed. This produces audio sidebands on
the nuclear induction signal which are proportional to the slope of the NMR line. In other words, as one sweeps through the NMR line, the magnitude of the audio sidebands on the nuclear induction signal will be proportional to either \( dx'/d\omega \) (u-mode) or \( dx''/d\omega \) (v-mode). The advantages of using this technique will become apparent as the discussion proceeds.

The nuclear induction signal is fed from the receiver coil to a straightforward TRF receiver\(^89\). Next the signal is processed through an AM detector circuit and an AF amplifier. This provides the first improvement in signal-to-noise since any slow changes in RF signal amplitude caused by circuit drifting are not passed by the detector. The audio signal is now fed to a narrow bandpass filter. Typically the bandpass is a few Hertz wide centered on the modulation frequency. There is no significant loss in line shape information if the magnetic field sweep rate is slow enough to cause only gradual changes in the sideband amplitudes. On the other hand, the signal-to-noise ratio is most often drastically improved by this technique.

\(^89\)All RF tuned circuits in the transmitter, probe, and receiver are "ganged" so that changes in frequency can be made with one dial.
The next stage is a phase sensitive detector. This is essentially a commutator switch circuit which periodically reverses polarity of the AF signal. This switch circuit is keyed by the AF modulator. In effect, the AF signal is multiplied by a square wave reference signal which has the same frequency and phase as the modulation. This provides full wave rectification of the NMR signal. Noise signals, which differ from the NMR signal in frequency and phase, have a D.C. component which tends to zero over a time interval that is long compared to the modulation period. The phase sensitive detector improves the signal-to-noise ratio by a factor of $\sqrt{2}$ if the noise is random. The rectified signal is now fed to an RC low-pass filter. The time constant is adjusted so that it is long compared to the modulation period but is short compared to the time of passage through the NMR line. The RC filter often improves the signal-to-noise by an order of magnitude. Its effect depends on the bandpass of previous stages.

The output signal from the RC filter is a D.C. voltage which is proportional to either $dx'/d\omega$ or $dx''/d\omega$. This is usually fed to the y input of a Varian F80A x-y recorder. The x input is a voltage from the Fieldial sweep circuit which is proportional to the sweep current. The resulting plot is the derivative of the $x'$ or $x''$ line shape.
The above discussion establishes a nominal configuration for the Varian V4200B Spectrometer. Several variations on this configuration were also used. In almost all cases, auxiliary equipment was employed to replace some of the Varian apparatus in order to extend or improve its capability.

One such variation utilized a Lock-in Amplifier model HR-8, manufactured by Princeton Applied Research, Inc. This device replaced the Varian signal processor and the modulation AF oscillator. It performed no new functions; however, it proved to be more versatile and to sometimes provide a better signal-to-noise figure.

Another variation required replacement of the Fieldial sweep system. The minimum sweep time on the Fieldial is 30 seconds. This was adequate for measuring $T_1$ longer than about 15 seconds. For a shorter $T_1$, a faster sweep time is desired. The auxiliary system made use of the modulation-sweep coils on the V4230B probe. A triangular ramp current was added to the modulation signal to provide the sweep. The triangular ramp was generated by a Wavetek Oscillator, model 111. A General Radio Tone Burst Generator (model 1396B) was used as a gate to switch the ramp signal on or off according to a preset prescription (details about this procedure will be discussed later). The ramp signal out of the gating device was
added to the modulation signal and then amplified by a Hewlett-Packard model 6824A Power Supply/Amplifier. This device fed the modulation sweep coils on the probe. The Wavetek Oscillator has a frequency range of .00015 Hz to 1.0 MHz. For this application, only frequencies between .05 and 5 Hz were used.

When faster sweep times were utilized, it was necessary to increase the bandpass and decrease the filter time constant on the signal processor. This invariably led to much poorer signal-to-noise figures on a given sweep through the resonance line. In order to recover signal-to-noise it was necessary to make repeated passages through the NMR line and then average the results. This procedure increases the signal-to-noise ratio by \( \sqrt{N} \) where \( N \) is the number of passages. A Varian C1024 Time Averaging Computer was employed to store and average the data. This device was inserted between the signal processor and x-y recorder; it was keyed by pulses from the tone burst gate. The C1024 has a delayed-time data read-out system which is compatible with the x-y recorder.

NMR measurements at cryogenic temperatures were accomplished by utilizing a four wall - two chamber vacuum pyrex dewar. The outer chamber may be filled with liquid nitrogen whereas the inner volume may contain either liquid helium or liquid nitrogen. The dewar includes a small
single-jacked tail which can be inserted into the sample holder on the V4230B probe. The inner dewar will hold up to 5 liters of liquid. Most NMR measurements were made at room temperature 300°C, at 77°C (liquid N₂) and 4.2°C (liquid He). A few measurements were made near 2°C by lowering the vapor pressure above the liquid helium. This was accomplished with a 50 cfm single stage forepump marketed by Fisher Scientific Corporation.

The V4012A electromagnet and the cryogenic dewars were also used for making measurements of the electrical properties of CdS:Cl. In addition electrical measurements were made at approximately 50°C temperature intervals between 100°C and 350°C. These temperatures were accomplished using a Varian model V4540 Variable Temperature Controller. This device can supply a dry nitrogen gas flow at a controlled temperature between 100°C and 525°C. For the lower temperatures, the dry nitrogen is pre-cooled by passing it through a heat exchanger submerged in liquid nitrogen.

On one particular sample of CdS:Cl, it was necessary to obtain electrical property measurements at temperatures between 4.2°C and 77°C. This required the design and

90This variable temperature device was used here only for electrical measurements. However, it was designed to be used in the V4230B probe for making NMR measurements.
construction of a "cold-finger" variable temperature device.

A simplified diagram of the cold-finger device is shown in Figure 7. The body is a 3/8 inch diameter, 4 inch long copper rod with a side-flat surface on one end. The CdS:Cl sample was attached to the flat surface with thermally conducting cement. The cold-finger was fitted with a thermometer and heating coils. The heat exchanger is a 3 inch length of #12 copper wire. In operation the cold-finger is submerged in liquid nitrogen with about one half of the heat exchanger above the surface. Liquid helium is then added. This cools and freezes the nitrogen. Solid nitrogen is a relatively poor heat conductor so that the main heat leak is through the copper to the heat exchanger. A heater coil is used to maintain a pre-selected temperature on the lower part of the cold-finger. The temperature is measured with a germanium resistance thermometer. Tests were conducted to show that the cold-finger does maintain a uniform temperature over the length below the heater coil\(^{91}\).

The cold-finger performed as designed, although it did use (vaporize) helium at a rather extravagant rate. At

\(^{91}\text{The CdS:Cl sample was replaced with a second thermometer.}\)
Figure 7. Simplified Drawing of Cold-Finger Device
temperatures above 20°K, the device vaporized liquid helium at rates above 10 liters per hour. The helium expenditure rate can be decreased by raising the nitrogen level on the heat exchanger or by decreasing the diameter of the heat exchanger. It should be cautioned, however, that this causes the system to be somewhat "sluggish" in terms of coming to an equilibrium temperature. This is particularly true below 20°K. Since only a few measurements were needed for this research, no attempt was made to optimize the cold-finger design.

The investigation of electrical properties in a semiconductor can, in itself, be a sizable experimental effort if high precision measurements are required. Many researchers have developed sophisticated equipment and methods for obtaining resistivities and Hall coefficients. For this problem, however, highly accurate data were not necessary.

92 This cold-finger device was also designed to allow NMR measurements. The side-flat on the end of the copper body is replaced with a one inch sapphire cylinder. The sample is mounted on the bottom of the cylinder. Sapphire is a good thermal conductor but a poor electrical conductor. The latter property allows the device to be inserted into the V4230B probe with only a minimum disturbance of the tuned circuits. This feature was not exploited for this research program; however, it has been used here, by Look, Locker and Adams, to obtain NMR data on chromium doped and also cobalt doped CdS (data unpublished).

93 These data were basically used to determine how $T_1$ depends on the electron concentration $n$. Measurements made on $T_1$ were rarely better than $\pm 10$ percent.
Figure 8 is a schematic diagram of the circuit used to obtain electrical property measurements. Figure 9 shows, in more detail, where the leads were attached to a CdS:Cl sample. Typical sample dimensions were 1.0x0.5x0.4 centimeters. Current $I_C$ measurements were obtained by reading the voltage across $R_1$. Voltage $V_C$ measurements were obtained between points 1 and 2. The resistivity $\rho$ of the sample is

$$\rho = \frac{V_C A}{I_C L} \quad (107)$$

where $A$ is the cross sectional area (yz plane), and $L$ is the distance between points 1 and 2. The total resistance of $R_2$ was selected to be large compared to that of the crystal. The tap on $R_2$ was adjusted so that the meter $V_2$ read zero when the magnetic field was zero. In the presence of a magnetic field, $V_2$ read the Hall voltage. Note that (104) can be written in terms of the measured quantities and is

$$R_H = \frac{V_2 Z}{H_2 I_C} \quad (108)$$

where $Z$ is the z dimension of the sample.
Figure 8. Electrical Diagram of Circuit used to Obtain Electrical Property Measurements.

- **V1**: Voltmeter for measuring crystal voltage and current.
- **V2**: Voltmeter for measuring Hall voltage.
- **S1**: Voltage/current switch.
- **R1**: 1 ohm.
- **R2**: See text.
Figure 9. Drawing of Sample with Leads Attached
2. **Experimental Methods**

From an experimental view-point, there were four major tasks to perform for this research effort:

a. Obtain ten or more samples of crystalline CdS:Cl with a large range in doping concentrations.

b. Determine the spin-lattice relaxation times of these samples as a function of temperature.

c. Measure the Knight shift (if any) exhibited by these samples as a function of temperature.

d. Determine the electrical properties of these samples; in particular, the electron concentration as a function of temperature.

The categorization and listing order used above is arbitrary. Work on all of these tasks was performed concurrently. Each item will now be discussed.

The chore of securing appropriate samples was a continuous one over a one and one-half year period. The first
crystal obtained for this research was donated by Dr. Donald Reynolds of ARL\textsuperscript{94}. The precise history of this sample could not be traced, but it was apparently grown prior to 1967 by the Eagle Picher Company of Miami, Oklahoma under a contract with ARL\textsuperscript{95}. Later analyses showed that it was highly doped with chlorine and had an impurity content in excess of 30 ppm (parts-per-million atomic). This sample was eventually designated as sample J.

The next samples were grown on request by Mr. Donald Nass of ARL. These were grown by the vapor deposition method. Chlorine doping was accomplished by mixing CdCl\textsubscript{2} with the CdS in the furnace "charge". The furnace was operated at about 1300\degree C with an argon atmosphere of 10 to 20 psi (absolute). A crystalline boule was deposited on a "C plate" located in a cool region (about 900\degree C) of the furnace.

Seven different CdS samples were obtained using this method. These included one control sample (designated sample A) grown with no CdCl\textsubscript{2} added to the charge. Later

\textsuperscript{94}Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio.

\textsuperscript{95}No records concerning the crystal could be found. Dr. Reynolds indicated that it was "probably" grown by the vapor deposition method in a chlorine atmosphere.
analyses showed that this method is rather inefficient for doping of CdS. None of the crystals contained more than a few ppm (parts-per-million atomic) of chlorine even when the charge contained up to one percent (by weight) of CdCl₂. However, five of these samples were later used for experimentation on lightly doped CdS. They were designated samples B through F.

At this point it should be noted that analysis of contingent samples on a day-to-day basis was not feasible. The most accurate method of determining the impurity content of a sample is probably to use a mass spectrometer. This instrument was not readily available. As an alternative, samples were classified by making measurements on the spin-lattice relaxation time T₁ at room temperature. This is a rough inverse measure of the conduction electron concentration or the donor concentration (see equations (101) and (102)). From previous work done by Look it was anticipated that the room temperature values of T₁ would range from a few hundred seconds for pure CdS to less than one second for heavily doped samples.

96 All CdS samples were eventually analyzed with a mass spectrometer by the Bell and Howell Electronic Material Division of Pasadena, California under a contract with ARL. The results are discussed in Chapter IV.

97 Private communication.
In an effort to obtain some moderately doped and heavily doped CdS, Mr. Nass modified the atmosphere used in the furnace. Chlorine gas was added to the argon, and on several occasions a pure chlorine atmosphere was used. Most of the samples obtained with this technique had a room temperature $T_1$ of about one second which is the same as that measured for sample J. In addition, most of the new samples appeared to have poor spatial uniformity of color. Only one of these samples was eventually used for experimentation. It was designated sample K and had a room temperature $T_1$ of about $\frac{1}{2}$ second.

An HCl atmosphere in the furnace was also tried in an attempt to increase the doping level. The crystals obtained using this technique had measured values of $T_1$ close to one second but were, in general, less uniform than those obtained using a chlorine atmosphere. None of these crystals were used for experimentation.

The final source of crystals was Eagle Picher Company. Under a contract with ARL, six CdS crystals were melt grown with a specified chlorine impurity content. The chlorine was added by mixing CdCl₂ with the CdS charge. Crystals were pulled from a 1500°C melt charge under about 50 atmospheres of argon. Four of these samples were eventually used for experimentation. Sample L
was heavily doped and had a room temperature $T_1$ of about 0.3 second. Samples G, H, and I were moderately doped with measured values of $T_1$ between 20 and 3 seconds.

Over thirty different CdS:Cl samples were examined as potential candidates for experimentation. Twelve of these were finally selected and designated by the letters A through L. Sample A was the undoped control sample with a room temperature $T_1$ in excess of 200 seconds. Each successive letter after A denotes a sample with a shorter $T_1$ (higher impurity content) up to sample L with $T_1 \approx 0.3$ seconds. Table 1 is a list of the samples with information about the source and the method used to add doping material.

Samples were prepared for experimentation in the following manner. Each boule was examined for color uniformity. The most uniform portion of the boule was then separated from the remainder. This typically provided from two to eight cubic centimeters of sample material. In most cases the samples were not single crystals but usually contained several grains.

The moderately and highly doped samples were subdivided into two parts: one for electrical property measurements and the other for NMR measurement. The NMR samples were crushed into small grains in order to reduce their overall conductivity. This vastly improves the NMR signal-to-noise
Table 1

Information on CdS Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source and Doping Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Vapor grown at ARL - Undoped.</td>
</tr>
<tr>
<td>B</td>
<td>Vapor grown at ARL - Charge mixed with .00005 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>C</td>
<td>Vapor grown at ARL - Charge mixed with .0002 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>D</td>
<td>Vapor grown at ARL - Charge mixed with .01 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>E</td>
<td>Same as Sample D.*</td>
</tr>
<tr>
<td>F</td>
<td>Vapor grown at ARL - Charge mixed with .002 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>G</td>
<td>Melt grown by Eagle Picher Company - Charge mixed with .00001 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>H</td>
<td>Melt grown by Eagle Picher Company - Charge mixed with .000025 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>I</td>
<td>Melt grown by Eagle Picher Company - Charge mixed with .000050 g of CdCl₂ per g of CdS.</td>
</tr>
<tr>
<td>J</td>
<td>Vapor grown by Eagle Picher Company using a chlorine atmosphere in the furnace.</td>
</tr>
<tr>
<td>K</td>
<td>Vapor grown at ARL using a chlorine atmosphere in the furnace.</td>
</tr>
<tr>
<td>L</td>
<td>Melt grown by Eagle Picher Company - Charge mixed with .001 g of CdSCl₂ per g of CdS.</td>
</tr>
</tbody>
</table>

* Samples D and E were taken from different parts of the same boule. The growth was apparently very non-uniform since the values of T₁ are different by about a factor of two.
ratio for two reasons. First, the RF field can penetrate only to about the electrical skin depth of a conducting solid. Skin depths on the order of one millimeter are typical for the highly doped crystals; thus crushing of the sample can significantly increase the number of nuclei which "see" the RF field. Second, the AF field modulation can set up eddy currents in a solid, high-conductivity sample. These will interact with the field and may induce small mechanical vibrations in the sample. This type of noise is difficult to discriminate against since its frequency and phase is often coherent to the modulation and will not be filtered by the signal processor. Crushing of the sample will break up the eddy currents and improve the signal-to-noise ratio.

The second part of the sample was used for making electrical property measurements. Usually a single crystal was cleaved from this portion; typical dimensions were 1.0x0.5x0.4 centimeters.

For the undoped and lightly doped samples, it was not necessary to crush the sample to obtain an adequate NMR signal-to-noise ratio; notwithstanding, crushing usually did provide some improvement. With some of these samples, however, a significant variation was observed in the impurity concentration from different parts of the same boule.
For example, samples D and E were taken from the same boule and have measured values of $T_1$ which are different by a factor of two. For this reason the NMR and electrical property measurements were usually performed on the same sample. The dual purpose samples were cut into cylinders rather than rectangular blocks since this is the shape of the sample volume in the NMR probe.

The most time consuming task was that of measuring spin-lattice relaxation times. A particular measurement would take anywhere from one to fifty hours to secure. The amount of time needed was inversely related to the NMR signal-to-noise ratio.

The method used here to measure $T_1$ is a modification of the classical "direct" method which is sometimes used to make similar measurements in liquids. With the classical direct method, the NMR signal is continuously observed as the nuclear spin system is allowed to approach an equilibrium condition. Usually the spin system is first saturated with a large RF field $H_1$. Then the $H_1$ is suddenly reduced to a small non-saturating value. The NMR signal strength is then measured as a function of time as

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98 If separate samples were used for the two measurements, the NMR sample was subjected to at least one measurement on its electrical properties to ascertain that both samples had nearly the same impurity content.

99 E. R. Andrew, loc. cit. (page 107).
it exponentially approaches a steady-state level with a characteristic time $T_1$.

In many dielectric solids, and particularly in cadmium compounds, the signal-to-noise ratio is intolerably low for small non-saturating values of $H_1$. There are two reasons for this. First, the spin-lattice interaction mechanisms are usually weak compared to those in a liquid; therefore, a solid often saturates at a lower value of $H_1$. Second, natural cadmium is composed of five major isotopes and the most abundant two, Cd$^{112}$ and Cd$^{114}$, have no nuclear moments. The natural abundance of Cd$^{113}$ is 12.3%, and Cd$^{111}$ is present at 12.9%. The Cd$^{113}$ resonance was observed for all experiments reported here. Thus, only one cadmium atom in eight participates in the NMR process.

A substantial increase in signal-to-noise is obtained using a modified direct method. As before, the spin-system is saturated by using a large RF field $H_1$ at the NMR frequency. This brings the nuclear magnetization to zero. The main magnetic field $H_0$ is now moved to an off resonance value ($H_0-\Delta H$) where $\Delta H$ was typically 10 to 25 gauss. The magnetization will then proceed to recover in a characteristic time $T_1$. At a pre-selected time, the field is allowed to sweep through the resonance to "sample" the magnetization. This process will again saturate the
spin-system, but not before a transient signal is observed. The peak value of this signal is proportional to the magnetization. By varying the time at which a "sample" is taken one may obtain a time history of the magnetization recovery.

Two details should be mentioned at this point. First, as discussed in Chapter II, the dispersion is not saturated as easily as the absorption. For this reason, the spectrometer was always operated in the u-mode. In fact, this author was not able to detect the v-mode absorption signal except at liquid helium temperatures. The second detail concerns the line shape of the observed signal. This is best obtained by a step-by-step synthesis process. First, remember that the output signal of the spectrometer (at the recorder) is proportional to the instantaneous derivative of the line shape. Thus if it were possible to observe the dispersion signal with a low non-saturating RF field $H_1$ and a very slow sweep rate, the output would resemble the curve in Figure 10a. If the RF field is not small, the signal will be saturated at the center resonance point and the observed signal follows the curve in Figure 10b. If now the sweep rate is increased such that the time of passage through resonance is short compared to $T_1$,

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The signal-to-noise ratio is inversely related to temperature.
Figure 10. Shape of NMR Signal
then the observed signal will be the curve in Figure 10c. Essentially the magnetization is saturated as the resonance center point is passed, and it does not recover fast enough to provide the second peak of Figure 10b.

Figures 11 and 12 are typical data sheets (photo-reduced) showing the magnetization recovery. Figure 11 is representative of data taken at 4.2°K. Figure 12 shows data taken at 77°K and testifies to the inverse dependence on temperature of the signal-to-noise ratio. The signal-to-noise ratio at room temperature, 300°K, was comparable to that at 77°K. At 300°K the loss in signal-to-noise due to temperature was compensated by the use of larger samples. This was possible since a double-walled dewar is not required. Furthermore, the mechanical vibrations caused by the boiling of cryogenic liquids are major contributors to the noise.

The measured value of $T_1$ is obtained from the data in the following manner. The magnetization is sampled after a long waiting period (many times the length of $T_1$). The value of the signal is denoted by $M_\infty$. The magnetization is then sampled at pre-selected times $t$ where $t$ is usually less than $2T_1$. The corresponding signal values are denoted by $M(t)$. For an exponential recovery, a plot of $\ln(M_\infty - M(t))$ versus time $t$ will yield a straight line with a slope $-1/T_1$. 
FIGURE 11

Typical Magnetization Recovery Data at 4.2°K
FIGURE 12

Typical Magnetization Recovery Data at 77°K
It should be emphasized that a single measurement of $T_1$ usually required averaging of several times the amount of data shown in Figure 12.

A majority of the NMR data were obtained using an 8 MHz resonance (approximately 8460 gauss). Some selected measurements of $T_1$ were made at 4 MHz (4230 gauss) in order to check the frequency dependence of this parameter. Data were obtained on all samples at room temperature and on all but the very lightly doped samples at 77°K. Similar measurements were made on six of the more heavily doped samples at 4.2°K. Two measurements of the $T_1$ at 8 MHz and 4 MHz were acquired at 2.13°K on sample J.

The third experimental task to be discussed concerns measurements of Knight shifts. If a particular CdS:Cl sample has a Knight shift, its resonance field $H_0$ will be lower than that for a pure CdS crystal (sample A). In practice none of the lightly doped samples B through F exhibited a detectable Knight shift; therefore, sample C was often used as a standard. The shorter $T_1$ of sample C, as compared to sample A, accelerated the process of acquiring Knight shift data.

Figure 13 is a typical data sheet showing a Knight shift in sample J. Note that the field was swept in both directions (see arrows in Figure 13) so that the center of resonance could be determined. In general, several
FIGURE 13

Typical Knight Shift Data
CdS:Cl

Frequency 8 MHz
Temperature 77 K

Scale
1.0 gauss

Sample J

Sample C
measurements were made to increase the precision of the data.

Knight shift measurements were obtained on all CdS:Cl samples at room temperature. On those samples which exhibited a detectable Knight shift at 300°K, measurements were also performed at cryogenic temperatures. All measurements were obtained at an NMR frequency of 8 MHz.

The procedures used to obtain electrical property measurements were simple and rather straightforward. Some of these were discussed in the previous section along with the description of the apparatus. Electrical leads were attached to the sample using an ultrasonic soldering iron and indium solder. The connections were mechanically fragile, but adequate for these measurements. The crystal current \( I_c \) was always adjusted so that the total power dissipated in the sample was much less than one watt. A typical current in a lightly doped crystal was twenty milliamperes. Currents up to one-half ampere were used in the highly doped samples. The resistivity measurements (see equation (107)) were made with a zero magnetic field. Next, the Hall voltage meter \( V_2 \) was balanced to read zero by adjusting \( R_2 \) (see Figure 8). The magnetic field was then turned up to ten kilogauss and a Hall voltage reading was taken from \( V_2 \). Typical Hall voltages ranged from fifty microvolts to ten millivolts. Magneto-resistive
effects and misadjustments in the meter balance were com-
pensated by reversing the magnetic field and again reading
the Hall voltage\textsuperscript{101}. In practice the readings were
repeated several times and then averaged.

Electrical property measurements were made on all
samples at temperatures ranging from 350°K down to 77°K.
Measurements were also made on samples G, H, I, J, K and
L at 4.2°K. The "cold-finger" variable temperature device
was used to obtain electrical property data at tempera-
tures between 4.2°K and 77°K on sample I. The reason for
these "special" measurements will be discussed in the
next chapter.

\textsuperscript{101}Magneto-resistance will cause a transverse voltage
proportional to the square of the magnetic field strength.
This effect was observed only at 4.2°K.
3. **Data Reduction and Analysis Techniques**

From the inception of this research effort, it was obvious that a systematic data reduction method would be required to handle the rather substantial amounts of data generated when making spin-lattice relaxation measurements. Several hundred data sheets of the type shown in Figures 11 and 12 were acquired during the course of this program.

Raw data were processed in the following manner. Measurements were made of the signal height and designated as $M(t)$ or $M_\alpha$. The unit of measure is arbitrary but was usually taken as inches which corresponds to the scale on these data sheets. The quantity $M_\alpha - M(t)$ was immediately calculated by hand and plotted versus the time $t$ on semi-logarithm paper. This provided a rough estimate of $T_1$ and also an indication of the quality of the data. If the data showed a large scatter about a "best fit" straight line, more measurements were made to increase the signal-to-noise ratio. A typical plot of $\ln(M_\alpha - M(t))$ versus $t$ is shown in Figure 14.

The numerical values of $M_\alpha - M(t)$ and $t$ were entered in pairs on IBM computer cards. These data were then reduced by a computer which was programmed to provide:

---

102 This author had access to the IBM 7094 computer system at Wright-Patterson AFB, Ohio.
Figure 14. Typical Semilog Plot of Magnetization Recovery Data
(1) a semilogarithmic plot of the data; (2) a straight line least-squares fit; (3) computed values of $T_1$, and (4) a statistical analysis of the data scatter$^{103}$. The final reduced data were then tabulated as $T_1$ versus temperature for each sample. In most cases, two values of $T_1$ were recorded, one for an 8 MHz resonance and the other for a 4 MHz resonance.

One important detail should be mentioned here. The quantity $M_x-M(t)$ is a difference between two experimentally determined values and should decrease in magnitude as $t$ increases. Since the noise in the experimental apparatus can usually be characterized by a constant rms amplitude, the "signal-to-noise" ratio of the quantity $M_x-M(t)$ is a decreasing function of $t$. This leads to larger and larger fluctuations in $\ln(M_x-M(t))$ as $t$ is increased. In practice measurements of $M(t)$ were normally taken in a range $0<t<2T_1$. This usually prevented the statistical occurrence of a negative value for $M_x-M(t)$. In cases where the signal-to-noise ratio was very poor, repeated measurements were made on both $M_x$ and $M(t)$ to obtain more precise values.

$^{103}$A Fortran IV computer program had been written several years earlier by this author for another purpose. It was essentially a "plotting" program with a wide variety of options in the output format. It was easily adapted for use here by adding a subroutine for calculating $T_1$ from the input data.
In fact, it became a standard procedure to take repeated measurements of $M_a$ and also of $M(t)$ for the larger values of $t$. This tended to compensate for the decreasing signal-to-noise ratio, and it negated the necessity to include weighting factors in the least-squares curve fit calculations\(^{104}\).

A difficulty which was encountered in the data reduction procedure involved a slight tendency for the magnetization recovery process to be non-exponential. In much of the data this tendency was difficult or impossible to detect. However, at liquid helium temperatures the improved signal-to-noise ratio revealed that the recovery process appears to slow-down with time. This is shown in Figure 15. It should be noted, however, that substantial changes in the slope occur at late times where $t > 2T_1$ or after the magnetization has recovered more than 80% of its final value\(^{105}\). For this reason the effect is difficult to detect.

\(^{104}\)A common straight-line least squares fit assumes that an error in the measurement of a variable is independent of the value of the variable itself. If this assumption cannot be made, it is necessary to weight the data according to how the error distribution changes with the variable.

\(^{105}\)A $T_1$ cannot be defined for non-exponential recovery, but it is convenient for this discussion to calculate a $T_1$ based on the initial portion of the recovery curve.
Figure 15. Semilog Plot of Magnetization Recovery Data Showing Non-Exponential Behavior
at higher temperature where the signal-to-noise ratio hampers measurements beyond $t = 2T_1$.

Furthermore, this effect may go undetected unless special care is taken in securing the data. In particular, the measurement of $M_\alpha$ is made after the magnetization is "completely" recovered. Normally, a measurement of $M$ at $t = 4T_1$ will suffice (98% of the magnetization is recovered). If the above $T_1$ is based on the initial slope of the semilogarithmic recovery curve, this measurement of $M$ will be smaller than the true $M_\alpha$ by much more than 2%. In practice the difference was more like 5 or 10%. If an experimenter plots $\ln(M_4 - M(t))$ versus $T$ where $M_4 = M(t)$ at $t = 4T_1$, the curve corresponding to Figure 15 would tend to be more of a straight line, especially for $t < 2T_1$. Thus, the entire effect could go undetected in the presence of noise signals.

It became obvious to this experimenter than an investigation of the non-exponential behavior could in itself become a complete research project. Detection of this effect at higher temperature severely taxed the capability of the available equipment. Several months were spent in securing only a few measurements, and these were of poor quality. In addition, these measurements on non-exponential behavior did not appear to provide any relevant information on the semiconductor-to-metal transition. The entire
matter became a problem of devising a suitable data reduction procedure.

It was ultimately decided that $T_1$ would be measured by fitting a straight line to the initial part of the magnetization recovery semilogarithmic curve. The cut-off point was $t = 2T_1$. There are, in fact, good physical reasons why this interpretation of data is reasonable. First, remember that $T_1$ is normally an inverse measure of the strength of the relaxation mechanism. Second, the non-exponential behavior is a second order effect in the sense that most of the magnetization has been recovered before any appreciable change in slope can be detected. Therefore, it seems plausible that $1/T_1$ as measured here is a good approximation to the strength of the relaxation mechanism. Third, it is possible to postulate a reasonable physical model to explain the non-exponential behavior, and this model is consistent with the above statements.

A brief description of a physical model will be given here; a more detailed discussion is presented in the Appendix. It is assumed that the total magnetization recovery process is a sum of the individual recovery processes in each particle of the "crushed" NMR sample. If there is a variation in the average impurity concentration from particle to particle, the total magnetization will be a sum of
exponential terms with a distribution in values of $1/T_1$. A rather simple calculation indicates that the initial slope of the semilogarithmic recovery curve is given by $-\bar{1}/\bar{T_1}$ where the bar indicates the mean value of the distribution.

There are several pieces of experimental evidence which support the above model. First, all of the samples showed some spatial variation in color, and on several occasions, $T_1$ measurements on specimens from various parts of a boule were different. Second, the non-exponential behavior seemed to be much more apparent when a particular sample was crushed as compared to a measurement made on a bulk crystal\textsuperscript{106}. Third, the non-exponential behavior could not be detected in the very lightly doped samples where other spin-lattice relaxation mechanisms strongly compete with those related to one specific impurity species. Fourth, mass spectrometer data on "chips" from various parts of a sample boule invariably yielded different values for the chlorine impurity concentration. These measurements are discussed in the next chapter. For more information on non-exponential behavior, the reader is referred to the Appendix.

\textsuperscript{106}The spin-spin interaction in a single crystal will keep the entire spin system in internal equilibrium.
An estimate of the standard error associated with a particular measurement of $T_1$ is not a trivial task. The data reduction computer program has a built-in routine which calculates a standard error associated with the least squares fit slope. This calculation is based on the scatter of data about the best fit curve. Repeated $T_1$ measurements were made on one sample at the same temperature and resonance frequency. These showed that the precision of an individual measurement is not as good as that indicated by the least squares fit analysis. Some further experiments indicated that the discrepancy between the two methods of computing standard error was larger when the apparent signal-to-noise ratio increased. The key word here is "apparent". Very low frequency noise does not usually make the data curves look "noisy". In addition, this kind of noise will not generally cause random scatter in the measurements of $M(t)$ unless random sampling techniques are used when taking the data. It can, however, produce errors in the measurement of $T_1$.

A very low frequency noise source was detected in the NMR spectrometer. It was a slow change in the amplification factor or gain of the electronic system. The direction of change was random on a day-to-day basis, but during any particular measurement period (several hours) it often proceeded in the same direction. This tended to bias
magnetization recovery data which were taken in sequence with respect to the "time off resonance". The result was an error in the measured value of $T_1$.

By making repeated measurements on a "standard" signal over a period of several days, data were obtained which indicated that errors in the measurement of $T_1$ caused by changes in the amplification factor would usually be less than 7%. It was also found that an alert experimenter can often detect changes in the amplification factor when apparent signal-to-noise ratio was more than about 25/1. It was estimated that for a given signal-to-noise ratio ($R$), that the largest contribution to an error in the measurement of $T_1$ caused by undetected changes in the amplification factor would be roughly $(2/R)100\%$.

Other factors affecting the precision of $T_1$ were assessed to be negligible compared to random noise and changes in the amplification factor. Therefore, error estimates from these two sources were utilized to calculate an rms standard error for each measurement of $T_1$.

The reduction of raw data on the Knight shift was a straightforward process. The center of resonance was determined by bisecting the distance between the signal peaks (see Figure 13). The shift in resonance was determined relative to the standard sample C. The Knight shift $K = \Delta H/H_0$ was tabulated versus temperature for each sample.
The precision of a single measurement was ±0.1 gauss. This estimate was determined by taking into account the field stability ratings on the Varian Fieldial. In practice, five or more measurements were taken in each case to increase the precision. The standard error is ±0.1/√N where N is the number of individual measurements.

Electrical property data are measured values of Ic, Vc, V_H, T and the physical dimensions of a sample. These were reduced via (108) and (107) and tabulated as R_H and ρ versus T for each sample. Estimates were then made of the conduction electron concentration n. If the Hall coefficient was independent of temperature, it was assumed that the sample had metal properties and that the electrons were degenerate. The value of n was obtained from (105). If, however, R_H increased monotonically with decreasing temperature, it was assumed that the conduction electrons were non-degenerate and (106) was used to calculate n.

With sample I the Hall coefficient was only weakly dependent on temperature and displayed a maximum value near 77°K. This sample probably possessed an impurity conduction band. A fair estimate of n is obtained by using (106) and the value of R_H measured at the highest temperature (350°K)\textsuperscript{107}.  

\textsuperscript{107}At room temperature and above, most of the conduction electrons are in the CdS conduction band and not in the impurity conduction band. The electrons are probably non-degenerate.
It is then assumed that \( n \) is independent of temperature and that the variations in \( R_H \) at lower temperatures are a result of having two contributions to the observed mobility when some of the electrons drop into the impurity conduction band.

As indicated in the previous section, the techniques used here to obtain electrical property measurements were rather crude. On some of the highly doped samples, the Hall voltage was less than 0.1 millivolts and accurate readings were difficult to obtain because of electrical noise in the measuring apparatus.

These uncertainties, together with the fact that variations in impurity content were observed with several samples, were used to make a standard error estimate of about 15% for the electrical property measurements.

In order to analyze results, plots were made of \( \log(T_1) \) versus \( \log(n) \) at different constant temperatures. The slopes of these curves were studied to determine whether the relaxation was due to non-degenerate or degenerate conduction electrons (see Equations (101) and (102)) or even paramagnetic impurities\(^{108}\). Therefore, these plots are

\(^{108}\)If \( T_1 \) is insensitive to changes in \( n \), mechanisms other than those associated with conduction electrons are most likely responsible for the spin-lattice relaxation process.
useful in ascertaining the value of $n$ associated with a semiconductor-to-metal transition. A plot of $\log(T_1)$ versus $\log(n^{2/3}T)$ was made for some of the more highly doped samples; these curves were correlated with (102) to test for degeneracy in the conduction electrons.

The Knight shift data were analyzed by plotting $\log(K)$ versus $\log(n)$; these curves were correlated with (103) to find those samples with metal properties (slope = 1/3). As discussed in the previous chapter, the transition to a semiconductor is marked by a sharp drop in the value of $K$ as $n$ decreases below the transition.

Similar log-log plots were made for the Korringa product versus $n$. The Korringa product is a constant for metals, and it also decreases sharply at the transition concentration.

Some of the techniques employed to analyze the experimental data were suggested by the nature of the data itself. It is convenient to discuss these in the next chapter after the data have been presented.
CHAPTER IV
RESULTS, ANALYSES AND DISCUSSION

For the sake of completeness, the experimental results are first presented in tabular form. In the second part of this chapter, the results are analyzed and discussed in detail; many of the measurements are exhibited again in the form of appropriate graphs which expose important features in the data.

1. Experimental Results

In Table 2, NMR data on CdS samples A through D are presented. NMR measurements on these undoped and lightly doped samples were made only at 300°K (room temperature). No Knight shifts were observed with any of these samples.

NMR data for 300°K and 77°K are given for CdS:Cl Samples E and F in Tables 3 and 4 respectively. A Knight shift could not be detected at 300°K for either sample; Knight shift measurements were not attempted at 77°K.

Tables 5 through 10 contain the NMR data taken on the moderately and highly doped CdS:Cl Samples G through L. A blank space indicates that no measurement was attempted. All Knight shift measurements were made at a resonance frequency of 8 MHz.

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Table 2

NMR Data on CdS Samples A through D at 300°K

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>240. ± 11.</td>
<td>218. ± 10.</td>
</tr>
<tr>
<td>B*</td>
<td>162. ± 5.</td>
<td>148. ± 3.</td>
</tr>
<tr>
<td>C*</td>
<td>132. ± 7.</td>
<td>117. ± 4.</td>
</tr>
<tr>
<td>D*</td>
<td>123. ± 10.</td>
<td>-</td>
</tr>
</tbody>
</table>

* A Knight shift was not detected.
Table 3

NMR Data on CdS:Cl Sample E*

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>60. ± 4.</td>
<td>59. ± 6.</td>
</tr>
<tr>
<td>77.</td>
<td>218. ± 24.</td>
<td>182. ± 18.</td>
</tr>
</tbody>
</table>

* A Knight shift was not detected at 300°K.

Table 4

NMR Data on CdS:Cl Sample F*

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>37.5 ± 1.5</td>
<td>38. ± 3.</td>
</tr>
<tr>
<td>77.</td>
<td>123. ± 7.</td>
<td>102. ± 8.</td>
</tr>
</tbody>
</table>

* A Knight shift was not detected at 300°K.
Table 5

NMR Data on CdS:Cl Sample G

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
<th>Knight Shift $(10^{-4}K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.</td>
<td>18.3 ± 1.4</td>
<td>-</td>
<td>0.07 ± 0.04</td>
</tr>
<tr>
<td>77.</td>
<td>69. ± 6.</td>
<td>55. ± 4.</td>
<td>-</td>
</tr>
<tr>
<td>4.2</td>
<td>713. ± 76.</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6

NMR Data on CdS:Cl Sample H

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
<th>Knight Shift $(10^{-4}K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.</td>
<td>7.7 ± 0.5</td>
<td>-</td>
<td>0.2 ± 0.05</td>
</tr>
<tr>
<td>77.</td>
<td>36. ± 3.</td>
<td>32. ± 4.</td>
<td>0.18 ± 0.05</td>
</tr>
<tr>
<td>4.2</td>
<td>374. ± 29.</td>
<td>186. ± 21.</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 7
NMR Data on CdS:Cl Sample I

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
<th>Knight Shift ($10^{-4}K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.</td>
<td>3.1 ± 0.2</td>
<td>3.2 ± 0.3</td>
<td>0.32 ± 0.05</td>
</tr>
<tr>
<td>77.</td>
<td>16.4 ± 1.4</td>
<td>12.9 ± 1.5</td>
<td>0.39 ± 0.05</td>
</tr>
<tr>
<td>4.2</td>
<td>200. ±14.</td>
<td>102. ± 9.</td>
<td>0.32 ± 0.05</td>
</tr>
</tbody>
</table>

Table 8
NMR Data on CdS:Cl Sample J

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$T_1$ at 8 MHz (sec)</th>
<th>$T_1$ at 4 MHz (sec)</th>
<th>Knight Shift ($10^{-4}K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.</td>
<td>1.07 ± 0.04</td>
<td>1.07 ± 0.07</td>
<td>0.78 ± 0.05</td>
</tr>
<tr>
<td>77.</td>
<td>5.3 ±0.2.</td>
<td>5.2 ± 0.4</td>
<td>0.97 ± 0.07</td>
</tr>
<tr>
<td>4.2</td>
<td>104. ±8.</td>
<td>83. ±7.</td>
<td>0.95 ± 0.07</td>
</tr>
<tr>
<td>2.13</td>
<td>173. ±7.</td>
<td>136. ±6.</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 9
NMR Data on CdS:Cl Sample K

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>T₁ at 8 MHz (sec)</th>
<th>T₁ at 4 MHz (sec)</th>
<th>Knight Shift (10⁻⁴K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.53 ± 0.03</td>
<td>-</td>
<td>1.36 ± 0.05</td>
</tr>
<tr>
<td>77</td>
<td>2.5 ± 0.3</td>
<td>-</td>
<td>1.42 ± 0.06</td>
</tr>
<tr>
<td>4.2</td>
<td>47.4 ± 1.6</td>
<td>-</td>
<td>1.27 ± 0.07</td>
</tr>
</tbody>
</table>

Table 10
NMR Data on CdS:Cl Sample L

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>T₁ at 8 MHz (sec)</th>
<th>T₁ at 4 MHz (sec)</th>
<th>Knight Shift (10⁻⁴K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.34 ± 0.04</td>
<td>0.36 ± 0.04</td>
<td>1.67 ± 0.05</td>
</tr>
<tr>
<td>77</td>
<td>1.40 ± 0.10</td>
<td>1.35 ± 0.15</td>
<td>1.73 ± 0.06</td>
</tr>
<tr>
<td>4.2</td>
<td>32.8 ± 0.9</td>
<td>27.8 ± 0.6</td>
<td>1.66 ± 0.07</td>
</tr>
</tbody>
</table>
Electrical property measurements made on all samples A through L are presented in Tables 11 through 22 respectively. Note that the Hall coefficients are in units (cm$^3$/coul). These hybrid units are widely used in the literature in preference to the gaussian units of (105) and (106). Values of the conduction electron concentration were computed utilizing the methods discussed in Section 2 of Chapter III. Electrical property measurements were not attempted below 77°K on samples A through F.

Measurements were pursued at 4.2°K on samples G and H but with only partial success. Adequate data were obtained on the resistivities, but the Hall voltages could not be measured. Both samples exhibited magneto-resistance at 4.2°K, and the transverse voltages from this effect completely masked the feeble Hall voltages. Based on the magnitude and stability of the magneto-resistance voltage measured on each sample, it was possible to estimate a minimum detectable Hall voltage. Since no Hall voltage was detected, this minimum figure may be used, in turn, to calculate an upper bound value for the magnitude of the Hall coefficient $|R_H|$. This was done for both samples with the results $|R_H|<2.5\times 10^5$ cm$^3$/coul for sample G and $|R_H|<6.\times 10^3$ cm$^3$/coul for sample H. Since the resistivity of both samples was measured, (87) may be used to estimate their respective values of $R_H$ in terms of the Hall mobility.
### Table 11

**Electrical Properties Measured on CdS Sample A**

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient ($10^3$ cm$^3$/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration ($10^{15}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-1.6</td>
<td>5.0</td>
<td>4.7</td>
</tr>
<tr>
<td>300.</td>
<td>-1.6</td>
<td>4.3</td>
<td>4.7</td>
</tr>
<tr>
<td>250.</td>
<td>-1.6</td>
<td>3.6</td>
<td>4.6</td>
</tr>
<tr>
<td>200.</td>
<td>-1.7</td>
<td>2.5</td>
<td>4.4</td>
</tr>
<tr>
<td>150.</td>
<td>-1.9</td>
<td>1.7</td>
<td>3.9</td>
</tr>
<tr>
<td>100.</td>
<td>-2.5</td>
<td>1.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

### Table 12

**Electrical Properties Measured on CdS:Cl Sample B**

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient ($10^3$ cm$^3$/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration ($10^{15}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-0.74</td>
<td>2.9</td>
<td>10.</td>
</tr>
<tr>
<td>300.</td>
<td>-0.77</td>
<td>2.6</td>
<td>9.7</td>
</tr>
<tr>
<td>250.</td>
<td>-0.81</td>
<td>2.2</td>
<td>9.2</td>
</tr>
<tr>
<td>200.</td>
<td>-0.91</td>
<td>2.0</td>
<td>8.2</td>
</tr>
<tr>
<td>150.</td>
<td>-1.2</td>
<td>3.4</td>
<td>6.2</td>
</tr>
<tr>
<td>100.</td>
<td>-1.6</td>
<td>13.</td>
<td>4.0</td>
</tr>
<tr>
<td>77.</td>
<td>-3.6</td>
<td>25.</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Table 13

Electrical Properties Measured on CdS:Cl Sample C

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (10^2 cm^3/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration (10^16 cm^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-4.9</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td>300.</td>
<td>-5.2</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>250.</td>
<td>-5.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>200.</td>
<td>-5.8</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>150.</td>
<td>-6.5</td>
<td>.70</td>
<td>1.1</td>
</tr>
<tr>
<td>100.</td>
<td>-9.1</td>
<td>.43</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table 14

Electrical Properties Measured on CdS:Cl Sample D

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (10^2 cm^3/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration (10^16 cm^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-3.1</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>300.</td>
<td>-3.2</td>
<td>2.4</td>
<td>2.3</td>
</tr>
<tr>
<td>250.</td>
<td>-3.4</td>
<td>2.5</td>
<td>2.2</td>
</tr>
<tr>
<td>200.</td>
<td>-4.0</td>
<td>2.6</td>
<td>1.8</td>
</tr>
<tr>
<td>150.</td>
<td>-4.6</td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>100.</td>
<td>-7.4</td>
<td>2.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 15

Electrical Properties Measured on CdS:Cl Sample E

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (10^2\text{cm}^3/\text{coul})</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration (10^{16}\text{cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-1.8</td>
<td>0.79</td>
<td>4.1</td>
</tr>
<tr>
<td>300.</td>
<td>-1.9</td>
<td>0.67</td>
<td>3.9</td>
</tr>
<tr>
<td>250.</td>
<td>-2.0</td>
<td>0.57</td>
<td>3.7</td>
</tr>
<tr>
<td>200.</td>
<td>-2.3</td>
<td>0.46</td>
<td>3.3</td>
</tr>
<tr>
<td>150.</td>
<td>-2.8</td>
<td>0.35</td>
<td>2.6</td>
</tr>
<tr>
<td>100.</td>
<td>-4.4</td>
<td>0.32</td>
<td>1.7</td>
</tr>
<tr>
<td>77.</td>
<td>-9.0</td>
<td>0.43</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Table 16

Electrical Properties Measured on CdS:Cl Sample F

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (10^2\text{cm}^3/\text{coul})</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration (10^{16}\text{cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-0.87</td>
<td>0.35</td>
<td>8.5</td>
</tr>
<tr>
<td>300.</td>
<td>-0.90</td>
<td>0.29</td>
<td>8.3</td>
</tr>
<tr>
<td>250.</td>
<td>-0.96</td>
<td>0.24</td>
<td>7.8</td>
</tr>
<tr>
<td>200.</td>
<td>-1.1</td>
<td>0.19</td>
<td>6.6</td>
</tr>
<tr>
<td>150.</td>
<td>-1.3</td>
<td>0.15</td>
<td>5.6</td>
</tr>
<tr>
<td>100.</td>
<td>-2.3</td>
<td>0.17</td>
<td>3.2</td>
</tr>
<tr>
<td>77.</td>
<td>-5.1</td>
<td>0.26</td>
<td>1.5</td>
</tr>
</tbody>
</table>
### Table 17

**Electrical Properties Measured on CdS:Cl Sample G**

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (10 cm³/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration (10¹⁷ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-3.6</td>
<td>.13</td>
<td>2.1</td>
</tr>
<tr>
<td>300.</td>
<td>-3.8</td>
<td>.12</td>
<td>2.0</td>
</tr>
<tr>
<td>250.</td>
<td>-4.0</td>
<td>.10</td>
<td>1.9</td>
</tr>
<tr>
<td>200.</td>
<td>-4.7</td>
<td>.095</td>
<td>1.6</td>
</tr>
<tr>
<td>150.</td>
<td>-5.6</td>
<td>.090</td>
<td>1.3</td>
</tr>
<tr>
<td>100.</td>
<td>-9.7</td>
<td>.11</td>
<td>0.77</td>
</tr>
<tr>
<td>77.</td>
<td>-17.</td>
<td>.18</td>
<td>0.43</td>
</tr>
<tr>
<td>4.2</td>
<td>-</td>
<td>140000.</td>
<td>*</td>
</tr>
</tbody>
</table>

*Estimate is \( n \approx 4 \times 10^{13} \text{ cm}^{-3} \) (see text).

### Table 18

**Electrical Properties Measured on CdS:Cl Sample H**

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (10 cm³/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration (10¹⁷ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-1.5</td>
<td>.072</td>
<td>4.8</td>
</tr>
<tr>
<td>300.</td>
<td>-1.7</td>
<td>.065</td>
<td>4.4</td>
</tr>
<tr>
<td>250.</td>
<td>-1.8</td>
<td>.061</td>
<td>4.2</td>
</tr>
<tr>
<td>200.</td>
<td>-2.0</td>
<td>.056</td>
<td>3.8</td>
</tr>
<tr>
<td>150.</td>
<td>-2.3</td>
<td>.065</td>
<td>3.2</td>
</tr>
<tr>
<td>100.</td>
<td>-3.0</td>
<td>.147</td>
<td>2.5</td>
</tr>
<tr>
<td>77.</td>
<td>-3.9</td>
<td>.209</td>
<td>1.9</td>
</tr>
<tr>
<td>4.2</td>
<td>-</td>
<td>9500.</td>
<td>**</td>
</tr>
</tbody>
</table>

**Estimate is \( n \approx 10^{15} \text{ cm}^{-3} \) (see text).
Table 19

Electrical Properties Measured on CdS:Cl Sample I

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (cm$^3$/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration* ($10^{18}$cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-4.7</td>
<td>0.021</td>
<td>1.6</td>
</tr>
<tr>
<td>300.</td>
<td>-4.8</td>
<td>0.020</td>
<td>1.6</td>
</tr>
<tr>
<td>250.</td>
<td>-5.0</td>
<td>0.019</td>
<td>1.6</td>
</tr>
<tr>
<td>200.</td>
<td>-5.2</td>
<td>0.018</td>
<td>1.6</td>
</tr>
<tr>
<td>150.</td>
<td>-5.3</td>
<td>0.018</td>
<td>1.6</td>
</tr>
<tr>
<td>100.</td>
<td>-6.3</td>
<td>0.016</td>
<td>1.6</td>
</tr>
<tr>
<td>77.</td>
<td>-6.6</td>
<td>0.018</td>
<td>1.6</td>
</tr>
<tr>
<td>63.</td>
<td>-5.8</td>
<td>0.020</td>
<td>1.6</td>
</tr>
<tr>
<td>53.</td>
<td>-5.8</td>
<td>0.024</td>
<td>1.6</td>
</tr>
<tr>
<td>40.</td>
<td>-5.8</td>
<td>0.027</td>
<td>1.6</td>
</tr>
<tr>
<td>32.</td>
<td>-4.7</td>
<td>0.027</td>
<td>1.6</td>
</tr>
<tr>
<td>27.</td>
<td>-4.7</td>
<td>0.025</td>
<td>1.6</td>
</tr>
<tr>
<td>21.</td>
<td>-5.0</td>
<td>0.027</td>
<td>1.6</td>
</tr>
<tr>
<td>13.</td>
<td>-5.2</td>
<td>0.029</td>
<td>1.6</td>
</tr>
<tr>
<td>9.</td>
<td>-5.2</td>
<td>0.074</td>
<td>1.6</td>
</tr>
<tr>
<td>4.3</td>
<td>-3.8</td>
<td>0.068</td>
<td>1.6</td>
</tr>
<tr>
<td>4.2</td>
<td>-4.4</td>
<td>0.057</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*See text concerning the method of estimating the electron concentration.
# Table 20

Electrical Properties Measured on CdS:Cl Sample J

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (cm³/coul)</th>
<th>Resistivity (ohm·cm)</th>
<th>Electron Concentration ($10^{18}$ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>-2.7</td>
<td>0.015</td>
<td>2.4</td>
</tr>
<tr>
<td>300</td>
<td>-2.7</td>
<td>0.015</td>
<td>2.4</td>
</tr>
<tr>
<td>250</td>
<td>-2.7</td>
<td>0.015</td>
<td>2.4</td>
</tr>
<tr>
<td>200</td>
<td>-2.7</td>
<td>0.015</td>
<td>2.4</td>
</tr>
<tr>
<td>150</td>
<td>-2.7</td>
<td>0.015</td>
<td>2.4</td>
</tr>
<tr>
<td>100</td>
<td>-2.7</td>
<td>0.019</td>
<td>2.4</td>
</tr>
<tr>
<td>77</td>
<td>-2.7</td>
<td>0.020</td>
<td>2.4</td>
</tr>
<tr>
<td>4.2</td>
<td>-2.6</td>
<td>0.022</td>
<td>2.4</td>
</tr>
</tbody>
</table>

# Table 21

Electrical Properties Measured on CdS:Cl Sample K

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (cm³/coul)</th>
<th>Resistivity (ohm·cm)</th>
<th>Electron Concentration ($10^{19}$ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-0.94</td>
<td>0.0044</td>
<td>6.7</td>
</tr>
<tr>
<td>200</td>
<td>-0.95</td>
<td>0.0042</td>
<td>6.6</td>
</tr>
<tr>
<td>100</td>
<td>-0.94</td>
<td>0.0043</td>
<td>6.7</td>
</tr>
<tr>
<td>77</td>
<td>-0.95</td>
<td>0.0043</td>
<td>6.6</td>
</tr>
<tr>
<td>4.2</td>
<td>-0.95</td>
<td>0.0038</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Table 22
Electrical Properties Measured on CdS:Cl Sample L

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Hall Coefficient (cm$^3$/coul)</th>
<th>Resistivity (ohm-cm)</th>
<th>Electron Concentration ($10^{19}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.</td>
<td>-0.49</td>
<td>.0038</td>
<td>1.3</td>
</tr>
<tr>
<td>300.</td>
<td>-0.49</td>
<td>.0036</td>
<td>1.3</td>
</tr>
<tr>
<td>250.</td>
<td>-0.49</td>
<td>.0034</td>
<td>1.3</td>
</tr>
<tr>
<td>200.</td>
<td>-0.49</td>
<td>.0033</td>
<td>1.3</td>
</tr>
<tr>
<td>175.</td>
<td>-0.49</td>
<td>.0033</td>
<td>1.3</td>
</tr>
<tr>
<td>150.</td>
<td>-0.49</td>
<td>.0033</td>
<td>1.3</td>
</tr>
<tr>
<td>125.</td>
<td>-0.49</td>
<td>.0033</td>
<td>1.3</td>
</tr>
<tr>
<td>100.</td>
<td>-0.49</td>
<td>.0033</td>
<td>1.3</td>
</tr>
<tr>
<td>77.</td>
<td>-0.49</td>
<td>.0035</td>
<td>1.3</td>
</tr>
<tr>
<td>4.2</td>
<td>-0.49</td>
<td>.0041</td>
<td>1.3</td>
</tr>
</tbody>
</table>
A reasonable lower bound value for $\mu$ in CdS at 4.2°K is $\mu > 1. \text{cm}^2/\text{volt sec}$. Published experimentally measured values for $\mu$ differ, but all are greater than unity$^{109,110}$. This provides lower bound values of $|R_H| > 1.4 \times 10^5 \text{cm}^3/\text{coul}$ for sample G and $|R_H| > 9.5 \times 10^3 \text{cm}^3/\text{coul}$ for sample H.

The upper and lower bound values of $|R_H|$ are amazingly close in both cases. In fact, for sample H, the lower bound value is slightly larger than the upper bound value; however, this is inconsequential in view of the "order of magnitude" arguments given here. These values were used to estimate the conduction electron concentration at 4.2°K for each sample. The estimates are quoted in footnotes to Tables 17 and 18.

If measurements on samples A through F had been attempted at 4.2°K, it is very probable that problems similar to those just discussed would have been encountered. As mentioned in Chapter III, the methods and circuit utilized here were rather crude and are particularly inadequate when the sample has a high resistivity. Fortunately, these data were not required for this research effort since the non-degenerate nature of the conduction electrons can be derived from higher temperature data.


$^{110}$S. Toyotomi and K. Morigaki, loc. cit.
With regard to samples I through L, the resistivities remain relatively small even at 4.2°K, and reasonable measurements of the Hall voltages were secured. For samples J, K, and L, the Hall voltages were independent of temperature. With sample I a weak temperature dependence was noted between 77°K and 350°K; therefore, the "cold finger" device was employed to obtain more detailed data below this range.

As discussed in Chapter III, the average precision of the electrical properties measurements is about 15%. The data taken with the cold finger device were somewhat more erratic and 25% is probably a better estimate of precision.

The primary reason for making electrical property measurements was to secure estimates of the conduction electron concentration. These were required to analyze the NMR data. However, the electrical property measurements, by themselves, reveal much about the CdS band structure and an analysis of these data will be discussed later in this chapter.

One or two "chips" from each CdS sample boule were sent to Bell and Howell Electronic Material Division in Pasadena, California. These were analyzed with a mass spectrometer to determine the types and quantities of impurities. The results are presented in Tables 23 and 24.
Table 23
Impurity Concentrations in CdS Samples A through F

<table>
<thead>
<tr>
<th>Element*</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D/E**</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.12</td>
<td>0.14</td>
<td>0.39</td>
<td>0.85</td>
<td>0.22</td>
</tr>
<tr>
<td>C</td>
<td>10.</td>
<td>2.0</td>
<td>0.44</td>
<td>27.</td>
<td>4.8</td>
</tr>
<tr>
<td>N</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>F</td>
<td>18.</td>
<td>3.2</td>
<td>2.6</td>
<td>45.</td>
<td>20.</td>
</tr>
<tr>
<td>Na</td>
<td>1.1</td>
<td>0.38</td>
<td>1.6</td>
<td>2.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Al</td>
<td>0.4</td>
<td>n.d.</td>
<td>0.11</td>
<td>0.97</td>
<td>0.11</td>
</tr>
<tr>
<td>Cl</td>
<td>0.38</td>
<td>0.2</td>
<td>0.18</td>
<td>1.2</td>
<td>0.60</td>
</tr>
<tr>
<td>K</td>
<td>0.35</td>
<td>0.24</td>
<td>0.7</td>
<td>1.1</td>
<td>0.27</td>
</tr>
<tr>
<td>Cr</td>
<td>3.0</td>
<td>0.28</td>
<td>0.28</td>
<td>11.</td>
<td>2.6</td>
</tr>
</tbody>
</table>

* Small amounts of H and Ca were detected in some samples. Analyses for Au and Ta are not given because gold electrodes and tantalum slits are used in the spectrometer. Background lines of CdS interfere with analyses for O, Mn, Fe, Zn. Unlisted impurities were not detected and have concentrations less than 0.3 ppm.

** Samples D and E were obtained from the same boule.

n.d. - Not detected.
Table 24

Impurity Concentrations in CdS Samples G through L

<table>
<thead>
<tr>
<th>Element*</th>
<th>Impurity Concentration (part per million atomic)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G</td>
</tr>
<tr>
<td>Li</td>
<td>0.23</td>
</tr>
<tr>
<td>C</td>
<td>1.5</td>
</tr>
<tr>
<td>N</td>
<td>0.36</td>
</tr>
<tr>
<td>F</td>
<td>n.d.</td>
</tr>
<tr>
<td>Na</td>
<td>5.7</td>
</tr>
<tr>
<td>Mg</td>
<td>n.d.</td>
</tr>
<tr>
<td>Al</td>
<td>n.d.</td>
</tr>
<tr>
<td>Cl</td>
<td>2.2</td>
</tr>
<tr>
<td>K</td>
<td>0.26</td>
</tr>
<tr>
<td>Cr</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* Small amounts of H and Ca were detected in some samples. Analyses for Au and Ta are not given because gold electrodes and tantalum slits are used in the spectrometer. Background lines of CdS interfere with analyses for O, Mn, Fe, Zn. Unlisted impurities were not detected and have concentrations less than 0.3 ppm.

n.d. - Not detected.
For most of the samples, only one analysis was performed. Two analyses were made on samples A, B, C and F; three were made on sample J. The impurity concentrations given in Tables 23 and 24 are mean values.

Different "chips" from various parts of the boule were used when more than one analysis was performed on a sample. These invariably yielded different quantitative results for the same sample. For example, the chlorine impurity concentration in sample J was measured three times with values of 12, 23 and 70 ppm respectively. Similar variances were observed for all impurity elements in this sample, and for any sample where more than one analysis was performed. Since the precision of these measurements is better than 10%, these results suggest that the impurity concentration is not uniform throughout the volume of a sample on a macroscopic scale\textsuperscript{111}.

In order to verify that the impurity distribution is non-homogeneous on a macroscopic scale, Bell and Howell Corporation performed special analyses on samples A, F and J using a "direct imaging mass analyzer". This instrument

\textsuperscript{111}Impurities are randomly distributed on a microscopic or atomic scale but would tend to a homogeneous average concentration on a macroscopic scale if the crystal growing process was uniform.
is a combined mass spectrometer and ion emission microscope\textsuperscript{112}. It provides a separate image of the surface from each element present in a sample. The viewed area is about 300 microns in diameter.

Figure 16 is a photograph of the image obtained for chlorine ions in sample $\text{J}^{113}$. Note that the chlorine impurities tend to cluster in regions of various sizes. The larger dark regions indicate little or no chlorine was detected. The significances of these results as well as those reported in Tables 23 and 24 are discussed later in this chapter.

\textsuperscript{112}This instrument, which is also called a "ion microanalyzer", was recently developed by the French firm CAMECA and is being distributed in the U.S. by CEC/Analytical Instruments Division of Bell and Howell. A brief description of the device may be obtained from an article by F. W. Kararek, Research/Development Magazine, Vol 21, Nr. 2, 32 (Feb 1970).

\textsuperscript{113}These data were secured by Eleanor Masumoto, Electronic Material Division of Bell and Howell, Pasedena, California.
Figure 16. Image of Chlorine Impurities in Sample J Obtained by Bell and Howell Corporation Using a Direct Imaging Mass Analyzer
2. **Analyses and Discussion**

All of the primary NMR data were obtained using an 8 MHz resonance frequency. Measurements made at 4 MHz were made only to determine the degree of frequency dependence and were often secured with less precision. For these reasons, values of $T_1$ and Knight shift quoted in this section are for an 8 MHz resonance unless it is stated otherwise.

Figure 17 is a plot of $\log(T_1)$ versus $\log(n)$ at 300°K. Each datum point was obtained from a different sample, A through L. In a region \((2 \times 10^{16} < n < 1.6 \times 10^{18} \text{cm}^{-3})\), the data are consistent with a straight line which has a slope close to negative one. This suggests that the dominant spin-lattice relaxation mechanism is a coupling between the spin system and non-degenerate conduction electrons and that $T_1$ is proportional to $n^{-1}$ as given by (101).

For lower concentrations \((n < 2 \times 10^{16} \text{cm}^{-3})\), the data fall below the $n^{-1}$ line. This indicates that another mechanism is competing with the conduction electrons to relax the spin system. The second mechanism is probably due to an interaction with paramagnetic impurities. This interpretation is consistent with measurements of the frequency dependence of $T_1$ which are discussed later in this section.
FIGURE 17

Spin-Lattice Relaxation Time versus Conduction Electron Concentration at 300°K
For higher electron concentrations, there is a rather abrupt transition in the neighborhood of \( n = 2 \times 10^{18} \text{cm}^{-3} \). For \( n \geq 2.4 \times 10^{18} \text{cm}^{-3} \), the data again fall on a straight line, but in this case the slope is a negative two-thirds. This implies that the spin-lattice relaxation mechanism is due to degenerate conduction electrons and that \( T_1 \) is proportional to \( n^{-2/3} \) as given by (102).

Figure 18 is a log-log plot of \( T_1 \) versus \( n \) for measurements made at both 77°K and 4.2°K. These curves have two features in common with the 300°K curve in Figure 17. First, a transition is clearly evident in the neighborhood of \( n = 2 \times 10^{18} \text{cm}^{-3} \). Second, the \( T_1 \) is proportional to \( n^{-2/3} \) for \( n \geq 2.4 \times 10^{18} \text{cm}^{-3} \). On the other hand, at these lower temperatures (77°K and 4.2°K), \( T_1 \) has a much weaker dependence on the conduction electron concentration for \( n < 1.6 \times 10^{18} \text{cm}^{-3} \). This indicates that the non-degenerate electrons become less dominant as a relaxation mechanism when the temperature is decreased\(^{114} \). The spin system is probably relaxed by paramagnetic impurity sites. At low temperatures the extra electron associated with a chlorine impurity is less likely to gain the conduction band, thus the chlorine itself can be paramagnetic.

\(^{114}\) The \( T_1 \) measurement on sample G at 4.2°K is not included in Figure 18 because of the small value of \( n \) required on the logarithmic abscissa; this data point does not significantly change the slope of the curve for \( n < 10^{15} \text{cm}^{-3} \).
FIGURE 18

Spin-Lattice Relaxation Time versus Conduction Electron Concentration at 77°K and 4.2°K
Before proceeding, the reader should note that although detailed measurements on the temperature dependence of the electron concentrations are contained in Tables 11 through 22, Figures 17 and 18 graphically display some of these data. In particular, these figures show that the concentration is independent of temperature in samples I, J, K and L, whereas it decreases with temperature in the more lightly doped samples.

In Figure 19, the data for samples I, J, K and L are presented on a log-log plot of $T_1$ versus $n^{2/3}$T. Except for those points associated with sample I, the data fall near a straight line with a slope of negative one. This further substantiates that the conduction electrons in samples J, K and L are degenerate and that (102) is applicable. It is reasonable to presume that the Fermi level is in the CdS conduction band and that the impurity band and conduction band are merged. These three samples are basically metallic in character.

The data points for sample I fall above the line in Figure 19. This denotes a change (weakening) in relaxation

\[115\] A $T_1$ measurement on sample J at 2.13°K is included in Figure 19. It was assumed that the conduction electron concentration continues to be independent of temperature below 4.2°K.
FIGURE 19

Spin-Lattice Relaxation Time versus (Conduction Electron Concentration)$^{2/3}$ x Temperature
mechanisms, and it provides further evidence that the merging of the impurity conduction band and CdS conduction band (N\textsubscript{cb} transition, see Eq. (77)) is bounded by samples I and J. On the other hand, the conduction electron concentration is independent or at least nearly independent of temperature. These results suggest that this sample possesses an impurity conduction band. Furthermore, since the electron concentration in sample H is highly dependent on temperature, it may be concluded that sample H and sample I bound the Mott transition (76), that is, the region where the impurity conduction band is formed.

The T\textsubscript{1} measurements made at 4 MHz tend to support the arguments presented above. First consider the data obtained at 300\degree K. It was suggested that the dominant relaxation mechanisms are due to both non-degenerate electrons and paramagnetic impurity ions in samples A, B, and C. In Table 2, the data show that T\textsubscript{1} is slightly dependent on the frequency. This indicates that the conduction electrons are not solely responsible for the spin-lattice relaxation.

For samples D through I, the relationship T\textsubscript{1} \propto n\textsuperscript{-1} depicted in Figure 17 suggests that non-degenerate electrons do dominate the relaxation processes. No frequency dependence was detected for these samples at 300\degree K (Tables 3 through 7).
The highly doped samples J, K and L also have measured values of \( T_1 \) which are independent of the resonance frequency (Tables 8 and 10). This is consistent with a relaxation process caused by conduction electrons. In fact, \( T_1 \) for these three samples continues to be frequency independent at 77°K. This provides further support for the suggested model. For the lighter doped samples, a frequency dependence of \( T_1 \) is observed at 77°K. Here again the data are consistent with the idea that the relaxation process is shared by both non-degenerate conduction electrons and paramagnetic impurity ions.

At 4.2°K, all of the samples on which 4 MHz \( T_1 \) data were obtained showed some degree of frequency dependence. However, for the highly doped samples, \( T_1 \) decreased only about 20% for a frequency change from 8 MHz to 4 MHz. This indicates that paramagnetic processes may be weakly competing with degenerate electrons to relax the spin system. This is not unreasonable since the strength of the interaction with paramagnetic sites is not a monotonically increasing function with temperature (see discussion in Chapter II). In fact, \( 1/T_1 \) increases with decreasing temperature if \( \omega t < 1 \), whereas \( 1/T_1 \) always directly proportional to temperature for an interaction with degenerate conduction electrons. The paramagnetic contribution to the relaxation process is apparently small, however, since
the $1/T_1 \propto n^{2/3}$ holds very well for samples J, K and L.

In contrast, the measured values of $T_1$ for samples H and I decrease by a factor of two when the frequency changes from 8 MHz to 4 MHz at 4.2°K. This implies that the conduction electrons may be relatively ineffective in relaxing the nuclear spin system. This was anticipated for sample H since very few impurity electrons can gain the conduction band at 4.2°K. Most of the electrons are trapped near the chlorine atoms and create paramagnetic sites.

In sample I, however, the number of conduction electrons is independent of temperature, and the electron concentration is moderately large even at 4.2°K. A key point in this case is that these electrons are not free in the CdS conduction band but are confined to an impurity conduction band when the temperature is low. These electrons are "free" charge carriers in the sense that no activation energy is required, but they do not have free access to the entire spatial volume of the sample. The impurity conduction band may be pictured as an interconnecting maze of "tunnels" between the donor impurity sites. Thus, many of the nuclear spins do not "see" the electrons in this impurity conduction band. It should be re-emphasized that spin-lattice relaxation by conduction electrons is normally a contact interaction.
Two models will be discussed; either one provides for a frequency dependent $T_1$ in sample I. Additional data is required to validate or reject either of these models.

The first model is due to Jerome, Ryter and Winter$^{116}$. They assume that the nuclear spins in or near impurity band tunnels are strongly relaxed by conduction electrons$^{117}$. It is further assumed that the remaining spins are relaxed by rapid spin diffusion$^{118}$. However, spin diffusion away from the tunnel regions is inhibited since spins which are inside the tunnels will experience a Knight shift due to polarization of the conduction electrons; those spins which are outside will be unshifted. To be more precise, the tunnel boundaries are not sharply defined but have peaks in the electron concentration near impurity centers. Effective spin-spin coupling is disrupted if the difference in Knight shifts between neighboring nuclei is more than

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$^{117}$The electron density in the "tunnels" is greater than the measured value of $n$ since they are concentrated in a spatially limited region.

$^{118}$The term "rapid spin diffusion" is used here in the same sense as it was used in Chapter II concerning spin-lattice relaxation via paramagnetic interactions.
the "local line width". This suggests a spin diffusion barrier concept similar to that used to model the paramagnetic spin-lattice interaction. The range of this barrier depends directly on the polarization of the conduction electrons which, in turn, has a Curie low dependence. In fact, the range of the barrier (b) is directly proportional to \((H/T)^{1/3}\) and, therefore, dependent on the resonance frequency\(^{119}\). For rapid spin diffusion, \(1/T_1\) is proportional to \(b^{-3}\) (see Equation (67)). Thus the frequency dependence is \(T_1 \propto \omega_0\). This is consistent with the experimental data.

The ideas concerning a second model to explain the low temperature \(T_1\) data on sample I may be obtained through the following train of thought. It is interesting to note that the \(T_1\) data as plotted in Figures 17 and 18 tend to naturally place each sample in one of two groups. In this respect, sample I seems to fall-in with samples A through H rather than with the high concentration samples J, K, and L. Only because of the temperature independence of the electron concentration is this sample considered unique. Nevertheless, samples I and H do not appear to have major differences from an NMR viewpoint. Even at 4.2°K, both of

\(^{119}\text{W. E. Blumberg, loc. cit.}\)
these samples have about the same frequency dependence of $T_1$. It is, therefore, tempting to assume that the relaxation mechanisms in both samples are very much alike. Although such a model cannot be strictly valid, it is suggested that this line of reasoning has considerable merit.

At 4.2°K the spin-lattice relaxation mechanism in sample H is most likely associated with paramagnetic chlorine atoms. The paramagnetism arises from the unpaired donor electrons which are trapped at low temperatures. When the impurity band is formed in the higher doped sample I, it seems reasonable to accept that the paramagnetism should be quenched due to delocalization of the donor electron. In this second model, it is assumed that this is not the case, and localized magnetic moments are still possible around the chlorine impurity sites. In other words, some - if not all - of the paramagnetic character of the impurity levels is maintained when an impurity conduction band is formed. Such a model is qualitatively consistent with the observed $T_1$ measurements in that a frequency dependence is anticipated.

Localized-magnetic-moment models have been suggested by Yosida$^{120}$ and by Toyozawa$^{121}$; however, quantitative

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agreement is lacking for both theories. Nevertheless, Khosla and Fischer\textsuperscript{122} recently demonstrated that low temperature negative magnetoresistance measurements obtained in degenerate CdS can be explained, at least partially, by extending the Toyozawa model. It, therefore, appears reasonable that such localized magnetic moments do exist and that the impurity conduction band may possess sufficient paramagnetic character to contribute to the spin-lattice relaxation process at 4.2°K in sample I.

The Knight shift measurements will be discussed next. As is noted in Tables 2, 3, and 4, no Knight shift could be detected for samples B through F. The conduction electrons in these samples are undoubtedly non-degenerate. Since the electron concentrations are less than \(10^{17}\text{cm}^{-3}\), the corresponding Knight shifts should be exceedingly small and undetectable with the apparatus used here.

Small Knight shifts were detected with sample G at 300°K and with sample H at both 300°K and 77°K (see Tables 5 and 6). The Knight shift of sample H diminished to a value below the detection limit when the temperature was decreased to 4.2°K. The fact that even a small Knight shift was detected for either of these samples was, at first, surprising since the conduction electrons are not

degenerate. According to (72), the Knight shift should be more than an order-of-magnitude smaller than the detection limit of the apparatus\(^\text{123}\). However, (72) was derived under the assumption that Boltzmann statistics were appropriate to describe the electron energy distribution in the conduction band\(^\text{124}\). This would require that the temperature be such that \(kT \gg E_f\), the Fermi energy. For CdS the electron effective mass \(m^* = 0.19m\). Thus, an approximate expression for the Fermi temperature \(T_f = E_f/k\) is given by

\[
T_f \approx \frac{n^2 (3\pi^2 n)^{2/3}}{2m^*k}, \quad (109)
\]

or

\[
T_f \approx 2.2 \times 10^{-10} n^{2/3}. \quad (110)
\]

At 300°K, both samples G and H have electron concentrations which are in excess of \(10^{17}\) cm\(^{-3}\); the Fermi temperatures are approximately 75°K and 125°K respectively. One must, therefore, question the validity of (72) for calculating Knight shifts associated with these samples. On the other hand, the conduction electrons are not degenerate; thus (70) is also not appropriate.

\(^\text{123}\)A Knight shift of less than \(5 \times 10^{-6}\) would be very difficult to detect with the apparatus used here.

\(^\text{124}\)D. A. Zhogolev, loc. cit.
A valid theory for computing the Knight shift for samples G and H would require a perturbation calculation on the Hamiltonian (59) using Fermi statistics but without the simplifying degeneracy assumption $T << T_f$ that is used to derive (70). At this writing, no theoretical calculations of this nature have been reported.

Knight shifts were also measured for sample I at $300^\circ K$, $77^\circ K$ and $4.2^\circ K$ (Table 7). The shifts were relatively independent of temperature. Here again, existing theory is not adequate. Boltzmann statistics are not valid and the electrons are not degenerate at $300^\circ K$ or $77^\circ K$. At $4.2^\circ K$ the conduction electrons may be degenerate; however, in this case they are confined to a spatially limited impurity conduction band. This would dictate a modification of the interaction Hamiltonian given by (59).

The Knight shifts measured for samples J, K and L indicate that the conduction electrons are degenerate. Figure 20 is a plot of $\log (K)$ versus $\log (n)$. The data points for samples J, K and L fall very near a straight line with a slope of one-third. This is consistent with (103). Note that the measured Knight shifts for samples G, H and I fall below the line for degenerate conduction electrons. The $N_{cb}$ transition associated with a merger of the impurity conduction band and the CdS conduction band is rather evident in Figure 20. This is particularly
FIGURE 20

Knight Shift versus Conduction Electron Concentration
CONDUCTION ELECTRON CONCENTRATION (cm$^{-3}$)

KNIGHT SHIFT (K = $\Delta H/H_0$)

$10^{-5}$

$10^{-4}$

$10^{-3}$

$10^{17}$

$10^{18}$

$10^{19}$

3000$^\circ$K

4.2$^\circ$K

O

□

H

□

L

K

$\mathrm{O}_2$

$\mathrm{OH}$

$\mathrm{I}$

$\mathrm{K}$

$\mathrm{K}_3\mathrm{S}$
true if only the 300°K and 77°K data are considered. The $N_{cb}$ transition, as marked by a departure from the $K=n^{1/3}$ relationship, is clearly bounded by samples I and J. On the other hand, the Mott transition (formation of the impurity conduction band) is distinguished by the onset of a measurable Knight shift at 4.2°K; it is bounded by samples H and I.

One deviation was noted for the Knight shift data on the high concentration samples. Measurements made on samples J, K and L were almost independent of temperature except for the 300°K measurement made with sample J. The Knight shift in this case was about 20% lower than the value obtained at 77°K and 4.2°K. This variation is more than can be attributed to experimental error. Here again, the measurement may be explainable in terms of the Fermi temperature. For sample J the Fermi temperature is approximately 400°K. Thus at 300°K the degeneracy inequality $T<T_f$ is not satisfied. The conduction electrons may, therefore, take on some non-degenerate character and cause a corresponding decrease in the observed Knight shift. Here again, detailed theoretical calculations have not been reported for Knight shifts when the temperature is near the Fermi temperature.
The spin-lattice relaxation time data and the Knight shift measurements were used to calculate Korringa products. Figure 21 is a plot of \( \log(T_1T_K^2) \) versus \( \log(n) \). These data points tend to exhibit more scatter due to the fact that the \( T_1T_K^2 \) is a product of three experimentally measured parameters which are all subject to error. The \( K^2 \) factor tends to amplify errors in the Knight shift measurement.

For degenerate conduction electrons, the Korringa product should be a constant in accordance with (71). The data for samples J, K and L fall reasonably close to a constant value \( T_1T_K^2 = 3.3\times10^{-6} \text{ sec }^{-\circ}\text{K} \). This is somewhat smaller than anticipated. The Landé g-factor is defined by \( \tilde{\gamma}_e = g\mu_0 \) where \( \mu_0 \) is the Bohr magneton. Experimental values of the g-factor between 1.7 and 1.8 are commonly reported for CdS\textsuperscript{125,126}. This corresponds to a Korringa product \( T_1T_K^2 = 4.1\times10^{-6} \text{ sec }^{-\circ}\text{K} \). A discrepancy of this nature is commonly observed in metals where the electron-electron interactions are important\textsuperscript{127}. However, for


FIGURE 21
Korringa Product versus Conduction Electron Concentration
**Conduction Electron Concentration (cm$^{-3}$)**

- **Korringa Product $T_1 T K^2$**
  - $T_1 T K^2 = 3.3 \times 10^{-6}$

**Legend:**
- $300^\circ K$
- $77^\circ K$
- $4.2^\circ K$
electron concentrations on the-order-of $10^{19} \text{cm}^{-3}$, these effects are probably not significant\textsuperscript{128}.

A possible explanation for the above discrepancy is that the reported values for the g-factor are usually measured in CdS samples with low or moderate doping levels. In heavily doped CdS:Cl the value of the g-factor may be smaller. For example, it is reasonable to assume that in heavily doped CdS:Cl the band gap is decreased when the impurity conduction band and CdS conduction band are merged. Cardona has shown that, other things being equal, a smaller band gap will effect a corresponding decrease in the g-factor\textsuperscript{129}. For the measured value $T_1 T K^2 = 3.3 \times 10^{-6} \text{sec}^{-1} \text{K}$, the Landé g-factor would be about 1.6.

As with the Knight shift, the onset of a non-zero Korringa product at 4.2°K locates the Mott transition. Likewise, the 300°K and 77°K data mark the $N_{\text{cb}}$ transition by a sharp departure from a constant value. The $N_{\text{cb}}$ transition is evident in Figure 21 and as before is bounded by samples I and J.

In the analyses of NMR data discussed thus far, the measurements of conduction electron concentrations have been indispensable. In fact, some of the conclusions

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\textsuperscript{128} D. C. Look, \textit{loc. cit.}

drawn from these analyses are apparent from the electrical measurement data alone. For example, both the Mott transition and transition associated with the merging of conduction bands can usually be roughly identified from temperature dependent measurements of the Hall coefficient.

Figure 22 is a log-log plot of $|R_H|$ versus temperature and contains data on all of the samples A through L. From these curves it is immediately obvious that $|R_H|$ is a monotonically decreasing function of temperature for samples A through H. This behavior is typical of semiconductors. The temperature dependence of $|R_H|$ is radically changed in a region bounded by samples H and I such that the latter has only a weak temperature dependence. This is characteristic of a sample which possesses an impurity conduction band. As was discussed in Chapter II, the electron concentration in this sample is very likely independent of temperature, and the weak temperature dependence of $|R_H|$ is a result of having two conduction bands. For samples J, K, and L, $|R_H|$ is independent of temperature. This indicates that in a region bounded by samples I and J the two conduction bands are merged. Samples J, K and L have electrical properties which are characteristic of a metal.
FIGURE 22

Magnitude of Hall Coefficient versus Temperature
One further comment should be made concerning the temperature dependence of $|R_H|$ in sample I. The data secured between 4.2°K and 77°K were obtained using the cold-finger apparatus described in Chapter III. These were not precision measurements and were made only to bracket the range over which $|R_H|$ varies with temperature. The detailed structure in this curve may or may not be real. The data do show that a weak temperature dependence is present and that a maximum $|R_H|$ occurs near the liquid nitrogen temperature of 77°K. No attempt was made to analyze these measurements beyond this point.

For a final discussion, consider the mass spectrometer measurements made at Bell and Howell Corporation. These data were presented in Tables 23 and 24 in the first section of this chapter. It was also noted in this section that the repeatability of these measurements is rather poor\(^{130}\). Thus quantitative analyses are of limited value.

The alphabetical order used in naming each sample was derived from measurements of $T_1$ at room temperature (see Chapter III). However, there is a strong correlation between the alphabetical order and the amount of chlorine

\(^{130}\)This is attributed to spatial clustering of the impurity (see Figure 16).
dopant that was used in the growing process (see Table 1). It is very probable that each successive sample A through L has an increased amount of chlorine impurity. However, for the lightly doped samples A through F, the mass spectrometer measurements of the chlorine concentration showed almost no correlation to this order. On the other hand, the chlorine impurity concentrations measured in the more heavily doped samples G through L are at least increasing monotonically with the alphabetical order.

Figure 23 is a log-log plot of $T_1$ versus the chlorine impurity concentration $N_i$ for the more heavily doped samples G through L. These graphs display two interesting features. First, there are comparatively steep slopes to the curves in a concentration region ($15 < N_i < 35$ ppm) which contains the samples H, I and J. This corresponds to a strengthening of the spin-lattice mechanism as the impurity concentration is increased through both of the aforementioned transition regions. Second, the general shape of the individual curves is similar and they are nearly parallel at all three temperatures. This indicates that a chlorine impurity atom contributes to the spin-lattice relaxation mechanism in almost equal measure independent of whether it donates an electron to the conduction band or becomes a paramagnetic site. Transitions and changes in the relaxation mechanisms may affect the value of $T_1$. 
Figure 23. Spin-Lattice Relaxation Time versus Chlorine Impurity Concentration
by a factor of two, but the overall trend is for \( T_1 \) to be inversely related to both \( N_i \) and \( T \). This latter observation suggests that a measurement of \( T_1 \) can provide a rough estimate on the chlorine concentration at least for moderately doped and heavily doped CdS:Cl. In fact, the data shown in Figure 23 can be roughly fit to the simple empirical equation

\[
\frac{1}{T_1} \approx 6 \times 10^{-5} N_i T \text{ (sec)}^{-1} . \tag{111}
\]

This formula is accurate to about a factor of two for concentrations \((2<N_i<30 \text{ ppm})\) and is better than \( \pm 50\% \) for \((30<N_i<120 \text{ ppm})\). For concentrations of less than 2 ppm it is doubtful whether (111) could be useful. Other impurities are always present and they may compete with the chlorine to relax the spin system. In addition, compensation becomes an appreciable factor in lightly doped semiconductors. For very heavily doped CdS:Cl, it is reasonable to expect that (111) may be useful slightly beyond a concentration of 120 ppm. However, on theoretical grounds the correct formula should have \( 1/T_1 \propto N_i^{2/3} T \) because for large impurity concentrations \( N_i \approx n \). Thus, (111) will probably yield values of \( T_1 \) which are too small when \( N_i \) is very large.
It must be emphasized that the intended purpose for the empirical relationship given by (111) is to provide an experimenter with an approximate method of estimating either \( N_i \) or \( T_1 \) if one of these quantities is known. The formula has little theoretical basis in that it does not relate to a specific relaxation mechanism. No information concerning the semiconductor-to-metal transition is furnished by (111) since this feature in the data was averaged out by the curve fitting procedure. Nevertheless, it is suggested that (111) may be useful in the laboratory and that, in fact, it may be employable with CdS doped with any of the halogen elements\(^{131}\).

The photograph presented in Figure 16 was also obtained by personnel at Bell and Howell Corporation as part of their analyses on sample J. As previously discussed, this shows the two dimensional distribution of chlorine impurities from a 300 micron diameter region of the sample.

This photograph clearly reveals that chlorine impurities tend to cluster on a macroscopic scale. It is unlikely a randomly chosen small sample would have a chlorine concentration representative of the overall average concentration unless its volume were one cubic millimeter or

\(^{131}\)There are no data available to substantiate or refute this possibility.
greater. This accounts for the non-repeatability of the measurements obtained with the mass spectrometer. This instrument consumes much less than one cubic millimeter of sample for each measurement.

In Chapter III a model was suggested to account for a slight non-exponential recovery of the magnetization which was observed in the data. An explicit assumption in this model is that there exists a distribution in the impurity concentration of individual particles in a crushed sample of CdS:Cl. The particle sizes in samples used here were, in general, much smaller than one cubic millimeter. Thus, the photographic data in Figure 16 strongly supports the purposed model. No quantitative analyses were attempted with these data.

This concludes a detailed discussion of the results obtained during this research. In the next and final chapter a brief summary of the more important results is presented together with a few recommendations for future investigations.
CHAPTER V
SUMMARY AND RECOMMENDATIONS

An NMR investigation of the semiconductor-to-metal transition in CdS:Cl has been accomplished. The results are in reasonable agreement with theory and may be summarized as follows:

1. An impurity conduction band is formed (Mott transition) in CdS:Cl when the conduction electron concentration $n$ attains a value in the region $(5 \times 10^{17} < n < 1.6 \times 10^{18} \text{ cm}^{-3})$.

2. The impurity conduction band and the CdS conduction band are merged to complete a semiconductor-to-metal transition in a concentration region $(1.6 \times 10^{18} < n < 2.4 \times 10^{18} \text{ cm}^{-3})$.

3. For electron concentrations $n \leq 5 \times 10^{17} \text{ cm}^{-3}$, the electrical properties of CdS:Cl are basically those of a semiconductor. The spin-lattice relaxation mechanism is due to non-degenerate conduction electrons at $300^\circ$K. At lower temperatures, the conduction electrons are trapped, and the relaxation process is dominated by paramagnetic impurity sites. Knight shifts are very small or negligible.

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(4) For electron concentration \( n \cong 2.4 \times 10^{18} \text{cm}^{-3} \), the electrical properties of CdS:Cl are basically metallic in nature. The spin-lattice relaxation mechanism is due mainly to degenerate conduction electrons. Knight shifts are observed and consistent with existing theory. The Korringa product is \( 3.3 \times 10^{-6} \text{ sec}^{-1} \text{K} \). This corresponds to a Landé \( g \)-factor of 1.6. This value is somewhat lower than \( g = 1.8 \) which has been reported by most investigators. The discrepancy may be due to the very high doping level used here in contrast to the rather pure CdS used by others.

(5) For electron concentrations in the semiconductor-to-metal transition region, \( n \approx 1.6 \times 10^{18} \text{cm}^{-3} \), the electrical properties of CdS:Cl are "metal-like"; however, they exhibit more than usual temperature dependence. In this region, CdS:Cl undoubtedly possesses a narrow impurity conduction band located in the band gap just below the CdS conduction band. At 300\(^{\circ}\)K the dominant spin-lattice relaxation mechanism is non-degenerate conduction electrons. At lower temperatures the exact nature of the relaxation mechanism becomes less certain. The observed data are consistent with a model which assumes that nuclear spins in or near impurity band "tunnels" are strongly relaxed by impurity-band conduction electrons.
and that the remaining spins are then relaxed by rapid
spin diffusion. The data may also be interpreted in terms
of the existence of localized magnetic moments associated
with the impurity conduction band. Either one or both of
these mechanisms may be responsible for spin relaxation
at low temperatures. Small Knight shifts are observed but
existing theories are not adequate to interpret these
data.

Two interesting phenomena were observed during this
research which were not investigated completely. First,
the magnetization recovery in moderately doped and heavily
doped CdS:Cl was observed to be slightly non-exponential.
Strong evidence exists to suggest that the origin of this
behavior lies in the non-homogeneous distribution of
chlorine impurities in CdS. This evidence includes photo­
graphs obtained with a "direct imaging mass analyzer"
which show clustering of chlorine impurities on a macro­
scopic scale. It was also observed that the non-exponen­
tial behavior was less prevalent in single crystal samples
as opposed to crushed or powder samples. A model was pro­
posed (see Chapter III and Appendix) which roughly pre­
dicts the observed data. It is recommended that an NMR
investigation of the non-exponential behavior in CdS:Cl
could prove to be an interesting and worthwhile research.
If this effort can be coupled to experimentation using a
direct imaging mass analyzer, the investigation could be even more fruitful.

A second interesting phenomena concerns the $T_1$ measurements in sample I at 4.2°K. This sample possesses an impurity conduction band and the exact spin-lattice relaxation mechanism could not be determined. It is suggested that a detailed NMR investigation on several samples having conduction electron concentrations in a region $(5 \times 10^{17} < n < 2.4 \times 10^{18} \text{cm}^{-3})$ could reveal more fundamental information about the nature of an impurity conduction band and the semiconductor-to-metal transition.
APPENDIX

Consider a crushed or powdered sample of crystalline CdS:Cl in which there exists a variation from particle to particle in the average impurity concentration or more precisely in the average conduction electron concentration $n$. For simplicity it is assumed that all particles in the sample have the same volume but have electron concentrations varying from $n_0-a$ to $n_0+a$ where $n_0$ is the average electron concentration for the entire sample. The parameter $(a)$ is a measure of the half-width of the distribution. Let $s(n)$ be a normalized distribution function such that $\int_{\infty}^{\infty} s(n) \, dn = 1$. For simplicity it is assumed that

\[ s(n) = \frac{1}{2a} \quad \text{for } n_0-a \leq n \leq n_0+a \]
\[ s(n) = 0 \quad \text{elsewhere.} \]  

(112)

Now for non-degenerate conduction electrons, in one particle, the spin-lattice relaxation time $T_1$ is related to the electron concentration by

\[ \frac{1}{T_1} = qn \]  

(113)

where $q$ may be treated as a constant (see Equation (101)).
The magnetization $M(t)$ recovers from complete saturation in accordance with

$$M(t) = M_\alpha \left(1 - \exp\left(-t/T_1\right)\right) . \quad (114)$$

By combining (113) and (114), the following expression is obtained:

$$\frac{M_\alpha - M(t)}{M_\alpha} = \exp(-q_{nt}) . \quad (115)$$

Since the total magnetization in a crushed sample is a sum of the magnetizations from each particle, (115) may be replaced by

$$\frac{M_\alpha - M(t)}{M_\alpha} = \int_0^\infty s(n) \exp(-q_{nt})dn \quad , \quad (116)$$

or

$$\frac{M_\alpha - M(t)}{M_\alpha} = \frac{1}{2a} \int_{n_0-a}^{n_0+a} \exp(-q_{nt})dn \quad . \quad (117)$$

Upon integration,

$$\frac{M_\alpha - M(t)}{M_\alpha} = \exp(-q_{n_0}t) \cdot \frac{\sinh(aqt)}{aqt} . \quad (118)$$

Now for $aq_{t} < 1$

$$\frac{\sinh(aqt)}{aqt} \approx 1 + \frac{(aq_{t})^2}{6} \quad . \quad (119)$$

By taking a logarithm, (119) becomes
\[
\ln \left[ \frac{M_\infty - M(t)}{M_\infty} \right] \approx -qn_0 t + \ln(1 + (aqt)^2/6) , \quad (120)
\]

or
\[
\ln \left[ \frac{M_\infty - M(t)}{M_\infty} \right] \approx -qn_0 t + (aqt)^2/6 . \quad (121)
\]

If \( a \ll n_0 \), then for small values of \( t \),
\[
\ln \left[ \frac{M_\infty - M(t)}{M_\infty} \right] \approx -qn_0 t . \quad (122)
\]

The above equation indicates that if the width of the distribution \( (a) \) is small compared to value of the average concentration \( (n_0) \), then the initial slope of a plot \( \ln(M_\infty - M(t)) \) versus \( t \) is given by
\[
\text{slope} = -qn_0 = -\frac{1}{T_1} . \quad (123)
\]

where the bar indicates a mean value of the distribution of \( 1/T_1 \) throughout the crushed sample. If the above approximation remains valid until \( M(t) \) approaches to within 80% or more of \( M_\infty \), then \( \frac{1}{T_1} \) is a respectable measure of the strength of the relaxation mechanism. This suggests that an appropriate \( T_1 \) may be defined by
\[
\frac{1}{T_1} = qn_0 \quad . \quad (124)
\]
For degenerate conduction electrons, the equations are somewhat more complicated. The relationship between $T_1$ and $n$ is given by (102) and may be written

$$\frac{1}{T_1} = Qn^{2/3} \quad (125)$$

where $Q$ may also be treated as a constant. The magnetization recovery is given by

$$\frac{M_x - M(t)}{M_x} = \frac{1}{2a} \int_{n_0-a}^{n_0+a} \exp(-Qn^{2/3}t) dn \quad (126)$$

An analytical expression in closed form does not appear to be obtainable from (126). However, for $a \ll n_0$, the following change of variables will yield a tractable approximation to (126). Let

$$X = \left(\frac{n}{n_0}\right)^{2/3} - 1$$

where the integration limits

$$X_L = \left(\frac{(n_0-a)}{n_0}\right)^{2/3} - 1 \approx -\frac{2a}{3n_0}$$

$$X_U = \left(\frac{(n_0+a)}{n_0}\right)^{2/3} - 1 \approx \frac{2a}{3n_0}$$

and

$$W = \frac{2a}{3n_0}$$

$$A = kno^{2/3}t$$

This yields

$$\frac{M_x - M(t)}{M_x} \approx \frac{\exp(-A)}{2W} \int_{-W}^{W} (1+X)^{1/2} \exp(-AX) dX \quad (127)$$
Since \( a \ll n_0 \), \(|W| \ll 1\) and \( X \ll 1\), therefore, \((1+X)^\frac{1}{2} = 1 + \frac{1}{2}X\) and (127) becomes,

\[
\frac{M_\alpha - M(t)}{M_\alpha} \approx \exp(-A) \int_{-W}^{W} (1 + \frac{1}{2}X) \exp(-AW) dX \quad . (128)
\]

Upon integration,

\[
\frac{M_\alpha - M(t)}{M_\alpha} \approx \exp(-A) \left[ \frac{\sinh AW}{AW} + \frac{1}{2A} \left( \frac{\sinh AW - \cosh AW}{AW} \right) \right] . (129)
\]

By expanding the \( \sinh AW \) and \( \cosh AW \) terms in power series, (129) may be reduced to

\[
\frac{M_\alpha - M(t)}{M_\alpha} \approx \exp(-A) \left[ 1 - \frac{W^2}{6} A + \frac{W^2}{6} A^2 - \ldots \right] . (130)
\]

or

\[
\frac{M_\alpha - M(t)}{M_\alpha} \approx \exp(-Qn_0^{2/3}t) \left[ 1 - \frac{2Qa^2t}{27n_0^{4/3}} + \frac{2(Qat)^2}{27n_0^{2/3}} - \ldots \right] . (131)
\]

If for increasing time, the linear and higher order terms of the expansion remain negligible until the exponential factor decays, then for small values of \( t \) Eq. (131) further reduces to the form

\[
\frac{M_\alpha - M(t)}{M_\alpha} \approx \exp(-Qn_0^{2/3}t) \quad , (132)
\]

or following the previous line of reasoning,
\[
\ln \left( \frac{M_e - M(t)}{M_e} \right) \approx -t/T_1 \quad (133)
\]

where

\[
\frac{1}{T_1} = Qn_0^{2/3} \quad (134)
\]

Equations (122) and (132) reveal that for both non-degenerate and degenerate conduction electrons, if \( a \ll n_0 \), the initial phase of the magnetization recovery is very nearly exponential. Once more, \( T_1 \) measured by fitting a straight line to a semilogarithmic plot of the recovery data will be characteristic of the average concentration \( n_0 \) as is shown in (124) and (134) respectively.

One final comment should be made about the above derivation. Equation (122) was obtained by neglecting quadratic and higher order terms in \( t \) which are negligible if \( a \ll n_0 \) and \( Qa^2t \ll 1 \). This is clearly revealed by (118) and (119). A careful analysis of these equations shows that as \( t \) approaches zero, the slope of the curve in a semilogarithmic plot approaches \( (-qn_0) \) independent of the value of distribution half-width parameter \( a \). On the other hand, (133) was obtained by neglecting certain linear and higher order terms in \( t \) which are negligible if \( a \ll n_0 \) and \( Qa^{2/3}t \ll 1 \). Note that a linear term affects
the slope at $t = 0$. Therefore, unless the condition $a < n_0$ is strictly valid, the initial recovery will not be characteristic of the concentration $n_0$ in the same sense as previously described. The initial slope will be steepened as the half-width parameter $(a)$ becomes larger. This is because the concentration distribution in terms of the variable $n^{2/3}$ is not symmetric about $n_0$. This difference between the models for non-degenerate and degenerate conduction electrons may be worthy of further investigation from both an analytical and experimental point-of-view.
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