The University of British Columbia

FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE
FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

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FRIDAY, APRIL 28th, 1967, at 3:30 P.M.

IN ROOM 301, PHYSICS (HENNINGS) BUILDING

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NUCLEAR MAGNETIC RESONANCE IN SINGLE CRYSTALS
OF TIN AND CADMIUM

ABSTRACT

A systematic study of the Knight shift parameters has been carried out on single crystal specimens of tin and cadmium over a range from 1 K to just below the melting points. The line widths observed in cadmium are approximately half the widths quoted by other workers enabling more precise measurements to be made. These measurements show the anisotropy of the Knight shift in cadmium changes sign between 4 K and 77 K. Pronounced changes in the Knight shift parameters are observed upon alloying cadmium with mercury.

The temperature dependence of the isotropic Knight shift in tin can be explained by the volume effects and the phonon contributions when the temperature exceeds the Debye temperature. Comparing the temperature dependence data with pressure dependence results of other workers the explicit temperature dependence is extracted.

It appears that the variation in the anisotropy of the Knight shift above the Debye temperature is largely caused by a change in lattice parameters, specifically a change in c/a ratio.

Measurements of the line width at helium temperature in isotopically pure Sn\textsuperscript{119} and the same isotope in natural tin as a function of crystal orientation are reported. Second moments for the different crystal orientations have been computed. Analysis of the isotopically pure tin data leads to an evaluation of relative contributions from the various shells, to the pseudo-dipolar interaction.

For the isotopically pure tin, the measurements at the helium and room temperatures enable an evaluation of the spin lattice relaxation time T\textsubscript{1}. T\textsubscript{1} is constant over the temperature range and closely isotropic.
GRADUATE STUDIES

Field of Study: Nuclear Magnetic Resonance

Seminar in NMR - D.Ll. Williams
Quantum Theory of Solids - R. Barrie
Statistical Mechanics - R. Barrie
Advanced Magnetism - M. Bloom
Low Temperature Physics - J.B. Brown
Electronic Instrumentation - F.K. Bowers
"The Temperature Dependence of the Knight Shift in Tin and Cadmium"
NUCLEAR MAGNETIC RESONANCE IN SINGLE
CRYSTALS OF TIN AND CADMIUM

by

SURENDRA NATH SHARMA

M.Sc., The University of British Columbia, 1962

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
PHYSICS

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March, 1967

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ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. D. Ll. Williams for his constant help and encouragement throughout this work.

I am indebted to Prof. Myer Bloom for his valuable help in interpreting some of my results.

I am grateful to Dr. B. G. Turrell for helpful discussions, to Dr. R. Howard and Krishna M. Agrawal for helping in the computation of some of my data on the computer and to Dr. H. E. Schone for the loan of the isotopically pure tin single crystal.

The cheerful assistance of the Physics Workshops staff in technical matters is highly appreciated.

The financial assistance of the National Research Council of Canada in the form of summer research grants is gratefully acknowledged.
CHAPTER I

INTRODUCTION

When an assembly of identical nuclei, each possessing a magnetic moment $\mu$ and angular momentum $I$, is subjected to a d.c. magnetic field, the nuclei precess around the field with the Larmor frequency $\frac{\mu H}{\hbar I}$. If now an r.f. field is applied perpendicular to this d.c. field such that the radio frequency corresponds to the Larmor frequency, the system absorbs energy. This is the magnetic resonance phenomenon. In practice, however, the field seen by a given nucleus is different from the applied field because it also feels a 'local' field from surrounding electrons and neighbouring nuclei. The Larmor frequency then is defined in terms of the vector sum of the applied and local fields, and the nucleus can be used as a probe to measure this local magnetic field. The experiment consists of observing the rate of energy absorption with varying radio frequency and around the resonance frequency a spectral 'line' is observed. The shape of this line and the resonance frequency are parameters of physical interest.

While investigating NMR in metals W.D. Knight found that the resonance frequency of any particular isotope in a metal was shifted from the resonance frequency measured in a non-metallic compound in the same external magnetic field. This shift in frequency is known as the Knight shift and is usually positive. It can be explained by taking into account the hyperfine interaction between the nucleus and the conduction electrons. The applied magnetic field induces a polarization of the conduction electron spins which is then felt by the nucleus. Thus the Knight shift can provide valuable information about the conduction electrons near the Fermi surface in the metals.

In the past the experiments on the Knight shift measurements were limited to powdered samples with particle size less than the electro-
magnetic skin depth, in order to achieve substantial penetration of the r.f. field into the sample.

For a cubic crystal the Knight shift is independent of crystal orientation with respect to the external magnetic field. This is not true for metals with crystal symmetry lower than cubic. Experiments on the powders of such metals result in a broad line due to the random orientation of the crystallites. Any orientation dependence of the Knight shift and line shape can clearly be observed if single crystal specimens are used. This would result in considerably narrower lines hence increasing the accuracy of the measurements.

However, NMR experiments in single crystals are not as easy as it might appear from reading the last paragraph for the following reasons.

(i) In a single crystal experiment the fraction of the total number of nuclei participating in the resonance phenomenon is very small as compared to that in a powder specimen. Since only nuclei which happen to be situated in the skin depth region, which is a few microns only, take part while the rest of the nuclei in the crystal are sitting idle. This results in a poor signal to noise ratio which necessitates a sensitive set of equipment.

(ii) The observed resonance frequency is not the true resonance frequency. This is also caused by skin depth effects and complicates the analysis of the data. The first reason is a major hurdle and only because of this previous experiments have been limited to the powder specimens.

At the commencement of this work two experiments\(^{(32,42)}\) had been recently performed on metal single crystals but Schone\(^{(33)}\) has since also studied cadmium.

The object of the present work was (i) to study the Knight shift parameters in tin and cadmium from helium temperatures to just below the
melting point, and (ii) to study the line widths and shapes as a function of crystal orientation at various temperatures. The temperature dependence of the Knight shift and its anisotropy has been studied. Following Benedek and Kushida, the variation in the Knight shift with temperature has been attributed to volume effects and an intrinsic temperature dependence. The present results have been combined with other workers' results, on pressure dependence of the Knight shift, and the intrinsic temperature dependence has been derived over the entire temperature range.

We have investigated the line-width as a function of crystal orientation in isotopically pure Sn\textsuperscript{119} and line shapes of the same isotope in natural tin. Analysis of the isotopically pure tin data has enabled the evaluation of the relative pseudo-dipolar contributions from various shells. An analysis of the line-widths at liquid helium and room temperatures has enabled an evaluation of the spin-lattice relaxation time, T\textsubscript{1}, at room temperature.
CHAPTER II
EQUIPMENT

The apparatus used for the experimental work is conventional and standard in design. Figure 1 shows the schematic diagram. A brief description of each unit used is given below.

A PKW type oscillating detector \(^{(3,9)}\) with minor changes was constructed. A 6922 vacuum tube was used in place of 6J6 in the oscillator section. The cathodes of the oscillator and the amplifier, which feeds back to the oscillator, were coupled through a .1 \(\mu F\) low voltage mylar capacitor in order to tie the oscillator at a single operating point and at the same time the gain of the amplifier could be varied over a wide range. A small variable capacitor \(C_1\) of value 2-8pf in parallel with a voltage sensitive diode capacitor \(C_2\) (varicap) PC116 was used in the resonant circuit. \(C_1\) was kept roughly minimum during the experiments. Since \(C_2\) was always greater than \(C_1\) the resonance frequency was practically determined by \(C_2\). The oscillator was very stable in frequency \((2 \times 10^6\) over several hours\) and worked very well at 100mv peak-peak rf level with quite low noise. Experiments from 1.15\(^0\)K to 450\(^0\)K were performed and thus various rf levels had to be used. It was found that the above mentioned equipment was adequately sensitive even for high rf levels, up to 1V p-p, used for the high temperature experiments.

The frequency of the oscillator was swept by applying a variable amplitude (0-100 volts) linear sawtooth available from a modified Tektronix wave form generator type 162 \(G^2\) which could generate linear sweeps of from 1 m.sec. to several hours duration.

The audio output of the marginal oscillator was fed into a White twin-tee narrow band amplifier model 216A. To test the performance of the detector an Aluminum single crystal was used as the specimen at room temperature. Several 5% bandwidth White twin-tees with centre frequencies from 15 to 400c/s
Figure 1. Block Diagram of the Spectrometer.

- Power Amplifier
- Attenuator
- Audio Oscillator
- Horizontal Amp. and Phase Shifter
- PKW Oscillating Detector
- Modified Tektronix 162.
- Magnet
- Narrow Band Amplifier
- Phase Sensitive Detector
- Counter and Printer
- Recorder
- Field Monitoring Oscillator
- Battery and Helipot
were tried and it was found that the signal to noise ratio (S/N) was maximum for a twin-tee of 20 c/s, keeping other variables of the PKW detector the same. This rather peculiar behavior is not in agreement with the Watkin's findings and the Naval Research Lab. Report (15).

Following the narrow band amplifier is the phase sensitive detector which in principle is the same as that of Schuster's (35). The signal recorder used was a Varian recorder, model G11A.

The frequency measurements were made with Hewlett-Packard electronic counters, models 524C and 5245L. The frequency was recorded by Hewlett-Packard digital recorders models 516B and 5622A respectively, which in turn activated an indicator pen on the signal recorder every time it made a print. The measured frequency was an average over a period of .1 second.

The external magnetic field was supplied by a rotatable Varian magnet with 12" diameter pole faces and a 2-1/4" gap. The magnet is mounted on a graduated table so that field orientation relative to the sample in the plane of rotation can be determined. The magnet was switched on at least 24 hours before the actual experiment started. The cooling water for the magnet was supplied from a reservoir which in turn was cooled by the running tap water. This gave a field stability of about 1 in 10^6 over a period of several hours.

Field modulation was achieved by a pair of coils, each wound with 60 turns of No. 18 copper wire on bakelite forms, mounted around the magnetic pole faces. The modulation current was supplied by a Williamson type power amplifier driven by a Hewlett-Packard audio oscillator, model 202D.

The low temperature system used is shown in figure 2. An ordinary doubledewar glass cryostat was used to achieve low temperatures. The lowest temperature achieved was 1.15°K by pumping on the liquid helium with a three inch Kinney pump. The temperature was determined by measuring the pressure over the liquid helium bath using the oil manometer.
The sample was mounted on a coaxial line of stainless steel 3/8 inch in diameter. The central conducting wire of the coaxial line was a No. 36 copper wire held in place with teflon spacers.

The magnetic field measurements were made by displaying the proton signal on the oscilloscope directly. The sample used was glycerine which was situated just outside the liquid nitrogen dewar. The circuit used to monitor the field was assembled in a shock-mounted heavy brass box, to avoid microphonics, and was mounted permanently on the magnet until each experimental run was complete. The coaxial line used with the box was made of copper tubing about one foot in length and half inch outside diameter and had a No. 32 copper wire as the inner conductor. It had a BNC connector on one end which was directly hooked on to the box and on the other end of the coaxial line a glycerine sample was mounted permanently in a glass tube 5 mm. outside diameter. Four such probes were made which covered the frequency range from (11-60) Mc/s. Thus a suitable probe was available for each field used.

A small capacitor, 2-8pf, in parallel with a varicap No. 116 was used in the resonance circuit. The variable voltage for the varicap was obtained from a 90 volts dry cell and a 100K Helipot. A 2pf capacitor was used in series with the varicap. This enabled extremely fine control of the frequency and thus a very accurate measurement of the field. The proton resonance frequency was read on the Hewlett-Packard frequency meter. The circuit had excellent frequency stability, 3 in 10^6, and very high signal to noise ratio.

In all cases the magnetic field was measured before and after each run for a particular field orientation with respect to the crystal.

All the crystals used were cylindrical in shape. The natural tin crystal with axis of tetragonal symmetry parallel to the specimen axis, axis of symmetry perpendicular to the specimen axis and the cadmium crystal with hexagonal axis of symmetry perpendicular to the specimen axis were obtained.
Figure 2. Schematic of Low Temperature System.
commercially from Metals Research Ltd., Cambridge and had a purity of 99.999%. Each crystal was one inch in length and 3/8" in diameter and was etched before making measurements.

The isotopically pure tin crystal was grown in the form of a hollow cylinder. The axis of tetragonal symmetry made an angle of 30° with the specimen axis. Two suitable mounts were made to make the measurements in the basal plane and with the tetragonal axis of symmetry in the plane of the field rotation.

The Cd-Hg alloy crystal, with 12 atomic percent mercury was obtained from Semi Elements Inc. Saxonburg, U.S.A. It was .5 inch long and 4 mm. in diameter. The hexagonal axis of symmetry was perpendicular to the specimen axis.

In all the experiments a copper wire No. 40 was used for the coil around the specimen. One layer of .001 inch thick mylar was used as insulator between the coil and the specimen for helium and liquid nitrogen experiments. For higher temperature experiments five or six layers of mylar were used between the coil and the specimen.

The oscillator did not oscillate at room temperature with only one layer of mylar as insulation between the coil and specimen. It was found necessary to put the specimen in liquid nitrogen for the oscillator to operate and to know the resonance frequency of the coil. After two or three trials a coil of desired resonance frequency could be wound. For high temperature experiments, five layers of mylar made the Q of the circuit high enough for the oscillator to work at high temperatures. It was experimentally observed that optimum signal to noise was obtained with the lowest Q coil. The coil was wound as closely as possible so that the oscillator would still oscillate at the temperature of the experiment.
The wire used for the coil was not strong enough to support the weight of the crystal and to keep it in the desired position. A cylindrical copper bomb was designed to hold the crystal. The mounting of the crystal is very important. If the axis of symmetry of the crystal does not lie in the plane of field rotation, and is off even by a couple of degrees, it will give wrong results of the Knight shift and anisotropy. The copper bomb not only served as a support for the crystal but also enabled the sample to be rigidly mounted in the correct orientation.

As already described the PKW detector worked very well with 20 cycle twin-tee and signal to noise was no problem for any of the specimens used. In case of isotopically pure tin the signal could even be displayed on the oscilloscope. Time constants of .5 sec., 2.5 sec. and 5.0 seconds were used in the phase sensitive detector for isotopically pure tin, natural tin and cadmium respectively. In all the experiments at helium temperatures a modulation less than one fifth of the line width was used. However, for isotopically pure tin very small modulation was used. For high temperature experiments time constants up to 30 seconds and higher modulation amplitudes were used.
CHAPTER III
REVIEW OF THE THEORY OF THE KNIGHT SHIFT

In the following sections a brief review of the theory of the Knight shift is given. A detailed and comprehensive treatment is given by Abragam and Slichter. In the last section the temperature dependence of the Knight shift is treated.

3.1 The Knight Shift:

The Knight shift has been explained in terms of the hyperfine interaction between the nuclei and conduction electrons. Let us consider an assembly of n conduction electrons and N ion cores. Under the adiabatic approximation, the ion cores can be treated as stationary lattice points. The motion of the electrons can be assumed to be uncorrelated and the free electron approximation may be used. The electrons feel the potential due to ion cores plus some over all value of electron repulsion. The Hamiltonian of the system in presence of external magnetic field $H_0$ can be written as,

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_n + \sum_{i=1}^{n} \beta H_0 (L_z + 2S_z) + \sum_{j=1}^{N} \gamma H_0 I_z + \sum_{i=1}^{n} \sum_{j=1}^{N} \mathcal{H}_{ij}^{(i,j)}$$

3.1.1

where $\mathcal{H}_e$ is the Hamiltonian for the conduction electrons in the field of ion cores, $\mathcal{H}_n$ is the Hamiltonian of the ion cores. The third and fourth terms are the Zeeman energies of the conduction electrons and the nuclei and $\mathcal{H}_{ij}^{(i,j)}$ is the interaction Hamiltonian between ith electron and jth nucleus. It represents the hyperfine interaction energy and is of interest here. The energy of the jth nucleus $\mathcal{H}_{i}^{(j)}$ can be written as,

$$\mathcal{H}_{i}^{(j)} = -\gamma H_0 I_z^{(j)} + 2\beta \gamma (r_{ij}^3 \mathcal{I}_{i}^{(j)} \mathcal{I}_{i}^{(i)}) \frac{\gamma g_i S_i^{(j)} \mathcal{I}_{i}^{(i)}}{r_{ij}^3} - \sum_{i=1}^{n} \gamma g_i S_i^{(i)} \mathcal{I}_{i}^{(i)} \frac{\gamma g_i S_i^{(j)} \mathcal{I}_{i}^{(i)}}{r_{ij}^3} + \frac{8\gamma g_i S_i^{(j)} \mathcal{I}_{i}^{(i)} \mathcal{I}_{i}^{(j)}}{3}$$

3.1.2

The electron operators are labelled with superscript i and nuclear operators with j. The prime on the 3rd term means that it does not contain singularity. It has already been evaluated at the origin and the value included in the last term.

The expectation value of $\mathcal{H}_{i}^{(j)}$ with respect to the electron wave function
\( \Psi_n \) gives the Knight shift. Since the sum is over all the conduction electrons, \( \Psi_n \) is normalized over the crystal volume. The electron wave functions are simply Bloch functions \( \psi(\mathbf{k}, \mathbf{r}) = \psi_k(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}} \) where \( \psi_k(\mathbf{r}) \) is a function having same periodicity as lattice. Since the orbital angular momentum in most metals is quenched, (rare earths are exception), the second term does not contribute. For metals with cubic symmetry, the contribution of the primed term is zero but it does contribute to the Knight shift in the metals with symmetry lower than cubic and is responsible for anisotropy. This will be treated in one of the following sections. The last term in (3.1.2) known as the contact term is the only term, contributing to the isotropic Knight shift. If only contact term is considered, the expectation value of \( \mathbf{M}_1 \) may be written as,

\[
\langle \mathbf{M}_1 \rangle = -\gamma H_0 I_z \left( 1 + \frac{\beta \gamma H_0 I_z}{3} \right) \text{VN}(E_F) P_F
\]

where \( P_F \) is the probability of an electron, with Fermi energy, being found at the site of the nucleus. Thus we get

\[
\langle \mathbf{M}_1 \rangle = -\gamma H_0 I_z \left( 1 + \frac{\beta \gamma H_0 I_z}{3} \right) \text{VN}(E_F) P_F
\]

The Pauli susceptibility \( \chi_p = \beta N(E_F). \) Therefore

\[
\langle \mathbf{M}_1 \rangle = -\gamma H_0 I_z \left( 1 + \frac{\beta \gamma H_0 I_z}{3} \right) \text{VN}(E_F) P_F
\]

The first term in the above expression can be recognized as the nuclear Zeeman energy. The second term is the contribution of only s electrons at the Fermi surface. It can now be seen that the nucleus j feels an additional magnetic field \( \Delta H, \) due to these electrons, which can be written as

\[
\Delta H = \frac{8 \pi}{3} H_0 \text{VN} P_F
\]
This is known as isotropic Knight shift ($K_{iso}$).

3.2 Orbital Paramagnetism.

In the previous section the theory of the isotropic Knight shift has been outlined. It was assumed there that the orbital angular momentum is quenched and hence does not contribute to the paramagnetism. This is not true in general. For metals with partially filled non s bands, the orbital magnetic moment contributes to the paramagnetic susceptibility. This is because, as Kubo\(^{(22)}\) has pointed out, in metals the spin paramagnetism is reduced by a factor $T/T_0$, where $T_0$ is the degeneracy temperature and in metals with degenerate bands, orbital paramagnetism can be an appreciable fraction of the total paramagnetism. This can be shown by considering the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e^2}{2mc^2} \mathbf{A}^2 + \frac{e}{2mc}(\mathbf{p} \cdot \mathbf{\tilde{A}} + \mathbf{\tilde{A}} \cdot \mathbf{p}) + 2\beta \mathbf{S} \cdot \mathbf{H}$$

where $\mathcal{H}_0 = \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e^2}{2mc^2} \mathbf{A}^2$

and $\mathcal{H}_1 = \frac{e}{2mc}(\mathbf{p} \cdot \mathbf{\tilde{A}} + \mathbf{\tilde{A}} \cdot \mathbf{p}) + 2\beta \mathbf{S} \cdot \mathbf{H}$

$\mathbf{A}$ can be be written as $2\mathbf{A} = Hx\mathbf{r}$, where $\text{div}\mathbf{A} = 0$ and $\text{curl}\mathbf{A} = \mathbf{H}$. Using this value of $\mathbf{A}$ one gets

$$\mathcal{H}_1 = \frac{e\hbar}{2mc} \mathbf{H} \cdot (L + 2\mathbf{S})$$

$$= \beta \mathbf{H} \cdot (L + 2\mathbf{S})$$

3.2.1

The magnetic moment of the metal is given by $M = \langle \mathbf{\tilde{A}} \rangle$ and the susceptibility by $\chi = -\langle \frac{\partial \mathcal{F}}{\partial H^2} \rangle$ = const, $H \to 0$

where $\mathcal{F}$ is the free energy and is given by

$$\mathcal{F} = N\xi - kT \sum \log(1 + \exp((\xi - E_i)/kT))$$

3.2.2

and the summation taken over all the states. $N$ is the total number of electrons and $\xi$ is the thermodynamic potential. $\xi = E_F$ at $0^\circ K$ only. $E_i$
is an eigenvalue of $\mathcal{H}$ and eqn. (3.2.2) can be written as a function of $\mathcal{H}$, denoted by $\varphi(\mathcal{H})$ below.

$$F = N \varphi + \text{Tr}(\varphi(\mathcal{H}))$$

where $\varphi(\mathcal{H}) = -kT \sum \log(1 + \exp((\xi - \mathcal{H})/kT))$

Now using the representation in which $\mathcal{H}_0$ is diagonal and $\mathcal{H}_1$ is diagonal in vector $\mathbf{r}$,\(^\text{(16,29)}\) in tight binding approximation, $\text{Tr}(\varphi(\mathcal{H}))$ can be expanded in the following way

$$\text{Tr}(\varphi(\mathcal{H})) = \text{Tr}(\varphi(\mathcal{H}_0 + \mathcal{H}_1))$$

$$= \text{Tr} \varphi(\mathcal{H}_0) + \sum_{m} \varphi_1(E_m) \langle m | \mathcal{H}_1 | m \rangle + \frac{1}{2} \sum_{m,m'} \frac{\varphi'(E_m) - \varphi'(E_{m'})}{E_m - E_{m'}} |(m | \mathcal{H}_1 | m) |^2$$  \hspace{1cm} \text{3.2.3}

The first term contributes to the diamagnetic susceptibility of the conduction band electrons. Since we are looking for paramagnetic contributions, it will not be considered here. The second term requires a permanent magnetic moment to be present and so only occurs for ferromagnetic metals, a case which we are not interested in.

The last term gives the paramagnetic susceptibility. To evaluate the summation over all possible energy values it is changed into an integration over $\mathbf{k}$ space and a summation over all the values of $E_n(\mathbf{k})$ which correspond to each value of $\mathbf{k}$. Substituting the thermodynamic relation for $\chi$ gives

$$\chi_{\text{para}} = \sum_{n,n'} \int \frac{d\mathbf{k}}{8\pi^3} \left( \frac{f(E_n(\mathbf{k})) - f(E_{n'}(\mathbf{k}))}{E_n(\mathbf{k}) - E_{n'}(\mathbf{k})} \right) (n \mathbf{k} | \mathbf{S} | n' \mathbf{k}) (n' \mathbf{k} | \mathbf{S} | n \mathbf{k})$$  \hspace{1cm} \text{3.2.4}

where $\varphi(E) = f(E)$. $f(E)$ is the Fermi function and for $E_m$ the value in the absence of $H$ has been substituted. The factor $\frac{1}{8\pi^3}$ is the density of states per unit crystal volume per spin state in $\mathbf{k}$ space.

$\chi_{\text{para}}$ consists of three terms:

$$\chi_{\text{s}}^{(a)} = \sum_{n,n'} \int \frac{d\mathbf{k}}{8\pi^3} \left( \frac{f(E_n(\mathbf{k})) - f(E_{n'}(\mathbf{k}))}{E_n(\mathbf{k}) - E_{n'}(\mathbf{k})} \right) (n \mathbf{k} | \mathbf{S} | n' \mathbf{k}) (n' \mathbf{k} | \mathbf{S} | n \mathbf{k})$$  \hspace{1cm} \text{3.2.5}

This is the well known Pauli-spin susceptibility and arises because of surplus electron spins with their magnetic moments parallel to $\mathbf{H}$.

$$\chi_{\text{s}} = \beta^2 N(E_F)$$  \hspace{1cm} \text{as before.}
\[ \chi_{So} = \beta^2 \sum_{nn'} \int \frac{dK}{8\pi^3} \frac{f(E_n(K)) - f(E_{n'}(K))}{E_{n'}(K) - E_n(K)} \left( \langle nK|L|n'K \rangle \langle n'K|2\bar{S}|nK \rangle + \langle nK|2\bar{S}|n'K \rangle \langle n'K|L|nK \rangle \right) \]

\[ \chi_{So} \] is the contribution of spin-orbit coupling. This coupling lifts slightly the queching of the orbital angular momentum by mixing in other states of appropriate angular momentum and symmetry. The contribution is negligibly small as compared to \( \chi_s \) and it is not an important term.

\[ \chi_o = \beta^2 \sum_{nn'} \int \frac{dK}{8\pi^3} \frac{f(E_n(K)) - f(E_{n'}(K))}{E_{n'}(K) - E_n(K)} \langle nK|L|n'K \rangle \langle n'K|L|nK \rangle \]

This arises because of mixing of the un-occupied excited states, by the orbital angular momentum operator, into an occupied ground state with quenched orbital angular momentum. In the tight binding approximation \( \bar{L} \) has matrix elements between the states which have the same value of \( K \) and differ in magnetic quantum number \( n' \). This means that there are only contributions from matrix elements between levels in the same partially filled band. Most of the metals have mainly s electrons in the conduction band and for them \( \chi_o \) is negligible. Transition metals are exceptions as they have a partially filled d band and \( \chi_o \) has significant value.

3.3 Core Polarization:

In section 3.1 where the contribution of the contact term to the Knight shift is outlined, it is assumed that the unpaired s type electrons at the Fermi surface have no coupling with the closed shell electrons or core electrons. This is not strictly true. The unpaired electron spins interact with the core electron spins through the exchange interaction. As a result, the core electrons get polarized and contribute to the magnetic field at the nuclei.

This can be explained qualitatively as follows. Suppose the conduction s electron has spin \( \uparrow \) because of the magnetic field \( H_0 \). Let us consider its effect on \( n=2, l=0 \) closed shell electrons. There are two electrons in this shell,
one with spin $\uparrow$ denoted by $S_{2\uparrow}$ and the other with spin $S_{2\downarrow}$. The $S_{2\downarrow}$ electron will be pulled a bit outside and $S_{2\uparrow}$ electron pushed in as a result of exchange forces. In other words the wave functions are distorted in such a fashion that $\langle |\Psi_{2S_{\uparrow}}(0)|^2 - |\Psi_{2S_{\downarrow}}(0)|^2 \rangle$, for example, will no longer be zero at the nuclear site which it would otherwise have been but for the presence of the polarized conduction electrons. This will also be true for $\langle |\Psi_{1S}(0)|^2 - |\Psi_{1S}(0)|^2 \rangle$. Thus, due to the renormalization of the wave functions, the nucleus sees a net magnetic field due to the core polarization. The extent of this field seen will depend upon the degree of polarization of the conduction electrons. This extra field experienced by the nuclei is always in the direction of the applied magnetic field and paramagnetic in character.

Cohen et al have worked out the contribution due to core polarization in Li and Na. They have used self consistent field wave functions and calculate a 31% and 5.5% increase in the hyperfine coupling constant for Li and Na respectively. The comparison between Li and Na shows that the contribution should be smaller for higher atomic number.

The 2P electrons are also polarized, but do not contribute to the hyperfine coupling as they have a node at the nuclear site.

3.4 Anisotropy:

So far, we have been discussing the contributions to the Knight shift which do not depend upon the direction of the external magnetic field relative to the axis of symmetry of the crystal. If we go back to eqn. (3.1.2) we find that the primed term, not considered so far, depends upon the direction of the applied magnetic field $H_0$ and contributes to the anisotropy of the Knight shift. The cause of this orientation dependent shift is the energy of the nuclear dipole in the dipolar field of the unpaired electron spins outside the nucleus in the metal. The only term left unconsidered thus far is $H_{\text{aniso}}$. 
where
\[ H_{\text{aniso}} = -\gamma g \beta \left( \frac{3}{2} - 3 \frac{F_{ij}(s_{ij})}{r_{ij}} \right) r^{-3} \]  \hspace{1cm} (3.4.1)

Let the angle between the radius vector \( r \) and \( H \) be denoted by \( \alpha \), then eqn. (3.4.1) becomes
\[ H_{\text{aniso}} = \pm \gamma \beta M_T (1 - 3 \cos^2 \alpha) r^{-3} \]  \hspace{1cm} (3.4.2)
The \( \pm \) sign designates whether the electron spin is anti-parallel or parallel to \( H \). The expectation value of eqn. (3.4.2) with respect to the electron wave function \( \psi \) and sum over all the \( \mathbf{k} \) states gives the anisotropic Knight shift. Bloembergen (5) has worked this out for axially symmetric case. The result is,
\[ H_{\text{aniso}} = \beta N(E_F) q_F (3 \cos^2 \Theta - 1) \]  \hspace{1cm} (3.4.3)
where
\[ q_F = \left( \int \psi^* \left( 3 \cos^2 \alpha - 1 \right) r^3 \psi \, dV \right)_F \]  \hspace{1cm} (3.4.4)

\( q_F \) is the measure of the anisotropy in charge distribution and is related to the conduction electron wave functions (3.4.4). In the discussion the axis of symmetry has been chosen to be the \( z \) axis. The angle appearing in (3.4.3) is the angle between the magnetic field \( H \) and the symmetry axis. The total Knight shift is given by
\[ \Delta H = \Delta H_{\text{iso}} + \Delta H_{\text{aniso}} \]
or
\[ \Delta H = K_{\text{iso}} + \beta N(E_F) q_F (3 \cos^2 \Theta - 1) \]
\[ = K_{\text{iso}} + \frac{1}{2} K' (3 \cos^2 \Theta - 1) \]  \hspace{1cm} (3.4.5)
For any arbitrary angle, the field is
\[ \Delta H = H_{||} \cos^2 \Theta + H_{\perp} \sin^2 \Theta \]
For positive \( q_F \), \( \Delta H_{||} \) is greater than \( \Delta H_{\perp} \) and, therefore, the resonance frequency is higher when the crystal is oriented with \( \Theta = 0 \). This is seen in case of white tin. The relationship reverses when \( q_F \) is negative, which is seen in the case of thallium.

The expression for the isotropic Knight shift contains the Landé \( g \) factor. If \( g \) is anisotropic, it would also produce an anisotropy in the Knight shift as a result of an anisotropic Pauli spin paramagnetism. \( g \) can
be expressed as
\[ g(\theta) = (g_{\parallel} \cos^2 \theta + g_{\perp} \sin^2 \theta)^{1/4} \]
which approximates the form of eqn. (3.4.5) and hence it is not possible to
distinguish between these two contributions.

3.5 Temperature Dependence of the Knight Shift:

\( K_{\text{iso}} \) is given by
\[ K_{\text{iso}} = \frac{8\pi}{3} \chi_p P_F \]
where \( J \) is the volume over which \( \psi(K, o) \) is normalized and \( \chi_p \) is the Pauli
spin susceptibility. In the free electron model it is temperature indepen­
dent to a very good approximation. \( P_F \) is the probability of finding the
electron at the nuclear site and is also considered to be temperature
independent.

Soon after the discovery, experiments were undertaken to measure the
Knight shift as a function of temperature\(^{(27)}\). Preliminary experiments revealed
that the Knight shift was a weak function of temperature and the variation
with temperature was attributed to the thermal expansion of the sample.

In 1958 Benedek and Kushida\(^{(4)}\) made measurements on volume dependence
of the Knight shift in Na, Rb, Cs, Li and Cu by using pressures up to \( 10^4 \)
Kgm/cm\(^2\) while keeping the temperature constant. They were in a position to
examine the validity of the assumption that the temperature dependence comes
solely from thermal expansion. Use was made of the thermodynamic relation
\[ \frac{2\ln K}{2T} = \left( \frac{2\ln K}{2\ln V} \right)_T \left( \frac{2\ln V}{2T} \right)_P + \left( \frac{2\ln K}{2\ln V} \right)_V \]
\[ \text{3.5.1} \]
where the left hand side of the equation is experimentally measured, \( \left( \frac{2\ln K}{2\ln V} \right)_T \left( \frac{2\ln V}{2T} \right)_P \)
is the contribution of the thermal expansion and \( \left( \frac{2\ln K}{2\ln V} \right)_V \) is the intrinsic temp­
erature dependence of the Knight shift.

\[ \therefore \left( \frac{2\ln K}{2T} \right)_V = \left( \frac{2\ln P_F}{2T} \right)_V + \left( \frac{2\ln (\chi_p J)}{2T} \right)_V \]
\[ \text{3.5.1A} \]

The following model was proposed to explain the intrinsic temperature
dependence. The characteristic period of lattice vibration is of the order
of $10^{-12}$ sec., while the spin-lattice relaxation time of electron spins varies between $10^{-6}$ and $10^{-9}$ seconds. Thus the electron spins cannot follow the lattice vibration and hence no change in $\chi$ is expected. Under this assumption the second term on the right of eqn. (3.5.1A) can be neglected. Then it should be $P_F$ which is changing with temperature.

As the lattice vibrates, it produces rapid changes in the volume occupied by an atom in the lattice. The electron wave functions adjust themselves almost instantaneously to this local state of thermal strain. Thus $P_F$ is a time varying function and can be expanded around the equilibrium atomic volume $V_0$ at temperature $T$ and then a time average taken, as below

$$P_F(t) = P_F(V_0) + \frac{\partial P_F(V_0)}{\partial (V/V_0)} \frac{\partial (V/V_0)}{V_0} + 2 \frac{\partial^2 P_F}{2 \partial (V/V_0)^2} \frac{(V(t) - V_0)^2}{V_0} + \ldots$$

The second term in the expansion averages to zero and $P_F(t) = P_F(V_0)$ only in the first approximation otherwise $P_F(t) \neq P_F(V_0)$ because of zero point vibrations. $(\Delta V/V_0)$ is just the dilation. Using the value of the dilation operator, it can be shown that $(\Delta V/V_0)^2 = \beta U$, where $\beta$ is the adiabatic compressibility and $U$ is the internal energy density associated with the longitudinal phonons and $C$ is the contribution of the longitudinal phonons to the specific heat of the metal. What fraction of specific heat comes from the longitudinal phonons is not exactly known.

Making the crude assumption, that one third of the total specific heat $C_v$ comes from the longitudinal phonons,

$$\langle \frac{\partial \ln K}{\partial T} \rangle_v = \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0) \cdot \frac{\partial (V/V_0)}{V_0} \cdot \frac{\partial^2 P_F}{\partial (V/V_0) \cdot \frac{\partial (V/V_0)}{\partial T}}} \left( \frac{BC_v}{3} + \frac{U \beta}{\partial T} \right). \quad 3.5.3$$
CHAPTER IV
EXPERIMENTAL RESULTS AND DISCUSSION

In the experiments reported here a systematic study of the Knight shift parameters was carried out as a function of temperature in both tin and cadmium single crystals. The temperature range covered was from 1.1°K to just below the melting points.

Temperatures at which the experiments were carried out were 1.15°K, 4.2°K, 77°K, 195°K, 300°K, 380°K and 450°K. For experiments at 4.2°K and 77°K the specimen was in thermal contact with liquid helium and liquid nitrogen baths respectively at the atmospheric pressure. For the experiments at dry ice temperature and above, the temperature was measured by a copper-constantan thermocouple. To achieve temperatures higher than room temperature a high temperature oil bath was used. The temperature of the bath could be controlled to within ±1°C.

4.1 Tin

The first direct measurement of the Knight shift parameters in tin was made by Jones and Williams (42). A sliced sandwich single crystal was used and the measurements were limited to helium temperatures only. Barnes and Borsa (3) have made experiments using a powdered sample and the crossed coil technique. The present measurements were made on a single crystal, without slicing it, and the temperature range was extended to just below the melting point of tin. The results for the isotropic knight shift and the anisotropy in the knight shift are shown as a function of temperature in figures 3 and 4 together with the results of the above mentioned experiments.

For the single crystal experiments the observed resonance frequency, i.e. the frequency at which the derivative of the observed signal is zero, is not the true resonance frequency because of mixing of modes. For constant magnetic field the correct resonance frequency is higher by a fraction of the line-width. The experimental results have been corrected for this (Appendix B).
Figure 3. The Isotropic Knight Shift in Tin as a Function of Temperature.
Figure 4. Anisotropy in the Knight Shift in Tin as a Function of Temperature.
Figure 5. The Knight Shift in Tin, for Various Temperatures, as a Function of Crystal Orientation at 10 K Gauss.
Plots of the Knight shift as a function of the field orientation with respect to the (001) axis at the different temperatures are shown in figure 5 to indicate the accuracy and the completeness of the data. The reference used for these experiments was Sn₂Cl₂.

4.2 Cadmium:

Measurements on Cd¹¹³ have been made by quite a few workers. Masuda was the first to measure the Knight shift. He also estimated the contribution of s and p-type wave functions. Styles and Seymour measured only the isotropic Knight shift, using a super-regenerative detector, until the melting point. Barnes and Borsa also made measurements of these parameters but in all the above experiments powdered specimens were used. Schone measured the Knight shift in a sliced sandwich single crystal of cadmium for the first time.

Experiments were carried out on Cd¹¹³ in a natural cadmium single crystal without slicing it and were similar almost in all respects as the tin experiments. The reference for cadmium resonance experiments was CdCl₂.

Figures 6 and 7 show the Knight shift and anisotropy as a function of temperature. Results of the previous experiments are also plotted there for comparison. Figure 8 shows the plot of the Knight shift as a function of field orientation relative to the (0001) axis for various temperatures.

The present experiments have revealed that the anisotropy in the Knight shift in Cd changes in sign between 4.2 K and 77 K. In figure 9 the results, without line-width correction, have been plotted on an extended scale just to
emphasize this. This result is in contradiction with the results of other workers and it is not clear why the discrepancy exists. In view of the substantially narrower lines observed in this work it is felt that the present results are more reliable.

It has been found that the observed signal changes in shape with the orientation of the magnetic field. This means that the mixture of the modes changes. The reason for this is not presently understood but it seems likely that this is connected with the anisotropy of the magnetoresistance of Cd since this governs the penetration of the electromagnetic field. Two extreme cases are shown in figure 10. The line is almost symmetric when the magnetic field is parallel to (0001), the other orientation being with field perpendicular to (0001).

Cd-Hg alloy crystal:

To explore the relationship between the variation of the Knight shift parameters in hexagonal systems a study of a Cd-Hg single crystal with 12 atomic percent Hg was undertaken. Pure cadmium has a c/a ratio, at room temperature, equal to 1.8857 whereas Cd-Hg has 1.9023. The temperature variation of c/a ratio in cadmium can be calculated for helium temperature but the helium value is not known for Cd-Hg.

At helium temperatures the Knight shift was found to be \(0.371 \pm 0.002\%\), 9.44\% higher than natural cadmium at the same temperature, and the anisotropy \(0.0404\%\). Both are considerably higher than cadmium and these values coincide with corresponding values for cadmium at about 170°K. An attempt was also made to make these measurements at liquid nitrogen temperature but the signal to noise ratio was, unfortunately, only about 2:1. This was because of the fact that the line width at the helium temperature varied from four to six kc/s whereas the line width in natural cadmium varied between 0.5-0.7 kc/s.
Figure 6. The Isotropic Knight Shift in Cd as a Function of Temperature.
Figure 7. Anisotropy in the Knight Shift in Cadmium as a Function of Temperature.
Figure 8. The Knight Shift in Cadmium, for Various Temperatures, as a Function of Crystal Orientation at 10 K Gauss.
Figure 9. The Knight Shift in Cadmium, at Liquid Nitrogen and Helium Temperatures, as a Function of Crystal Orientation.
Observed signal when $H_0$ is perpendicular to (0001)

Observed signal when $H_0$ is parallel to (0001)
Thus the experiment at liquid nitrogen temperature was not a success so far as the accurate measurement of the Knight shift and anisotropy is concerned but it showed un-ambiguously that there was no change in the sign of the anisotropy.

4.3 Discussion:

(i) Comparison with other data.

(a) Tin

The most accurate results are obtained at 1.2°K where the signal to noise ratio is greatest. When comparing the present results with previous workers it is seen that the anisotropy observed at this temperature is higher than that previously measured. This is even true for the single crystal work of Jones and Williams \(^{(42)}\) where an anisotropy of 0.08\(\Omega\) was observed. The present value of 0.086±0.001 is believed to be a result of more careful crystal mounting to ensure that the plane of the field rotation contained the (001) axis. This indicates that a misalignment of about ten degrees occurred in the previous work.

For temperatures higher than helium, the only other results available are the powder measurements of Barnes and Borsa \(^{(3)}\). It is seen that there is some disagreement and it is felt that this indicates the degree of reliability of powder results. The powder analysis assumes an orientation independent line-width which is clearly not the case and possibly this is the source of error. At higher temperatures where the line width becomes dominated by the spin-lattice relaxation time it is to be expected that this approximation becomes more valid.

(b) Cadmium

For cadmium a considerable amount of data is available both in powder and single crystal form. A comparison is shown in figures 6 and 7 and it is
seen that large discrepancies exist. In particular at liquid helium temperatures the anisotropy is seen to have changed sign whereas other workers indicate zero anisotropy. It should be noted that the line-widths observed in the present work are nearly one half those quoted by others and it is felt that this alone vindicates the present results. Possibly the broad lines observed by others\(^{(3,33)}\) are due to oscillations in the Knight shift. An attempt to observe these oscillations in the specimen used did not reveal any significant evidence of their presence but probably the other specimens were of higher purity.

(ii) Analysis of temperature dependence:

As already stated in section 3.5, the temperature dependence of the Knight shift may be separated into two contributions, one due to thermal expansion and the other due to an explicit temperature dependence. These contributions may be separated by using the expression (3.5.1)

In both tin and cadmium the thermal expansion contribution can be determined from measurements of other workers\(^{(21,25)}\) and the explicit temperature dependence may be obtained. The analysis is concentrated upon this.

In the absence of any data available to sort out the explicit temperature dependence,\(\frac{\partial \ln K}{\partial T}V\), Barnes and Borsa made an attempt to work it out theoretically by putting\(\frac{\partial \ln K}{\partial n V}_T = -\frac{1}{3}\). This is correct under the free electron model where no zone boundaries are present. The result of volume effect under this model is a negative contribution to the Knight shift.

\textbf{Tin}

Recently Matzkanin and Scott\(^{(25)}\) have carried out experiments on the pressure dependence of the Knight shift at room temperature which determine the explicit volume contribution. They found that\(\frac{\partial \ln K}{\partial n V}_T (\frac{\partial n V}{\partial T}p) = 0.61 \pm 0.04\). This result is in contradiction to Barnes and Borsa's theoretical speculation
and is an indication that the free electron approximation is not capable of predicting reliable results for experimental quantities which are sensitive to the details of the model.

If the present results for \( \frac{\partial \ln K}{\partial T} \) are combined with Matzkanin and Scott's for the term \( \frac{\partial \ln K}{\partial \ln V} \) together with the thermal expansion results from reference (37), the intrinsic temperature dependence can be obtained over all the temperature range. In evaluating \( \frac{\partial \ln K}{\partial T} \) it has been assumed that \( \frac{\partial \ln K}{\partial \ln V} \) is constant. The results are shown in figure 11.

Various possible contributions to the Knight shift have been outlined earlier in sections 3.1 to 3.3. The facts that the results of the Knight shift measurements in superconducting tin (43) are explicable in terms of 90% contact contribution and that the Korringa relation is satisfied over a wide range of temperature, are very good indications that the contact contribution is the dominant term. Thus in the following treatment all other contributions will be neglected. The contact contribution to the Knight shift is

\[
K = \frac{2\pi}{3} \sum_p |\chi_p| P_F
\]

where the symbols have their usual meanings. Since \( \chi_p \propto g N(E_F) \),

\[
K = \frac{2\pi}{3} g \sum_p P_F N(E_F)
\]

Even after this simplification \( K \) contains too many variables i.e. \( g \), \( P_F \) and \( N(E_F) \). The problem appears to be formidable as they all can be a function of temperature.

There are two possible sources of an intrinsic temperature dependence; the influence of the lattice vibration spectrum and that of Fermi distribution function for the electronic states.

Let us try to analyse the accuracy of the model due to Benedek and Kushida (4) i.e. we assume \( \chi_p \) to be temperature independent and that the effect of the Fermi distribution function is negligible. The effect of the phonon spectrum is considered as a modulation of the atomic volume and as a result
Figure 11. Explicit Temperature Dependence of the Knight Shift in Tin as a Function of Temperature.
the probability of a Fermi electron interacting with the nucleus contains a term \( \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \left( \frac{\Delta V}{V_0} \right)^2 \), where \( P_F \) is the probability of a Fermi electron being found at the nuclear site at an instantaneous time \( t \) and \( \left( \frac{\Delta V}{V_0} \right)^2 \) is the mean square deviation of the volume from its equilibrium value \( V_0 \).

It has already been shown that

\[
\frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0} \left( \frac{\Delta V}{V_0} \right)^2 = \frac{1}{2P_F} \frac{\beta}{\gamma(V/V_0)^2} \bigg|_{V=V_0} \]

where \( \beta \) is the adiabatic compressibility and \( \gamma \) is the internal energy density associated with the longitudinal phonons.

In the case of tin \( \left( \frac{\partial \rho}{\partial T} \right) \) is very small and

\[
\left( \frac{\partial \ln K}{\partial T} \right)_V = \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \frac{\beta C}{V_0}
\]

where \( C \) is the specific heat due to longitudinal phonons. For the purpose of evaluating the approximate size of this term let us put \( C = C_V / 3 \) then

\[
\left( \frac{\partial \ln K}{\partial T} \right)_V = \frac{1}{6P_F} \frac{\beta C_V}{V_0}
\]

For temperatures higher than the Debye temperature \( \frac{\beta C_V}{V_0} = \frac{\beta k}{\mathcal{A} V} \), where \( k \) is Boltzmann's constant and \( \mathcal{A} \) is the atomic volume. It is thus seen that Benedek and Kushida's result, which is valid for temperatures higher than the Debye temperature, is a special case of the generalized theory outlined in the last chapter.

The result of the model is that \( \left( \frac{\partial \ln K}{\partial T} \right)_V \) should have the same temperature dependence as the specific heat. \( \left( \frac{\partial \ln K}{\partial T} \right)_V \) as well as the specific heat is plotted as a function of temperature in figure 11. It can be seen that the explicit temperature dependence does not obey the \( T^3 \) law at low temperatures.

It should be noted that \( \frac{\beta C}{V_0} = \frac{\beta C_V}{3V_0} = \frac{\mathcal{C}}{V} \) where \( \mathcal{C} \) is the coefficient of linear expansion and \( \mathcal{V} \) is the Grüneisen constant. Thus

\[
\left( \frac{\partial \ln K}{\partial T} \right)_V = \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0} \frac{\mathcal{C}}{V}
\]
and \( \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0} = \frac{\gamma}{\alpha} \left( \frac{\partial \ln K}{\partial T} \right)_V \)

The left hand side of the above expression is evaluated by combining \( \gamma \) for tin with the value of \( \frac{\partial \ln K}{\partial T} \bigg|_V \) from figure 11. For \( T \gg \Theta_D \)
\[
\frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0} = 3.8 \pm 0.2
\]

Matzkanin and Scott have plotted \( \frac{K_{iso}(V)}{K_{iso}(V_0)} vs \left( \frac{V}{V_0} \right) \). From their results
\[
\frac{1}{2K(V_0)} \frac{\partial K(V)}{\partial (V/V_0)^2} \bigg|_{V=V_0} = 4.3 \pm 0.5
\]

In our model, since \( K_0 \propto P_F \),
\[
\frac{1}{2K(V_0)} \frac{\partial K(V)}{\partial (V/V_0)^2} \bigg|_{V=V_0} = \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0}
\]

Thus it is seen that the value of \( \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0} \) obtained from the experiments at constant pressure is in good agreement with the value obtained from the pressure dependence of the Knight shift. However the determination of the second derivative from the pressure dependence requires very accurate data. It is felt that this can be better obtained from the pressure dependence experiments on a single crystal. The fact that the values of \( \frac{1}{2P_F} \frac{\partial^2 P_F}{\partial (V/V_0)^2} \bigg|_{V=V_0} \), obtained from two types of experiments, are equal indicates that there is little contribution due to \( \chi_p \) as a function of temperature. The model seems to work for \( T \gg \Theta_D \) while it does not for the low temperature results. It is possible that another contribution exists which is comparable in magnitude to the low temperature phonon contribution, but is dominated by the phonon contribution at higher temperatures.

Cadmium:

Figure 4 shows a \( K_{iso} \) vs temperature plot for cadmium. The experimental points of Barnes and Borsa are also shown there with the errors involved. The present results are in fair agreement with their results over all the temperature range but for the helium temperature. The present results show a change of slope at dry ice temperature. No measurements were made between liquid nitrogen and dry ice temperatures. If Barnes and Borsa's measurements in
this range are combined with our data, the $K_{iso}$ vs temperature plot will look as shown by the dotted line in this region.

Kushida and Rimai's (21) experiments on the pressure dependence of the Knight shift indicate that in cadmium the Knight shift is largely explicitly temperature dependent. If the present results for $\frac{\partial \ln K}{\partial T}$ are combined with their results for $\frac{\partial \ln c}{\partial T}$ at room temperature then $\frac{\partial \ln K}{\partial T}$ can be worked out. Treating $\frac{\partial \ln c}{\partial T}$ as constant over all the temperature range, the explicit temperature dependence has been worked out from $1^\circ K$ to $300^\circ K$. It is shown in figure 12 together with the variation of $\frac{\alpha}{\gamma}$ and $\left( \frac{\alpha}{\gamma} + \frac{\delta}{\partial T} \right)$. The values of $\alpha$ and $\gamma$, used in these calculations are from reference (24) and for $\gamma$, the Grüneisen constant, are from reference (11). The results for $\frac{\partial \ln K}{\partial T}$ are certainly some what inaccurate. It should be noted that $\frac{\alpha}{\gamma}$ vs $T$ has a hump in the same temperature region as $\left( \frac{\partial \ln K}{\partial T} \right)$. More and reliable data is required to establish the existence of a low temperature maximum.

For cadmium the compressibility is not independent of temperature (11) and the term in $\frac{\partial \delta}{\partial T}$ appearing in (3.5.3) can not be neglected at high temperatures. The contribution at $300^\circ K$ is about 10% of the total effect. The Grüneisen relation holds for cadmium (11) from $150^\circ K$ to $450^\circ K$. A calculation of $\frac{1}{2} \frac{\partial \delta}{\partial T}$ for $T=300^\circ K$, $\theta_D=172^\circ K$ (29), from present results gives a value equal to 48 which seems rather large. Unfortunately $\frac{1}{2K(\omega)} \frac{\partial K(\omega)}{\partial (\omega/\nu_0)^2}$ could not be evaluated from the pressure dependence results because of a large scatter and the figure obtained for it from the present results can not be compared. Pressure dependence in a single crystal can give more reliable results and then a comparison is possible. Perhaps a more sophisticated technique like that of Muto et al (30) is necessary to evaluate the lattice vibration effects.
Figure 12. Explicit Temperature Dependence of the Knight Shift in Cadmium as a Function of Temperature.
(iii) Anisotropy and Temperature dependence:

(a) Tin

No variation in anisotropy is observed between helium and liquid nitrogen temperatures. Since no measurements have been made between liquid nitrogen and dry ice temperatures, nothing can be said regarding its variation in this temperature range. Above the Debye temperature, $\Theta_D = 195^\circ K$ (14), it varies linearly and the results can be expressed as $K_{\text{aniso}} = (V(t)/V_0)^\alpha$, where $V(t)$ is the volume at $T^\circ K$ and $V_0$ at $0^\circ K$. $\alpha$ is some parameter and should not be confused with the coefficient of linear expansion. It is found that $\alpha = -7.3 \pm 0.2$. The values of the coefficient of thermal expansion have been used from reference (37). The volume dependence experiments, at constant temperature, for tin give a value $\alpha = -4.25 \pm 1.8$.

One of the possible contributions to the anisotropy can be the anisotropy in the Pauli susceptibility $\chi_p$. The measurements of Alexendrov (2) et al show that $\chi$ is positive. This is an indication that major contribution to $\chi$ comes from $\chi_p$. It should be noted, however, that $\Delta \chi = \chi_l - \chi_\perp$ increases in magnitude with a rise in temperature while $K_{\text{aniso}}$ decreases. Since they go in opposite directions, as a function of temperature, it is tempting to speculate that the anisotropy in $\chi$ is a diamagnetic anisotropy and is not related to $K_{\text{aniso}}$.

The mechanism which gives rise to $K_{\text{aniso}}$ is the dipole-dipole interaction at a distance and is described by the Hamiltonian $H_{\text{aniso}}$ eqn. 3.4.1. It has already been mentioned that the contribution of $H_{\text{aniso}}$ is non-zero only for metals with symmetry lower than cubic. In other words $H_{\text{aniso}}$ contributes only if $c/a \neq 1$. It seems reasonable to conclude that the contribution of $H_{\text{aniso}}$ should not change appreciably if $c/a$ remains constant. Any change in the $c/a$ ratio should have profound effects on the symmetry of the electron charge distribution in the lattice and hence on $q_p$. The changes in volume which keep $c/a$ unaltered should have little effect on $K_{\text{aniso}}$. Experiments on Mg single crystal
can provide valuable information in this regard. Mg has a c/a ratio equal to 1.6237\(^{(9)}\) which remains constant from 283°K to 473°K. However, experiments of Barnes and Borsa on the powdered specimen of Cd-Mg alloy, which has a different c/a ratio than that of pure Cd, do not indicate any change in anisotropy while our measurements on Cd-Hg alloy single crystal, to be described later, show a remarkable change in anisotropy. Thus it is not conclusive yet.

The variation in \(K_{\text{aniso}}\) can be written as

\[
\left( \frac{\partial K_{\text{aniso}}}{\partial T} \right) \approx \left( \frac{\partial K_{\text{aniso}}}{\partial (c/a)} \right) \frac{\partial (c/a)}{\partial T} + \left( \frac{\partial K_{\text{aniso}}}{\partial T} \right) \frac{c/a}{T}
\]

The first term on the right represents the contribution due to the change in c/a ratio as a function of temperature and the second term is explicit temperature dependence of \(K_{\text{aniso}}\) at constant c/a. As already mentioned the expected contribution from the second term should be negligible. Since \(\frac{\partial K_{\text{aniso}}}{\partial T}\) and \(\frac{\partial (c/a)}{\partial T}\) are known, the evaluation of \(\left( \frac{\partial K_{\text{aniso}}}{\partial (c/a)} \right) \frac{\partial (c/a)}{\partial T}\) would enable the evaluation of the explicit temperature dependence. Matzkanin and Scott's results could not be used to calculate \(\left( \frac{\partial K_{\text{aniso}}}{\partial (c/a)} \right) \frac{\partial (c/a)}{\partial T}\) because of the large errors involved.

It is felt that pressure dependence on a single crystal will give reliable data for \(\left( \frac{\partial K_{\text{aniso}}}{\partial (c/a)} \right) \frac{\partial (c/a)}{\partial T}\) which will enable the evaluation of the explicit temperature dependence of \(K_{\text{aniso}}\).

A plot in \(K_{\text{aniso}}\) vs c/a ratio for tin is shown in figure 13. It is seen that for \(T \gg \Theta_D\), \(\Theta_D=195°K\)(14), it is a straight line. It seems that above \(\Theta_D\) the change in c/a ratio is responsible for the variation in \(K_{\text{aniso}}\) and that there is little explicit temperature dependence. The values of c/a used from 273° to 450°K are from Lee and Raynor(23) and below 273°K have been worked out using White's(40) values for \(\lambda_{||}\) and \(\lambda_{\perp}\). The behaviour below \(\Theta_D\) is not understood at present.

Tin is tetragonal with c/a =0.5456 and can be compared with cubic structure. For c/a=1 the anisotropy is zero. If c/a of tin increases, by any means, the structure is becoming more nearly cubic and as a result the
Figure 13. Anisotropy of the Knight Shift vs. c/a Ratio for Tin.
anisotropy should go towards zero. The c/a does increase with temperature. Figure 13 shows that this is in fact true and the variation of $K_{\text{aniso}}$ is in the expected direction.

(b) Cadmium.

The anisotropy in the Knight shift of Cd is more temperature dependent as compared to tin. $q_F$ is positive above 77°K. As the temperature decreases, $q_F$ is also decreased. It goes to zero at some temperature and becomes negative at helium temperature. This implies that at some temperature between helium and nitrogen the charge distribution is spherically symmetrical. An explanation of this requires a detailed calculation of the electron wave functions for cadmium.

The variation in $K_{\text{aniso}}$ is linear above $\Theta_D$, $\Theta_D = 172°K$, and can be represented as $K_{\text{aniso}} = (V(t)/V_0) \lambda$. The value of $\lambda$ for cadmium is found to be $\lambda = 13.3 \pm 0.2$. By extrapolation it is found that $q_F$ is zero for a c/a ratio around 1.868. At 450°K c/a = 1.894 and as the temperature is decreased c/a ratio is also decreased. This means that with lowering of temperature the crystal structure is heading towards a c/a ratio which has a spherical charge distribution. Figure 14 shows a plot in c/a vs anisotropy.

Cd-Hg alloy single crystal.

To further the relationship between c/a ratio and the Knight shift parameters in hexagonal systems a study in Cd-Hg single crystal was done at helium temperature. The results have revealed that the addition of Hg changes the parameters drastically. At helium temperatures the values of the parameters coincide with that of pure Cd at about 170°K.

Experiments were undertaken by Barnes and Borsa on Cd-Mg alloy powder specimen with 1.0 atomic % of Mg. They did not observe any change in these parameters with in the experimental error. Cd, Cd-Mg and Cd-Hg have the
Figure 14. Anisotropy of the Knight Shift vs. c/a Ratio for Cadmium.
same crystal structure. All have the same valence so that alloying does not affect the number of electrons per atom and no charge re-distribution between the components is expected. However, the change in the lattice parameters should affect the symmetry of the charge distribution surrounding each nucleus. 1.0 atomic % Mg changes the c/a ratio to 1.8716 (17) (c/a for Cd=1.8857) and 12.0 atomic % Hg to 1.9023. Thus it is seen that the two types of impurities take the c/a ratio in opposite directions. In the light of the previous results it is natural to expect a larger anisotropy in Cd-Hg alloy single crystal. Since the Cd-Mg alloy has a lower c/a ratio, a smaller anisotropy is expected, in this case, as compared to Cd. Perhaps the effect could not be observed because of the broad lines encountered.

Since no thermal expansion data for Cd-Hg single crystal is available, the anisotropy vs c/a ratio at helium temperature could not be compared with the $K_{aniso}$ vs c/a plot for Cd.
CHAPTER V
THEORY OF THE LINE-WIDTH AND LINE SHAPES

The resonance frequency of a nucleus in an external homogeneous magnetic field \( H_0 \) is \( \omega_0 = \gamma H_0 \), where \( \gamma \) is the gyromagnetic ratio. If the nucleus is subjected to a variable frequency rf field \( H_1 \) perpendicular to \( H_0 \), resonance occurs at \( \omega_0 \) as the frequency is swept. The nucleus absorbs energy only at \( \omega_0 \), in the limit \( H_1 \to 0 \), causing the rf level to drop in a PKW box. The plot of rf level vs \( \omega \), in this case, goes through a very sharp minimum in the vicinity of \( \omega_0 \).

In practice the nuclei are embedded in bulk matter and experiments are made on an ensemble. In a crystal the nuclei are arranged in an orderly fashion and produce local magnetic fields, at each other's site, of a magnitude which depends upon the relative orientation and positions of the nuclei. Since each spin has several neighbours, with different relative orientations and positions the local magnetic field has different values at different sites. This causes a spread in the Larmor frequency and the absorption line is a function of \( \omega \) and has a finite width. The broadening is caused by the dipole-dipole interaction. However it is found that the experimental line-widths generally exceed the calculated dipolar width. This leads to the conclusion that there are other mechanisms responsible for broadening. This chapter is limited to the line-width studies in tin so that the discussion is limited to the spin \( \frac{1}{2} \) case.

Since there is no quadrupole moment present in a spin \( \frac{1}{2} \) system, broadening due to this interaction is absent. Another type of broadening is a consequence of a finite \( T_1 \). The spin-lattice relaxation time \( T_1 \) characterises the lifetime of a state. From uncertainty principle

\[
\Delta E \cdot T_1 \gg \hbar \\
\text{or } \Delta \omega \gg 1/T_1
\]
and shorter $T_1$ is, the more it will contribute to the line-width. In the case of tin $T_1=35$ ms. at $1^\circ K$ and its contribution to the line-width at this temperature is negligible.

The relevant contributions will now be discussed in detail.

5.1 Dipolar broadening.

The total Hamiltonian of a system having $N$ spins in a magnetic field $H_o$ is $H=H_Z+H_d$ where $H_Z$ is the main Hamiltonian representing the Zeeman energy and $H_d$ is the perturbing Hamiltonian responsible for line broadening.

$$H_d = \frac{\gamma_1 \gamma_2 h^2}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \left( \frac{\mathbf{I}_j \cdot \mathbf{I}_k}{r_{jk}^3} - \frac{3(\mathbf{I}_j \cdot \mathbf{F}_{jk})(\mathbf{F}_{jk} \cdot \mathbf{F}_{jk})}{r_{jk}^5} \right)$$

where $\mathbf{F}_{jk}$ is the radius vector joining $\mathbf{I}_j$ and $\mathbf{I}_k$. For simplicity, let us consider only two spins and omit the subscript from $r$. The dipolar Hamiltonian can now be written in a more familiar form:

$$H_d = \frac{\gamma_1 \gamma_2 h^2}{\gamma_3} (A+B+C+D+E+F)$$

where

$$A = \mathbf{I}_{1z} \mathbf{I}_{2z} (1 - 3 \cos^2 \theta)$$
$$B = \frac{1}{4} (I_{1z} I_{2z} + I_{1z} I_{1z}) (1 - 3 \cos^2 \theta)$$

$\theta$ is the polar angle describing the orientation of $\mathbf{r}$, the $z$ axis being parallel to $H_o$. $C$, $D$, $E$ and $F$ each have a similar form which can be found in a standard text on NMR.

The experimental data in NMR is expressed in terms of the rate of energy absorption vs the absorption frequency. Under the assumption of no saturation the total energy absorbed per unit time is $P = 2H_1^2 \kappa''(\omega)$, where $H_1$ is the amplitude of rf field and $\kappa''$ is the imaginary part of the rf susceptibility $\kappa' = (\kappa' + i \kappa'')$.

It is thus seen that $\kappa''$ is a good index, for a fixed $H_1$, of the power absorbed as the frequency is varied and contains all the information of the descriptive parameters in the absorption line such as line-width, shape and intensity. The expression for $\kappa''(36)$ is

$$\chi'(\omega) = \kappa \pi \omega (kT) \sum_{n,n'} \left| \langle n| \mu \gamma| n' \rangle \right|^2 \delta(E_n - E_{n'}, \omega)$$
The quantum numbers referring to the spin are \(n, n'\). Let
\[
\chi''(\omega) = \frac{\mathcal{T}_n(\omega)}{kT} \sum_{n, n'} |(n|\mu_x|n')|^2 \delta(E_n - E_{n'}) \gamma(\omega)
\]
then
\[
\chi''(\omega) = \frac{\mathcal{T}_n(\omega)}{kT} \sum_{n, n'} |(n|\mu_x|n')|^2 \delta(E_n - E_{n'}) \gamma(\omega).
\]
Since \(\chi''(\omega)\) and \(f(\omega)\) are related, a theoretical computation of \(f(\omega)\) enables one to determine \(\chi''(\omega)\) and the line shape. Use is made of the method of second moments. The \(n\)th moment is defined as
\[
\langle \Delta \omega^n \rangle = \frac{\int_0^\infty (\omega - \omega_0)^n f(\omega) d\omega}{\int_0^\infty f(\omega) d\omega}
\]
If \(n=2\), the above quantity is called the second moment. It is only necessary to retain the terms \(A\) and \(B\) in the dipolar Hamiltonian as discussed by Van Vleck. Thus
\[
H_d = \gamma \frac{\hbar^2}{2} \sum_{j<k=1}^N (A_{jk} + B_{jk}) r_{jk}^2
\]
It can be shown that
\[
\langle \Delta \omega^2 \rangle = \frac{\text{Tr}(H_d^2, \mu_x^2)}{\hbar^2 \text{Tr}(\mu_x^2)} = \frac{3}{4} \frac{\gamma^2}{\hbar^2} (I+1) \!\! \sum_{j<k} b_{jk}^2
\]
where
\[
b_{jk} = \left(\frac{1 - 3 \cos \theta_{jk}}{r_{jk}^3}\right) r_{jk}^3
\]
The summation is to be taken over the fraction \(F\) of the lattice sites occupied by spin \(I\). However, it is more convenient to sum over all \(N\) crystal sites and for second moment calculations use a restricted sum over only occupied sites which is just equal to \(F\) times the sum over all sites. Thus eqn. (5.1.3) reduces to
\[
\langle \Delta \omega^2 \rangle II = \frac{2}{25 \pi} \frac{\gamma^2}{\hbar^2} (I+1) F \Sigma b_{jk}^2
\]
If the sample contains two species of spins, denoted by primed and unprimed letters below, the total Hamiltonian is given by
\[
H = (H_z^I + H_z^{I'}) + (H_d^I + H_d^{I'I'} + H_d^{II'} + H_d^{II'})
\]
where \(H_z^I\) and \(H_z^{I'}\) are the Zeeman energies of the two spin systems \(I\) and \(I'\), \(H_d^I, H_d^{I'I'}\) are the dipolar interactions of the like nuclei and \(H_d^{II'}\) is the dipolar interaction between unlike nuclei. If the resonance of species \(I\) is under study, \(\mu_I\) represents the magnetisation of spin \(I\) system only. The
truncation of the perturbation Hamiltonian $H^{II}_{d}$ deserves special attention because its flip-flop term $B$ does not commute with the Zeeman Hamiltonian and should be dropped. The presence of the primed species gives an additional contribution to the second moment:

$$\langle \Delta \omega'^2 \rangle_{II} = \frac{1}{3} \gamma^2 I'I^2(I'+1) F' \sum_{jk} b^2_{jk} \gamma_{IJ}$$

$F'$ is the fraction of the lattice sites occupied by the primed spin system around a spin $I$. The total second moment is equal to $\langle \Delta \omega^2 \rangle_{II} + \langle \Delta \omega'^2 \rangle_{II'}$.

### 5.2 Indirect Exchange Interaction.

It has already been mentioned that the experimentally observed line-widths exceed the calculated dipolar line-width by a substantial amount for many elements. The line-widths are found to be field and temperature independent ruling out shift anisotropies and spin-lattice relaxation time effects. The conduction electrons are responsible for this behaviour. The nuclear spins are coupled together via these electrons. An electron passing through the lattice interacts with a nuclear spin and gets polarized. Moving further the same electron interacts with nuclear spins occupying different lattice sites thus coupling pairs of spins by an interaction which depends on their mutual orientations.

Computation of this indirect spin-spin interaction involves the conduction electron wave functions. The form and size of this coupling can be estimated by using second order perturbation theory.

Consider a pair of nuclear spins at the lattice sites $R_i$ and $R_j$. The spin dependent part of the nuclear-electron interaction Hamiltonian between the $i$th spin and the electron under consideration is

$$H_{i}S = \frac{8}{3} \gamma g_\beta \gamma_{ii} \vec{S}_i \cdot \vec{S}(\vec{r}_i) + 2 g_\beta \gamma_{ii} \vec{S}_i \cdot \left( \frac{\vec{S}}{r_i^3} - \frac{3}{r_i^5} \vec{r}_i \cdot (\vec{S} \cdot \vec{r}_i) \right)$$

where $\vec{r}_i = \vec{r} - \vec{R}_i$ is the radius vector from $i$th spin to the electron. The term in $\vec{L}$ has been omitted under the assumption that $\vec{L}$ is quenched. A similar
Hamiltonian can be written for the coupling between the jth spin and the same electron. Let us consider an electron-nuclear coupling \( H_{IS} \) through s-type electrons and involving spin i and j only. Then

\[
H_{IS} = \frac{8\pi}{3} g^p \gamma_i I_i \cdot \mathbf{s}(r_i) + \frac{8\pi}{3} g^p \gamma_j I_j \cdot \mathbf{s}(r_j)
\]

\[
= H_i + H_j
\]

The change in energy of the system due to the presence of \( H_{IS} \) is given by second order perturbation theory as

\[
\Delta E_{ks}^{(2)} = \sum_{k', s'} \sum_s \frac{(\psi^K|s'\rangle |H_{IS}|\psi^K\rangle (\psi^K|s\rangle |H_{IS}|\psi^K\rangle)}{E(k) - E(k')}
\]

\[
= \sum_{k', s'} \sum_s (E(k) - E(k'))^{-1} \left[ (\psi^K|s'\rangle |H_i|\psi^K\rangle (\psi^K|s\rangle |H_i|\psi^K\rangle' + (\psi^K|s'\rangle |H_j|\psi^K\rangle (\psi^K|s\rangle |H_j|\psi^K\rangle) \right] - 5.2.3
\]

The summation is over all the excited states \( k' \) and the two spin orientations \( s' \). \( \psi^K \) is the product of Bloch function and spin operator. The interest lies in the cross terms as the i\( \text{th} \) spin causes a transition of the electron to an intermediate excited state and spin j brings it back to the ground state.

Writing \( H_i \) and \( H_j \) explicitly we have

\[
\Delta E_{ks}^{(2)} = C \sum_{k', s'} \sum_s \frac{(\psi^K|s'\rangle \mathbf{s}(r_i) \psi^K\rangle (\psi^K|s\rangle \mathbf{s}(r_j) \psi^K\rangle)}{E(k) - E(k')}. \quad 5.2.3
\]

where \( C = \frac{64\pi^2}{9} \gamma_i \gamma_j \tau^4 \).

The energy \( \Delta E^{(2)} \) is what will be found as the first order contribution of an extra term \( H_{ex}^{ij} \), in the nuclear Hamiltonian, given by (5.1.1). To evaluate the total energy because of spin i and j, the summation over all initially occupied states \( k, s \) has to be performed. We therefore have

\[
H_{ex}^{ij} = C \sum_{k, s} \sum_{k', s'} \frac{\psi^K^i|s'\rangle \mathbf{s}(r_i) \psi^K\rangle (\psi^K|s\rangle \mathbf{s}(r_j) \psi^K\rangle)}{E(k) - E(k')}. \quad 5.2.3
\]

Let \( p(k, s) \) be defined as the probability, where \( p(k, s) = 1 \) if state \( k, s \) is occupied, zero otherwise. Then the restriction from the summation can easily be removed. \( H_{ex}^{ij} \) must be averaged over an ensemble to take into account its variation with the temperature of the electrons. This can be done by replacing
\[ i_{ij} = C \sum_{k,s,k',s'} \frac{(\psi_k f(k,s') | S(k') | \psi_{k,s}) (\psi_k f(k,s) | S(k') | \psi_{k,s'}) f(k,s) (1 - f(k',s'))}{E(k,s) - E(k',s')} \cdot \bar{I}_j \]

The Fermi levels of spin up and spin down distributions coincide. At absolute zero all the energy states \( E_{k,s} \) up to the Fermi level are occupied and all the \( E_{k',s'} \) above the Fermi level are unoccupied. The matrix elements of the delta-functions vary slowly with energy which makes the dependence of \( H_{ex}^{ij} \) on the electron spin energy very small. Thus to a good approximation the energy of the electron spin coordinate can be omitted and eqn. (5.2.4) may be written in a form as if the magnetic field were absent:

\[ H_{ex}^{ij} = C \frac{1}{2} \bar{I}_i \cdot \bar{I}_j \left( \sum_{k,k'} \frac{(\psi_k | S(k') | \psi_{k'}) (\psi_k | S(k') | \psi_{k'}) f(k,s) (1 - f(k',s'))}{E(k) - E(k')} \right) \]

where the factor \( \frac{1}{2} \) appears as a result of summation over \( s \) and \( s' \) for \( S=1/2 \).

It is seen that \( H_{ex}^{ij} \) has a scalar form

\[ H_{ex}^{ij} = \mathcal{H}_{ij} \bar{I}_i \bar{I}_j \]

\( J \) is known as the exchange constant and is independent of spin. In order to simplify the computation of \( J \) various assumptions have to be made. Assuming spherical energy surfaces, an effective electron mass \( m^* \) one gets for \( J_{ij} \)

\[ J_{ij} = \frac{2}{9 \pi} \gamma_e^2 \gamma_{Ii} \gamma_{Ij} m^* |U_{kF}(0)|^4 \left( \frac{2k_F \cos 2k_F a - \sin 2k_F a}{R^4} \right) \]

The exchange Hamiltonian with two magnetic ingredients is

\[ H_{ex} = \sum_{i>j} \mathcal{H}_{ij} \bar{I}_i \bar{I}_j + \sum_{k \neq i,j} \mathcal{H}_{k} \bar{I}_k \bar{I}_k + \sum_{j,k} \mathcal{H}_{jk} \bar{I}_j \bar{I}_k \]

where the exchange interaction has been separated into pairs of unprimed and primed variety alone and into mixed pair.

The total Hamiltonian for the system is now \( H = H_0 + H_d + H_{ex} \) where \( H_{ex} \) is
given by (5.2.5)

(a) Exchange interaction and the second moment:

The second moment of spin system I is

$$\langle \Delta \gamma \rangle = \frac{\text{Tr}(H_d^2 + H_{ex}, \mu_x^2)}{\text{Tr}(\mu_x^2)}$$

(i) If no primed ingredient were present then $H_{ex} = \sum_{j>l}^n \gamma J_{ij} I_i I_j$ and $H_{ex}$ and $\mu_x$ commute. Thus the presence of the exchange interaction does not change the second moment and it is still given by eqn. (5.1.4).

(ii) However if the primed ingredient is present then the cross term in $H_{ex}$ does not commute with $\mu_x$. As a consequence there is a net contribution to the second moment and the total second moment is

$$\langle \Delta \gamma \rangle = \left( \frac{3}{4} \gamma_I^2 \sum b_{1j}, + \frac{1}{3} I^2 \gamma_I' \sum J_{ik}' \right)$$

Neglecting the cross terms, the fourth moment is given by

$$\langle \Delta \omega^4 \rangle = \frac{\text{Tr}(H_d^4 + H_{ex}, (H_d^4, \mu_x^2))}{\text{Tr}(\mu_x^2)}$$

In the computation of the fourth moment, even if the primed variety is absent, $H_{ex}$ does not commute with $(H_d^4, \mu_x)$ and cannot be dropped. As a result it increases the fourth moment to an extent which depends upon J. Thus the presence of exchange coupling changes the line shape in such a way that the second moment remains unaffected while the fourth moment is increased. The resulting line is narrower, has a sharper peak and enhanced wings. The centre of the line has only a small effect on any of the moments. The fourth moment is more heavily weighted by the wings as compared to the second moment as a result $\langle \Delta \omega^4 \rangle$ is increased keeping $\langle \omega \rangle$ constant. This is known as exchange narrowing. According to Anderson-Weiss model (41), which has been verified, when $J > \text{half line-width}$, the resonance curve is Lorentzian with a cut off at $|\omega - \omega_0| \sim J$ which keeps the moments finite.
If more than one species of nuclei is present, then the second moment is increased, as already discussed, as well as the fourth moment. Thus roughly speaking, the exchange interaction between like nuclei narrows the line while that between unlike nuclei broadens it.

5.3 Pseudo-dipolar broadening.

While considering the coupling between two nuclei via the conduction electrons in the last section, the change in energy due to non-s electrons was neglected. The interaction Hamiltonian between an electron and nuclear spins i and j are again written below for the reader's convenience:

\[ H_{ij} = \frac{8}{3} \gamma_1 I_i \cdot S \cdot \mathbf{r}_i + 2 \gamma_1 I_i \cdot (S-3 \cdot \mathbf{r}_i \cdot (S \cdot \mathbf{r}_i) \cdot r_i) \cdot r_i \]

\[ = H_{i1} + H_{i2} \]

5.3.1a

Similarly

\[ H_{ij} = H_{j1} + H_{j2} \]

5.3.2b

The coupling energy between spin i and j is given by

\[ H_{IS} = (H_{i1} + H_{j1}) + (H_{i2} + H_{j2}) \]

\[ = H_1 + H_2 \]

where \( H_1 \) represents the sum of contact terms and \( H_2 \) the sum of dipolar terms.

The change in the energy of the system due to the presence of \( H_{IS} \) is given by second order perturbation theory as:

\[ E_{KS}^{(2)} = \sum_{K,s} \left( \frac{\langle \Psi_{K,s}^+ | H_1 + H_2 | \Psi_{K,s} \rangle \langle \Psi_{K,s}^+ | H_1 + H_2 | \Psi_{K,s}' \rangle}{E(K) - E(K')} \right) \]

\[ E_{KS}^{(2)} \]

can be separated into three parts

\[ a_1 = \sum_{K,s} \left( \frac{\langle \Psi_{K,s}^+ | H_1 | \Psi_{K,s} \rangle \langle \Psi_{K,s}^+ | H_1 | \Psi_{K,s}' \rangle}{E(K) - E(K')} \right) \]

\[ a_2 = \sum_{K,s} \left( \frac{\langle \Psi_{K,s}^+ | H_1 | \Psi_{K,s} \rangle \langle \Psi_{K,s} | H_2 | \Psi_{K,s}' \rangle + \langle \Psi_{K,s}' | H_2 | \Psi_{K,s} \rangle \langle \Psi_{K,s} | H_1 | \Psi_{K,s}' \rangle}{E(K) - E(K')} \right) \]

\[ a_3 = \sum_{K,s} \left( \frac{\langle \Psi_{K,s}^+ | H_2 | \Psi_{K,s} \rangle \langle \Psi_{K,s} | H_2 | \Psi_{K,s}' \rangle}{E(K) - E(K')} \right) \]

where \( E_{KS}^{(2)} = a_1 + a_2 + a_3 \).
The term (5.3.2a) has already been considered in the last section. The result indicated that $a_1$ could be calculated by adding a term $H_{\text{ex}}$ to the Hamiltonian. If one carries out a computation of $a_2$, which is the term of interest here, using the technique of the last section, it is found that $a_2$ can be taken into account by adding a term $H_{\text{pseudo-dip.}}$ to the Hamiltonian, where $H_{\text{p.d.}}$ has the form

$$H_{\text{p.d.}}^{ij} = (I_i^j - 3(I_i^j I_j^i - 3\alpha^2 I_{ij}^2) \alpha_{ij}^2)$$  \hspace{1cm} 5.3.3

The contribution of the contact term to the line-width, treated in the last section, is much larger than the pseudo-dipolar contribution. The contribution, $a_3$, which is quadratic in the dipolar Hamiltonian will be still smaller and can be neglected.

$\widetilde{B}_{ij}$ represents the pseudo-dipolar interaction constant and is a complicated function. It is zero for s-type electron wave functions and varies as $r_{ij}^{-3}$ for large $r_{ij}$. (5.3.3) has the same form as the dipolar Hamiltonian.

The total second moment, including all the interactions, for the resonance of unprimed species is given by (6)

$$\langle \delta \omega \rangle = \frac{5}{4} I (I+1) \frac{\hbar^2}{I_1} \sum_j B^2_{ij} + \frac{1}{3} I'(I'+1) \frac{h^2}{I_1} \sum_{1k} C^2_{1k},$$  \hspace{1cm} 5.3.4

where

$$B^2_{ij} = (\widetilde{B}_{ij} + g^2 \rho^2 r_{ij}^{-3}) b_{ij} r_{ij}$$

and

$$C_{1k} = \alpha_{1k} + (\widetilde{B}_{ik} + g g' \rho^2 r_{ik}^{-3}) b_{ik} r_{ik}^{-3}$$

Since $\widetilde{B}_{ij}$ and $g^2 \rho^2 r_{ij}^{-3}$ have the same dimensions, we can write $B^*$ as follows:

$$B^*_{ij} = (1 + B_{ij}) \gamma_{iij}^2 b_{ij}$$

and

$$C_{1k} = \alpha_{1k} + (1 + B_{ik}) \gamma_{iik}^2 b_{ik}.$$  \hspace{1cm} 5.3.5

For isotopically pure tin the second moment is,

$$\langle \delta \omega \rangle = \frac{3}{4} I(I+1) \frac{\hbar^2}{I_1} \sum_j (1 + B_{ij})^2 b_{ij}^2$$

This expression can also be written in the form (8) (Appendix A).

$$\langle \delta \omega \rangle = (A' \cos 4 \Theta + D') (1 - 2 \cos 2 \Theta) + E' \cos 2 \Theta \sin 2 \Theta + F' (3 \cos 2 \Theta - 1)$$  \hspace{1cm} 5.3.6
In the theoretical calculation of the second moment, so far, it has been assumed that the resonance frequency \( \omega_0 \) is exactly known. In the case of metal single crystal resonance this is not true. The reason is that the observed signal, \( f(\omega) \), is a mixture of modes i.e. \( f(\omega) = \chi''(\omega) + b \chi'(\omega) \) where \( \chi' \) and \( \chi'' \) are real and imaginary parts of the complex rf susceptibility and \( b \) is the fractional contribution of \( \chi' \). In a constant external magnetic field the observed resonance frequency is lower than \( \omega_0 \) by \( 1/3 \)rd of the line-width for equal mixture. If the line shape of the observed signal is known then the calculation of \( \omega_0 \) is straight forward. For unknown line shapes some approximation has to be made i.e. a fraction of the line-width has to be added to the observed resonance frequency. This may not give exactly \( \omega_0 \) and may be in error by \( \Delta \).

Let us examine how the experimental second moment will be affected by an error \( \Delta \) in \( \omega_0 \). The second moment in this case is

\[
\langle \Delta \omega^2 \rangle = \int (\omega - \omega_0 + \Delta)^2 f(\omega) d\omega
\]

where \( \int f(\omega) d\omega = 1 \)

\[
= \int (\omega - \omega_0)^2 f(\omega) d\omega + 2\Delta \int (\omega - \omega_0) f(\omega) d\omega + \Delta^2.
\]

\[
= M_2 + 2bM_1^2 + \Delta^2
\]

where \( M_2 \) is the required second moment. If \( \langle \omega^2 \rangle \) is computed for two known corrections which result in errors of \( \Delta_1 \) and \( \Delta_2 \) then

\[
\langle \Delta \omega^2 \rangle - \langle \omega^2 \rangle^2 = 2bM_1(\Delta_1 - \Delta_2) + (\Delta_1^2 - \Delta_2^2) = 2bM_1(\Delta_1 - \Delta_2).
\]

as \( (\Delta_1^2 - \Delta_2^2) \) is negligible. The left hand side is known and the \% error due to uncertainty in \( \omega_0 \) can be estimated.

Experimental computation of the second moment:

In the theory the second moment is calculated for \( f(\nu - \nu_0) \) while experimentally it's derivative is recorded and the second moment calculated from it. It can be shown that
\[ \langle \delta \mu^2 \rangle = \frac{\int (\nu - \nu_0)^2 f(\nu - \nu_0) d(\nu - \nu_0)}{\int f(\nu - \nu_0) d(\nu - \nu_0)} \]

\[ = \frac{1}{3} \frac{\int (\nu - \nu_0)^3 f'(\nu - \nu_0) d(\nu - \nu_0)}{\int f'(\nu - \nu_0) d(\nu - \nu_0)} \]

The above expression contains the derivative \( f'(\nu - \nu_0) \) which can be expressed in arbitrary units. For discrete frequency values

\[ \langle \delta \mu^2 \rangle = \frac{1}{3} \frac{\sum (\nu - \nu_0)^3 f'(\nu - \nu_0)}{\sum (\nu - \nu_0) f'(\nu - \nu_0)} . \]
CHAPTER VI

RESULTS AND DISCUSSION

Isotopically Pure Tin.

Figures 15 and 16 show the line-widths at the maximum slope \((\delta\nu)_{m.s.l.}\) at helium temperature as a function of crystal orientation with respect to the applied magnetic field. The line is Lorentzian in the centre and the cut off frequency \(J > (\delta\nu)_{m.s.l.}\). In order to set an experimental limit on \(J\), first the signal was observed with a small modulation amplitude. This enabled the evaluation of the correct resonance frequency. Keeping the crystal orientation fixed, the modulation amplitude was increased by more than the line-width. With increased modulation the signal could be seen, in the wings, 10 kc/s away from the centre of resonance after which it disappeared into the noise. Thus it is concluded that the cut off frequency \(J > 10\) kc/s. This sets an experimental lower limit on \(J\).

Line-width measurements were also made at room temperature with a modulation amplitude smaller than a sixth of the line-width. The data obtained combined with the helium temperature line-widths leads to the evaluation of the spin-lattice relaxation time at room temperature, as a function of crystal orientation.

Natural Tin.

Figure 17 shows the line-widths, in Sn\(^{119}\) isotope, in the basal plane. Measurements were also made 10° off the (001) axis. The signals recorded have been used in the computation of the second moments. The factor \(\sum_{J}^{} b_{ij}^2\) appearing in the second moment expression has been calculated for 21 shells. The results are shown in figures 18 and 19. The second moment results are shown in table 1.
Figure 15. The Line Width of the Isotopically Pure Sn$^{119}$ Resonance as a Function of Crystal Orientation.
Figure 16. The line Width of the Isotopically Pure Sn$^{119}$ in the Basal Plane.
Figure 17. The Line Width of Sn$^{119}$ in Natural Tin in the Basal Plane.
Figure 18. Plots of $\sum_{j}(1-3\cos^2\theta_{ij})^{2-6}r_{ij}$ vs. $\theta$ for Various Values of $\Phi$. 
Figure 19. Plot of $\sum (1 - 3\cos^2 \theta_{ij}) \sqrt{r_{ij}^6}$ vs. $\phi$ (in the Basal Plane).
Table 1.
The Second Moments

<table>
<thead>
<tr>
<th>Direction of $H_0$</th>
<th>Second Moment (Kc/s)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^\circ$ of (001)</td>
<td>3.9±0.4</td>
</tr>
<tr>
<td>(100)</td>
<td>3.7±0.4</td>
</tr>
<tr>
<td>(110)</td>
<td>1.2±0.1</td>
</tr>
</tbody>
</table>

It should be emphasized that these are lower limits of the second moments. This is because the wings can not be observed with a low modulation. If the modulation amplitude is too large, the signal recorded is not proportional to the slope of the absorption curve. Instead, the line is broadened resulting in an exaggerated second moment.

Discussion:

It has been observed that the line is Lorentzian in the centre and that the cut off frequency $J>>(|\nu-\nu_0|)$. It appears that we are observing extreme exchange narrowed lines to which the Anderson-Weiss model can be applied. According to this model the line is Lorentzian with a cut off $|\nu-\nu_0|\sim J$ which keeps the moments finite, and the second moment is proportional to the line-width. In order to examine whether the line is really exchange narrowed a further check was made by using the expression (5.3.6). The experimental line-widths along (001), (100), (110) and $\theta=75^\circ$, $\phi=25^\circ$ were used to evaluate the parameters $A'$, $D'$, $E'$ and $F'$. The values thus obtained were used in the calculation of the line-widths as a function of $\theta$ and $\phi$. The theoretical results are shown in figures 15 and 16 by the solid line together with the experimental $(|\nu|)_{m.s1}$. The excellent agreement between the two establishes that we are
indeed observing extreme exchange narrowing. According to the Anderson-Weiss model (Abragam pp. 107)
\[
\langle \delta^2 \rangle = \frac{2J^2}{\pi}
\]
where \( \delta \) is the half width at half intensity. For a Lorentzian line
\[
(2\delta) = \sqrt{3} (\delta^2)_{\text{m.s.l.}} \quad \text{and}
\]
\[
\langle \delta^2 \rangle = \frac{\sqrt{3}}{\pi} J (\delta^2)_{\text{m.s.l.}}.
\]

Theoretically the second moment in isotopically pure tin is given by (5.3.6) or alternately by,
\[
\langle \delta^2 \rangle = C \sum_j \left( 1 + B_{ij} \right) b_{ij}^2 = \frac{\sqrt{3}}{\pi} J (\delta^2)_{\text{m.s.l.}}.
\]
where \( C = \frac{3}{4} I (1+1) K^2 Y \)

\[
K \sum_j (1+B_{ij})^2 b_{ij}^2 = (\delta^2)_{\text{m.s.l.}}.
\]

The next step was to evaluate the relative pseudo-dipolar contributions, \( (1+B_{ij})^2 \), from various shells. Eqn. 5.3.6 contains only four independent variables which suggests that we can not form a set of more than four linearly independent eqns. out of system (ii). Since the second moment, eqn. (ii), can be described by only four variables, it was assumed that the values of \( B_{ij} \) for the first three shells are different from each other and that the values from the remaining shells are equal to a constant. Under this approximation eqn. (ii) can be written as
\[
K(1+B_{11})^2 \sum_1 b_{11}^2 + K(1+B_{12})^2 \sum_2 b_{12}^2 + K(1+B_{13})^2 \sum_3 b_{13}^2 + K(1+B_{1i})^2 \sum_{\text{rest}} b_{1i}^2 = (\delta^2)_{\text{m.s.l.}}.
\]

The experimental line-widths along (001), (100), (110) and \( \Theta = 54.7356^\circ \), \( \Phi = 25^\circ \) with appropriate values of \( \sum b_{ij}^2 \) were used to form a set of four linearly independent eqns. Solution of these equations gave the relative contributions from the various shells. The results obtained are summarized in table 2.

<table>
<thead>
<tr>
<th>( (1+B_{11})^2 )</th>
<th>( (1+B_{12})^2 )</th>
<th>( (1+B_{13})^2 )</th>
<th>( (1+B_{1i})^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>0.83</td>
<td>1.19</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Table 2.
The relative contributions from various shells.
These values were later used in the computation of the line-widths for all Θ's and φ's. The results plotted in figures 15 and 16 are in excellent agreement with the experimental values.

This is the first time these contributions have been evaluated.

An attempt was also made to evaluate the relative contributions by assuming that the values of $B_{ij}$ for the first two shells are different and those from the third shell, inclusive, onwards are all equal. The results thus obtained gave line-widths which were in marked disagreement with the experimental results.

A lower limit on the relative contributions and $\tilde{B}_{ij} = B_{ij} \frac{r^3}{k_F}$ can be set by using the experimental value for $J$, i.e. $J > 10$ kc/s. The results are tabulated in table 3. Let us assume the radial dependence of $\tilde{B}_{ij}$ is of the same form as that of $J_{ij}$. A rough estimate may be made of the contributions of the different shells to $J_{ij}$ by calculating $\tilde{J}_{ij}$ for the much simpler case of the spherical Fermi surface where $k_F$ is given by $E_F = \frac{\hbar^2 k_F^2}{2m^*}$. In place of a theory more appropriate to tin we shall use this expression to find $k_F$ from the following values: $m^* = 0.5m_e$ and $E_F = 0.370$ Rydberg (Phys. Rev. 149, 504 (1966)). This gives $k_F = 1.336 \times 10^8$ cm$^{-1}$. The radial dependence of $J_{ij}$ obtained from this value of $k_F$, as well as that of $\tilde{B}_{ij}$, is plotted in figure 20.

Table 3.

<table>
<thead>
<tr>
<th></th>
<th>$(1+B_{i1})^2$</th>
<th>$(1+B_{i2})^2$</th>
<th>$(1+B_{i3})^2$</th>
<th>$(1+B_i)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.80</td>
<td>4.56</td>
<td>6.59</td>
<td>4.89</td>
</tr>
</tbody>
</table>

Natural Tin.

In the computation of the experimental second moment, the observed resonance frequency has to be corrected by adding a fraction of the line-width to it. The fraction of the line-width to be added is determined by, the
fraction of mixture of $\gamma'$. 'b' can vary from $\frac{1}{3}$ to 1 depending whether the skin depth is anomalous or normal at helium temperature. The peak-to-peak ratio of the derivative for the normal skin depth is .55 and .39 for Gaussian and Lorentzian lines respectively whereas for the anomalous skin depth it is .66 and .535. We may deduce that the line is not Gaussian since the experimental second moments are approximately $2(\delta\nu)^2$, where $(\delta\nu)$ is the line-width, whereas a Gaussian line has a second moment $\pi(\delta\nu^2)/4$. Curve fitting using a Lorentzian function was tried but a good fit was not obtained even between the peaks of the derivative. The experimental peak-to-peak ratio is .53 and is the same for all orientations. This implies (i) that the line shape is not changing as a function of crystal orientation and (ii) that the skin depth is neither completely normal nor completely anomalous at helium temperatures. The true resonance frequency is related to the observed zero derivative by a correction of $(\delta\nu/3)$ for the normal case and $(\delta\nu/5)$ for the anomalous case. A correction of $(\delta\nu/4)$ was considered reasonable in this analysis.

In order to estimate the size of the error involved in an incorrect determination of $\omega$, the second moments were calculated using $(\delta\nu/5)$ and $(\delta\nu/6)$ as correction factors. Since the correction term $2bM_1\Delta$ is linear in $\Delta$, the difference between the two values gives the error due to a frequency error of $(\delta\nu/\omega)$. The results are shown in table 4 together with the percentage error arising from a frequency error of $(\delta\nu/3\omega)$ which would seem to be the absolute maximum possible error in the experiment. The errors quoted in table 1 are due to the probable errors in $\omega$.

<table>
<thead>
<tr>
<th>Direction of $H_0$</th>
<th>$&lt;\delta\nu&gt;_1$</th>
<th>$&lt;\delta\nu&gt;_2$</th>
<th>$&lt;\delta\nu&gt;_1 - &lt;\delta\nu&gt;_2$</th>
<th>$2bM_1 (\delta\nu)$</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>10° off (001)</td>
<td>3.733</td>
<td>3.711</td>
<td>0.022</td>
<td>0.066</td>
<td>2%</td>
</tr>
<tr>
<td>(100)</td>
<td>3.612</td>
<td>3.553</td>
<td>0.059</td>
<td>0.177</td>
<td>5%</td>
</tr>
<tr>
<td>(110)</td>
<td>1.100</td>
<td>0.968</td>
<td>0.032</td>
<td>0.096</td>
<td>9%</td>
</tr>
</tbody>
</table>

Table 4.
Numbers on the points indicate the shell number.

- $\bullet k_F = 1.35 \times 10^8 \text{ cm}^{-1}$
- $\circ k_F = 1.336 \times 10^8 \text{ cm}^{-1}$

$\approx_{\tilde{B}_{ij}}$ and $J_{ij}$ vs. $R_{ij}$
It is clear from table 4 that the upper limit in the error caused by using an
incorrect resonance frequency is around 9%. As the second moment is heavily
weighted by the wings, the inability of seeing the signal in the wings is like­
ly to cause much more error than this.

Making use of the technique which gave rise to the expression (5.3.6), the
second moment for natural tin can be written as

\[ -\frac{1}{\pi} \left( F + \frac{4}{3} F' \right) J(\delta \nu) \text{m.s.l.} + G'(3 \cos^2 \theta - 1) + 0.01917 \sum J_{ik}^2 = \langle \delta \nu^2 \rangle_{\text{expt.}} \]

where \( G' \) is a constant like \( F' \) in eqn (5.3.6). \( (\delta \nu) \text{m.s.l.} \) is known for \( \theta \) and \( \phi \). In principle it is possible to evaluate \( J, B, \) and \( \sum J_{ik}^2 \), using the experi­
mental second moments along three independent directions. Having found these
values, one can go back to the expression (5.3.5) and deduce the value of the
cross term in \( J \) and \( (1+B) \). However, as already stated, the present experimental
second moments are the lower limits only and using them reasonable values for
these parameters could not be estimated. The results even give a negative value
for \( \sum J_{ik}^2 \). It is felt that one may have to use some signal averaging device
in order to see the signal in the wings and get more accurate values of the
second moments. One of the best directions for the second moment calculation
would be \( \theta = \cos^{-1}(1/3) \), where \( \theta \) is measured from (001) direction. This would
eliminate the cross term contribution. It should be emphasized that with
sufficient accuracy in the second moments all the parameters can be determined
and should give useful information on the radial dependence of both \( J \) and \( B \).

Karimov and Schegolev (18) made measurements on the line-width in white
tin powder and compared the results with the calculated dipolar moments. They
obtained \( J = 2.5 \pm 0.1 \text{kc/s} \).

Spin-lattice relaxation time, \( T_1 \).

For a Lorentzian line the line-width is given by the expression

\[ T_{2}^{-1} = \sqrt{3} \pi (\delta \nu) \text{m.s.l.} \]  

This is true if there is no contribution to the line-width
because of \( T_1 \). However in presence of \( T_1 \) contributions, the line-width is des-
scribed by a $T_2$ as below:

$$T_2^{-1} = T_2^{-1} + T_1^{-1}$$

where $T_2'$ is the spin-spin contribution and $T_1$ is the spin-lattice contribution. From these, $T_1$ at a given temperature $T^0K$ can be worked out. It is equal to

$$T_1^{-1} = \frac{1}{3} \pi (\delta \nu' - \delta \nu)$$

where $(\delta \nu')$ is the line-width which includes $T_1$ contribution.

In case of isotopically pure tin the line is Lorentzian until well away from the centre at helium and higher temperatures. There is no appreciable contribution to $(\delta \nu)$ due to $T_1$, at helium temperature. Thus combining the line-width data at helium and room temperatures, $T_1$ at room temperature has been worked out. Results of helium and room temperature are summarized below.

Table 5.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Temperature °K</th>
<th>$(\delta \nu)$ in kc/s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>1</td>
<td>1.42</td>
</tr>
<tr>
<td>(001)</td>
<td>294</td>
<td>2.96</td>
</tr>
<tr>
<td>⊥ to (001)</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>⊥ to (001)</td>
<td>294</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Combining these results the following values for $T_1$ at room temperature, 294 °K, have been obtained.

$$T_1T \text{ along (001)} = 36 \pm 2 \text{ m. sec. °K} \quad \text{and}$$

$$T_1T \text{ ⊥ to (001)} = 37 \pm 2 \text{ m. sec. °K}.$$

It is known that $T_1T$ at 1°K = 35 m sec. °K. Present results indicate that $T_1T$ is constant over the temperature range and closely isotropic.
Suggestions for further experiments

a. Recently experiments on pressure dependence of the Knight shift at room temperature have been done on tin and cadmium powder specimens. The limitation of the powder technique in accuracy as well as the fact that the data are available only at room temperature is limiting the possibility of deriving general conclusions regarding the model proposed by Benedek & Kushida.

The most obvious experiments to try are the pressure dependence of the Knight shift on single crystals of tin and cadmium at various constant temperatures ranging from 77 K to just below the melting point. The results thus obtained would give dependable information (i) regarding the contribution of volume effects to the Knight shift and (ii) the effect of change in c/a ratio on the anisotropy at constant temperature.

The results obtained from these experiments combined with the present results would give explicit temperature dependence of the Knight shift over the whole temperature range. The calculation of the expression \( \left( \frac{\partial P_e}{\partial (V/V_0)} \right)^2 \) as a function of temperature will be a straight forward operation.

The results would also give us the contribution of volume effects on anisotropy over the entire range of temperature. One should be able to determine whether (i) the variation of anisotropy with temperature is purely due to change in c/a ratio, (ii) it is explicitly a temperature dependent phenomenon or (iii) it is a combined effect of the two. If it is found that the variation of anisotropy with temperature is due to both the phenomena then the contributions can be sorted out. The advantage of these experiments over others lies in the fact that all the information available would be accurate and dependable hence conclusive over the entire temp. range.

b. The variation of the Knight shift in Cd between 77 K & 195 K is not exactly known. An expected variation is shown by a dotted line in figure 4. Measurements in this range will resolve the ambiguity.
SECOND MOMENT IN ISOTOPICALLY PURE TIN AS A FUNCTION OF ORIENTATION

The second moment in isotopically pure tin can be written as,

\[
\langle \Delta \omega \rangle = \frac{2}{4} \left\{ \frac{1}{N} \sum_{i,j} \left( g^2 r_{ij}^2 + B_{ij} \right)^2 \right\} (3 \cos^2 \Theta_{ij} - 1)
\]

where \( N \) is a constant having the dimensions of frequency, the index \( i \) runs over the \( p \) non-equivalent sites (\( p = 2 \) in Sn), \( N \) = total number of spins in the crystal and \( r_{ij} \) is the distance between \( i \) and \( j \)th spin in reduced units, i.e. \( r_{ij} = r_{ij} / a \), 
\( \Theta_{ij} \) is the angle between \( r_{ij} \) and \( H_0 \). \( b_{ij} \) is a measure of the pseudo-dipolar interaction in units of \( ( \gamma \alpha^2 / a^3 ) \). Eqn. (i) can be re-written as follows:

\[
\langle \Delta \omega \rangle = \frac{-2}{4} \left\{ \frac{1}{N} \sum_{i,j} \left( 1 + b_{ij} \right) \right\} \left( \frac{r_{ij}^2}{r_{ij}^2} \right) \left( P_2 (\cos \Theta_{ij}) \right)^2
\]

where \( \Theta_{ij} = \frac{1}{4} \sum_{i,j} \left( 1 + b_{ij} \right) \left( r_{ij}^2 / r_{ij}^2 \right) \left( P_2 (\cos \Theta_{ij}) \right)^2 \)

We refer the applied field \( H_0 \) and \( r_{ij} \) to a coordinate system \((X_C,Y_C,Z_C)\) fixed with respect to the crystal. \( X_C, Y_C, Z_C \) are chosen along \((100), (010) \) and \((001)\) respectively. The three axes are mutually perpendicular.

Using the addition theorem for the spherical harmonics

\[
P_2 (\cos \Theta_{ij}) = \frac{2}{5} \sum_{m=-2}^{2} Y_{2m} \left( \Theta_{ij}, \Phi_{ij} \right) Y_{2m}^* \left( \Theta, \Phi \right)
\]

Substituting (iii) in (ii) we obtain

\[
\langle \Delta \omega \rangle = \left\{ \frac{2}{N} \right\} \sum_{i,j} \sum_{m=-2}^{2} \left( \Theta_{ij}^C, \Phi_{ij}^C \right) Y_{2m} \left( \Theta_{ij}, \Phi_{ij} \right) Y_{2m}^* \left( \Theta, \Phi \right) (iv)
\]

The crystal has reflection symmetry in the XZ and YZ planes. Reflection in the XZ plane means that for atom \( j \), there is another atom \( j' \) which has 
\( \Theta_{ij} = \Theta_{ij}' \), \( \Phi_{ij} = \Phi_{ij}' \) and \( \Phi_{ij} = \Phi_{ij}' \). Reflection in the YZ plane means that for
each atom \( j \) there is another atom \( j'' \) which has \( \mathcal{C}_{ij} = \mathcal{C}_{ij}' \), \( \theta_{ij}^c = \theta_{ij}^{c'} \) and \( \phi_{ij}^c = \pi - \phi_{ij}^c \). Since both symmetry operations hold, for each atom \( j \) there is an atom \( j''' \) which has

\[
\mathcal{A}_{ij} = \mathcal{A}_{ij}''' \quad \theta_{ij}^c = \theta_{ij}^{c''} \text{ and } \phi_{ij}^c = \pi + \phi_{ij}^c
\]

It is clear that the sum over \( j \) in eqn. (iv), for the above symmetry, involves terms of the following type for a fixed \( m, m' \)

\[
f_{mm'} = e^{i(m+m')\phi_{ij}^c} + e^{-i(m+m')\phi_{ij}^c} + e^{i(m+m')\pi} (e^{i(m+m')}\phi_{ij}^c - e^{-i(m+m')}\phi_{ij}^c)
\]

All terms with \( m+m' \) = odd are zero.

Now eqn. (iv) may be re-written, keeping only terms in which \( m+m' \) is even.

\[
\langle \omega \rangle = \frac{2\pi}{p} \sum_{n} \frac{4\pi}{5} \sum_{n=1}^{N} \sum_{j=1}^{\infty} \mathcal{A}_{ij} \sum_{m,m',m''} P_{2m} \theta_{ij}^c P_{2m'} \cos(m+m') \phi_{ij}^c e^{-i(m+m')\pi} (e^{i(m+m')}\phi_{ij}^c - e^{-i(m+m')}\phi_{ij}^c)
\]

The sum means that only \( m+m' \) even terms are kept.

Writing (v) explicitly we get

\[
\langle \omega^2 \rangle = \frac{2\pi}{p} \frac{4\pi}{5} \left( A (P_{22}(\theta))^2 \cos 4\phi + B P_{20}(\theta) P_{22}(\theta) \cos 2\phi + C (P_{21}(\theta))^2 \cos 2\phi \right)
\]

\[
+ D (P_{22}(\theta))^2 + E (P_{21}(\theta))^2 + F (P_{20}(\theta))^2
\]

where \( A = \frac{1}{p} \sum_{j=1}^{N} \mathcal{A}_{ij} A_{ij} \), etc.

\[
A_{ij} = (P_{22}(\theta_{ij}^c))^2 \cos 4\phi_{ij}^c
\]

\[
B_{ij} = 2P_{20}(\theta_{ij}^c)P_{22}(\theta_{ij}^c) \cos 2\phi_{ij}^c
\]

\[
C_{ij} = (P_{21}(\theta_{ij}^c))^2 \cos 2\phi_{ij}^c
\]

\[
D_{ij} = (P_{22}(\theta_{ij}^c))^2
\]

\[
E_{ij} = (P_{21}(\theta_{ij}^c))^2
\]

\[
F_{ij} = (P_{20}(\theta_{ij}^c))^2
\]

For tetragonal symmetry \( B = C = 0 \).
APPENDIX B

DETERMINATION OF THE CORRECT RESONANCE FREQUENCY IN TIN

Bloembergen \(^{(29)}\) has shown that in case of a conductor, with dimensions much larger than the r.f. skin depth, the observable absorption line shape is determined by both the real and imaginary parts of the nuclear rf susceptibility. The observed line shape function can then be represented by the expression

\[ f(\omega) = \chi'(\omega) + \chi''(\omega) \]  

(1)

where \(\chi'\) and \(\chi''\) are the real and imaginary parts of the r.f. susceptibility and 'a' is the mixing parameter.

The experimentally observed signal is the derivative of \(f(\omega)\). If there was no contribution from \(\chi'\), the zero of the derivative would correspond to the resonance frequency. The contribution due to \(\chi''\) makes the line asymmetric and now the zero of the derivative does not correspond to the correct resonance frequency\(^{(16)}\). In order to have a correct knowledge of the Knight shift parameters the knowledge of exact resonance frequency is essential.

In case of isotopically pure tin, it has been established that the line is Lorentzian until well away from the centre frequency. This fact immediately gives us the forms of \(\chi'\) and \(\chi''\) in eqn. (1) and the observed function can be represented by the expression

\[ y = \frac{df(\omega)}{d\omega} = K \left( \frac{\Delta^2 - (\delta\omega)^2}{\Delta^2 + (\delta\omega)^2} \right) \]  

(2)

where \(\Delta = (1/T_2)\), \(\delta\omega = \omega - \omega_0\), \(b = a^{-1}\) and \(K\) contains all the constants of the expression.

Our main interest lies in the evaluation of correct values of \(\Delta\), which gives us the line width, and \(\omega_0\), the resonance frequency. Expression (2) can be written as

\[ y_1 = f(\delta\omega, \omega_0) \]

where \(\delta\omega\)'s are the parameters \((\Delta, \omega_0, b\) and \(K\)) to be determined. Values of
are measured, in arbitrary units, as a function of $\omega_i$ in the frequency interval $\pm \Delta$ around the observed zero of the derivative. Since there will be some scatter, the information is fed in the form $y_i$ vs. $\omega_i$ and $(y_i - f(\omega_n, \omega_i))^2$ is minimized. To achieve this the derivatives with respect to $\omega_n$ must vanish so that

$$\sum_i (y_i - f(\omega_n, \omega_i)) \frac{\partial f(\omega_n, \omega_i)}{\partial \omega_n} = 0$$

for all $\omega_n$. Now the variations in $\omega_n$ from the initially guessed values are considered. Then

$$\sum_p \sum_i (((y_i - f(\omega_n, \omega_i)) \frac{\partial f(\omega_n, \omega_i)}{\partial \omega_n \partial \omega_p} - \frac{\partial f(\omega_n, \omega_i)}{\partial \omega_n} \frac{\partial f(\omega_n, \omega_i)}{\partial \omega_p}) \delta \omega_p ) = 0.$$

This is a set of simultaneous equations for corrections $\omega_n$ to the parameters. The Newton-Raphson method was extended to solve these equations by computer. Iteration was carried out until there was no change on the third decimal place of the desired parameters in kc/s.
PKW Oscillating Detector
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