Steady-state nuclear induction signal shapes in lithium metal

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Steady-state nuclear induction signal shapes in lithium metal

Abstract
A detailed theoretical and experimental study has been completed of the absorption and dispersion mode nuclear magnetic resonance signals for Li\textsuperscript{7} in solid lithium metal at room temperature. Calculations of resonance signal shapes, based on the Bloch Theory as modified by the small-amplitude modulation theory of Halbach, were made with an IBM 650 computer and were compared with the experimental results. A variety of experimental conditions and both the in-phase and quadrature components of the signal at the modulation frequency were studied. The Bloch-Halbach Theory appears to account very satisfactorily for the saturation behavior of the four types of resonance signals. In addition, the behavior of the complex absorption mode signal provides a convenient means of determining with precision the location of the quadrature phase signal.

Disciplines
Metallurgy
STEADY-STATE NUCLEAR INDUCTION SIGNAL SHAPES IN LITHIUM METAL

By
D. R. Torgeson
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November 1960

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Iowa State University
Ames, Iowa
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I. INTRODUCTION

A. Nuclear and Nuclear Magnetic Properties

In general (1) the atomic nucleus is found to have a mass \( M \), charge \( Q \), an intrinsic spin \( I \) or intrinsic angular momentum \( \mathbf{p} \), and a magnetic moment \( \mu \). Nuclei which have zero intrinsic spin are found to have zero magnetic moment. Classically, the atomic nucleus can be thought of as a small spinning spherical shell of mass \( M \) which has on its surface a uniformly distributed charge \( Q \). Using this simple picture of a spinning charged surface, a linear relation between the magnetic moment and angular momentum can be derived and is \( \mu = (Q/2Mc)p \), where \( c \) is a universal constant equal to the speed of light in a vacuum.

Different nuclear species are found to have different magnetic moments. The equation that is written to apply in general to all species is \( \mu = \gamma p \), where \( \gamma \) is a constant called the gyromagnetic ratio and is peculiar to a given nuclear species in a given energy state. The gyromagnetic ratio is sometimes expressed as \( \mu/\hbar \), where \( \hbar = h/2\pi \). \( h \) is called Planck's constant and is \( 6.625 \times 10^{-27} \) erg-sec.

The spin of the nucleus is formally defined as \( 1/\hbar \) times the largest observable value of the time average of the component of \( \mathbf{p} \) in a given direction. Experimentally, the given direction is taken to be that of an externally-applied magnetic field \( \mathbf{H} \).
the spin = \( \frac{1}{\hbar} (p_H)_{\text{max}} = I \)

Excluding ferromagnetic and antiferromagnetic substances and in the absence of an applied magnetic field, inside a given sample the magnetic moments \( \mu \) of the nuclei will be randomly oriented. In the presence of an externally-applied field the magnetic moment will tend to be aligned with the field direction. However, from the quantum mechanical space quantization effect, the values of \( p_H \), the components of the nuclear angular momentum in the direction of \( H \), do not form a continuous set of real numbers but form a finite closed set of real numbers. These are \( p_H = m\hbar \), where \( m = I, I - 1, \ldots, -I+1, \) and \(-I\).

From other quantum mechanical considerations it is seen that the value of \( p \cdot p = I(I+1)\hbar^2 \). Then the magnitude of the angular momentum vector is \( p = \sqrt{I(I+1)} \hbar \). Since \( (p_H)_{\text{max}} = I\hbar \) it is seen that the nuclear axis can never coincide with the field direction.

Although coincidence with the field \( H \) is impossible, the field \( H \) does exert a torque \( \mathbf{L} \) on a magnetic moment \( \mu \), that is,

\[ \mathbf{L} = \mathbf{\mu} \times \mathbf{H} \]

For a rigid body the torque \( \mathbf{L} \) is defined as the time rate of change of the angular momentum, i.e.,

\[ \mathbf{L} = \dot{\mathbf{p}} \]
Combining Equations 2 and 3, one has

\[ \dot{p} = \mu \times H. \quad 4 \]

Substituting \( \mu = \gamma p \) into Equation 4, one has

\[ \dot{p} = \gamma p \times H. \quad 5 \]

Because \( p \) has a constant magnitude, \( \dot{p} \) may be written as \( \omega \times p \), where \( \omega \) is the angular velocity of the magnetic moment and angular momentum vectors about the direction of \( H \). Therefore,

\[ \omega \times p = \gamma p \times H \quad 6 \]

which can be written as

\[ \omega \times p = -\gamma H \times p, \quad 7 \]

or in terms of magnitude only

\[ \omega = \gamma H. \quad 8 \]

This shows vividly that the frequency of precession of the nuclei in the presence of the field \( H \) is independent of the angle between the field and the magnetic moment. This precession frequency is called the Larmor precession frequency.

From Equation 2 it is possible to derive the potential energy \( U \) of a magnetic moment \( \mu \) in a magnetic field \( H \). Except for a zero point energy constant

\[ U = -\mu \cdot H = -\mu_H H. \quad 9 \]
Since the magnetic moment and the angular momentum of the nucleus are related in a simple one-to-one fashion, the set of values of $\mu_H$ is also a finite closed set of real numbers. This one-to-one relation also tells us that the magnetic moment can never coincide with the field direction.

The values of this discrete set of numbers given in terms of $m$ are

$$U(m) = -\mu m H / I$$

of which there are $2I + 1$ values, since $m = -I$ to $+I$. It is found that $I$ has integral and half-integral values.

Of the $2I + 1$ energy states one notes that for positive $\gamma$ the lowest energy state occurs when $m = I$, at which time the magnetic moment is most nearly aligned with the field. At this point one asks why these nuclei do not all move into the lowest energy state.

Thermodynamically the nucleus has at least 3 degrees of freedom and because of the equipartition of energy each degree of freedom has because of its temperature an energy of $\frac{1}{2}kT$, where $k$ is Boltzmann's constant and is equal to $1.380 \times 10^{-16}$ erg/deg and $T$ is the temperature in degrees Kelvin. At room temperature this value $\frac{1}{2}kT$ is much larger than the energy difference between the lowest and highest magnetic energy orientations with and against the field $H$. 
when $H$ is of the order of 10,000 gauss.

The thermal effect upon the nuclear magnetic energy levels is very great because of this very large energy of thermal agitation. Using the Boltzmann distribution condition, the relative population numbers $N_i$ and $N_j$ are related to the energies $U_i$ and $U_j$ of the $i^{th}$ and $j^{th}$ magnetic energy states and the temperature $T$ in the ratio

$$\frac{N_i}{N_j} = \frac{\exp (-U_i/kT)}{\exp (-U_j/kT)}.$$  

At room temperature $U \ll kT$ and an expansion of the ratio above can be made.

$$\frac{N_i}{N_j} = \frac{\exp (-U_i/kT)}{\exp (-U_j/kT)} \approx 1 + \frac{U_j - U_i}{kT}.$$  

An illustrative example is as follows: Consider a sample of protons which have spin $\frac{1}{2}$, $\mu = 1.41 \times 10^{-23}$ erg/gauss, and at room temperature, $T \approx 300^\circ K$, all in a field of 10,000 gauss then

$$\frac{N_{\frac{1}{2}}}{N_{-\frac{1}{2}}} = \frac{\exp (\mu H/kT)}{\exp (-\mu H/kT)} = 1 + \frac{2 \mu H}{kT} \approx 1 + 6.8 \times 10^{-6},$$  

or for every million nuclei in the $m = -\frac{1}{2}$ state there are one million and seven in the lower $m = \frac{1}{2}$ state.
B. Nuclear Magnetic Transitions

In Niels Bohr's early analysis of the hydrogen spectra, he made the hypothesis that the energy change $\Delta U$ between two atomic electron levels was related to the emitted or absorbed radiation in that the radiation had a frequency $\omega$ such that

$$\omega = \frac{\Delta U}{\hbar}.$$  \hfill (14)

The $2I + 1$ magnetic energy levels are of this type also, however, transitions do not occur between widely-separated levels, but only between adjacent levels. A transition between adjacent levels corresponds to a $\Delta m$ of +1 or -1. A selection rule (2) has been derived which allows only those transitions for which $\Delta m$ is +1 or -1.

The frequency of such a transition is then computed from Equations 9 and 14 to be

$$\omega = \frac{\Delta U}{\hbar} = \frac{\mu H}{I \hbar} = \gamma H = \omega_L,$$  \hfill (15)

which is also the Larmor precession frequency. For Li$^7$ the Larmor frequency, $\omega/2\pi$, is 16.547 Mc in a field of 10,000 gauss. If there is a radiation field of the proper frequency and orientation, a magnetic transition does occur. However, if that same radiation field is tuned to a frequency that is considerably different from that of the precession frequency, then no transitions will occur; hence, a magnetic transition...
of this kind is a resonance phenomenon.

The experimental arrangement with which one can induce transitions is as follows: Suppose there is a small radio frequency field $H_1$ that rotates with constant magnitude $H_1$ and angular frequency $\omega$ in a plane whose normal is parallel to the large field $H_0$ (see Figure 1). The field $H_1$ will induce a torque on the precessing magnetic moment $\mu$ such that

$$L_f = \mu \times H_1$$

and by the absorption or emission of energy $h\omega = \Delta U$ the magnetic moment will go to a higher or lower energy level where it will be oriented more nearly against or with the field $H_0$ respectively. Thus the torque $L_f$ is a flopping torque that can induce upward or downward transitions depending upon its relative vector orientation with respect to $\mu$.

If the frequency $\omega$ of the small field $H_1$ is different from that of the precessing nuclei, the torque $L_f$ will change its orientation with respect to $\mu$ with a frequency $\Delta \omega = \omega - \omega_L$. If $\Delta \omega$ is not too large, the radio frequency field will tend to induce upward transitions one half of the time and downward transitions the remainder of the time. This will result in a nutation of the precessing magnetic moment. The time average of this torque will be zero.
Figure 1. Vector model showing the relative orientations of the magnetic moment $\mu$, rotating magnetic field $H_1$, and the torque $\mathbf{L}_f$ all rotating about the large field direction $H_0$, at times $t'$ and $t''$.

Figure 2. Vector model illustrating the various components of $\mathbf{H}$ and $\mathbf{M}$ in a bulk sample at a given instant.
FLOPPING TENDENCY OF \( L''_f \)
FLOPPING TENDENCY OF \( L'_f \)
C. Nuclear Magnetic Resonance in Bulk Samples

Before giving a discussion of the complete mechanism for the recording of a nuclear resonance, one must realize that to speak of the resonance properties of a single nucleus or magnetic moment is experimentally naive. Only a discussion of the nuclear and magnetic properties of a material on a per unit volume basis will satisfy the reality of the experimental situation.

The magnetic flux density or magnetic induction $B$ within a sample can be written as

$$ B = H + 4\pi M, $$

where $H$ is the total magnetic field and $M$ is the volume density of magnetic moments or the magnetic moment per unit volume. In a simple isotropic substance the vector $M$ is linearly related to the magnetic field strength $H$:

$$ M = \chi H, $$

where $\chi$ is defined as the nuclear paramagnetic susceptibility per unit volume.

In the sample of two million and seven protons discussed before, which was in a field of 10,000 gauss, it is the extra seven magnetic moments in the lower energy state that contribute to $M$, the net magnetic moment per unit volume. It is
the time variation of $\mathbf{M}$ that is of particular interest.

Let $z$ be the direction of the large field $H_0$ and $x$ that of the radio frequency field of amplitude $2H_1$ and angular frequency $\omega$. The total magnetic field $\mathbf{H}$ has components

$$H_x = 2H_1 \cos \omega t$$
$$H_y = 0$$
$$H_z = H_0.$$

To obtain the time variation of $\mathbf{M}$ one need not solve a Schroedinger equation but recall that the quantum mechanical expectation value of an operator follows the classical equations of motion exactly and that the magnetic and angular moments are parallel to one another.

The resultant angular momentum $\mathbf{P}$ per unit volume of a given sample satisfied the classical equation of motion

$$\mathbf{\dot{P}} = \mathbf{T},$$

where $T$ is the total torque per unit volume acting on the nuclei. Now

$$\mathbf{T} = \mathbf{M} \times H_0,$$

which is similar to Equation 2.

An equation can be written to describe the relation between the angular momentum and magnetic moment per unit volume in strict analogy with the single nucleus case,
\[ \mathbf{M} = \gamma \mathbf{p}. \]

Combining Equations 20-22

\[ \dot{\mathbf{M}} = \gamma \mathbf{M} \times \mathbf{H}_0. \]

Of special interest is a special solution of Equation 23 when \( H_1 \ll H_0 \) and when the magnitudes \( H_1 \) and \( H_0 \) are constant. Assume that the frequency \( \omega \) of the r.f. field \( H_1 \) is in the neighborhood of the Larmor precession frequency \( \omega_0 \), where

\[ \omega_0 = \gamma H_0, \]

or such that

\[ |\omega - \omega_0| \ll \omega_0. \]

The \( x \) and \( y \) components of the actual field \( \mathbf{H} \) given by equation 19 can be replaced by the sum of

\[ H_x^+ = H_1 \cos \omega t \quad \text{and} \quad H_x^- = H_1 \cos \omega t \]
\[ H_y^+ = H_1 \sin \omega t \quad \text{and} \quad H_y^- = H_1 \sin \omega t \]

where the \( + \) indicates the positive or counterclockwise and the \( - \) indicates the negative or clockwise rotation about the \( z \) direction.

If the oscillating field has the same frequency as the precessing nuclei, one of the two oppositely-rotating components will rotate with the nuclei and the other against them. The component rotating against the nuclei will be very
13
different in relative frequency with respect to the nuclei and therefore its effect upon them will be zero. Using this concept, the total effective field that the nuclei "see" can be written

\[ H_x = H_1 \cos \omega t \]
\[ H_y = -H_1 \sin \omega t \]
\[ H_z = H_0 , \]

where the \( x \) and \( y \) components sum to give a component rotating in the \( xy \) plane with the rotation about the \( z \) direction in the negative or positive sense depending upon a positive or negative value of \( \gamma \) (see Figure 2).

The equation of motion of the rotating magnetic moment per unit volume (Equation 23) shows that the change in \( \vec{M} \) with respect to time is perpendicular to \( \vec{M} \). This can only mean that the magnitude of the polarization does not change as a function of time. The only change in \( \vec{M} \) is in its direction.

For constant magnitude of the r.f. field \( H_1 \) there is a special solution (3) of equation 23 where \( \vec{M} \) is given by

\[ M_x = M \sin \phi \cos \omega t \]
\[ M_y = -M \sin \phi \sin \omega t \]
\[ M_z = M \cos \phi . \]

Here \( \phi \) is a polar angle, i.e., the angle between the \( z \) or \( H_0 \) directions and \( \vec{M} \), and is constant and chosen such that
\[ \tan \phi = \frac{\gamma H_1}{(\gamma H_0 + \omega)} \]  

This also means that the z component \( M_z \) is also constant. The minus or plus sign before \( \omega \) in Equation 28 is chosen if the value of \( \gamma \) is positive or negative respectively.

Let \( H^* = \omega^* \) be the value of the field \( H_0 \) at which the precession frequency is the frequency of the r.f. oscillating field. Then Equation 28 can be written as

\[ \tan \phi = \frac{H_1}{H_0 - H^*} \]

The angle \( \phi \) between \( H_0 \) and \( M \) is small as long as \( H_0 \) is large compared to the resonance field \( H^* \). \( \phi \) is between 0 and 90 degrees if the difference \( H_0 - H^* \) is comparable to \( H_1 \). When \( H_0 = H^* \), \( \phi \) is 90 degrees. When \( H_1 \ll H^* - H_0 \), \( \phi \) is nearly 180 degrees.

Equations 26 and 29 can be rewritten as

\[ \delta = \frac{H_0 - H^*}{H_1} = \cot \phi \]

This equation gives a measure of the distance the large field \( H_0 \) is from \( H^* \) in units of \( H_1 \). Using this notation one now has
\[
M_x = \frac{M \cos \omega t}{(1 + \delta^2)^{\frac{1}{2}}}
\]
\[
M_y = \frac{M \sin \omega t}{(1 + \delta^2)^{\frac{1}{2}}}
\]
\[
M_z = \frac{M \delta}{(1 + \delta^2)^{\frac{1}{2}}}
\]

Although the solution (Equation 31) was found while working under the hypothesis that \( \omega, H_0 \), and therefore \( \delta \) were constant, one can show that Equations 31 are equally valid provided these quantities vary adiabatically or slowly enough so that

\[
|d \delta/dt| << |\gamma H_1|.
\]

Notice that as resonance is approached or as \( H_0 \) goes to \( H^* \), \( M_x \) and \( M_y \) have attained their maximum values. As \( H_0 \) begins to differ from \( H^* \) they decrease in amplitude.

Under these conditions several experimental procedures are possible. In all cases, \( H_1 \) is held constant, while for example, one could operate at fixed field \( H_0 \) and vary \( \omega \), or with fixed frequency and variable field \( H_0 \). In the Varian Model V-4200b Wide Line N-M-R Spectrometer used in the performance of the experiments to be described in this report \( \omega \) is held constant and \( H_0 \) is slowly varied.

In the induction type spectrometer (of which the Varian Spectrometer is an example) a coil is wound about the sample
with its axis in the y direction. Any radio-frequency flux which has a component in the y direction will then be seen as an induced radio-frequency voltage at the terminals of the coil. Thus, as the y component of the nuclear magnetic moment per unit volume, or polarization \( M_y \), grows in magnitude while approaching resonance and then decreases after passing resonance, this change of \( M_y \) will produce a voltage in the receiver coil. The induction associated with \( M_y \) is \( B_y = 4\pi M_y \). The receiver coil, as it is called, has \( N \) turns and a cross-sectional area \( A \). If the receiver coil is entirely filled with sample, the effective flux through the coil will be

\[
P = 4\pi N A M_y = \frac{4\pi N A M_y \sin\omega t}{1 + \delta^2}.
\]

The radio-frequency voltage induced in the receiver coils is then

\[
V = -\frac{1}{c} \frac{dP}{dt} = \frac{4\pi N A M \omega \cos\omega t}{c(1 + \delta^2)^{3/2}},
\]

where \( \delta \) is considered to vary extremely slowly with time as compared to \( \cos\omega t \).

Approaching resonance, the amplitude of the induced voltage \( V \) increases until \( H_0 = \omega/\gamma = H^* \), at which time \( V \) is a maximum, and as resonance is passed \( V \) decreases. Calculations show that \( V \) is of the order of millivolts under ideal conditions. This value of the induced voltage is an overesti-
mate because the physical picture described here is a gross oversimplification.

D. Spin-Lattice Interactions

In the foregoing discussion, it was implicitly assumed that the atomic electrons do not cause appreciable fields at the nucleus, that interactions between neighboring nuclei can be considered negligible, and that thermal agitation does not appreciably affect the nuclei.

Consider a given simple sample containing nuclei having spin $I$ at room temperature and in the earth's own magnetic field. The populations of the $(2I+1)$ magnetic energy levels will be practically identical (to about 3 parts in $10^{11}$). If the sample is quickly put into a field of 10,000 gauss, how long will it take for the equilibrium excess number of nuclei to appear at the lower energy level? Thus, what is the mechanism of the relaxation process necessary for this equilibrium distribution to be established? In a thermodynamic sense, a relaxation process is any process of energy exchange between the nuclear spins and the lattice. The material sample of which the nuclei are a part, whether gas, liquid, or solid, is conventionally called the lattice.

Immediately after placing the sample in the 10,000 gauss magnetic field, the $(2I+1)$ magnetic energy level populations
have not yet changed and are still nearly equal. Recall Equation 12

\[ \frac{N_i}{N_j} \exp \left( \frac{-U_i}{kT} \right) = 1 + \frac{U_j - U_i}{kT} \]

For \( I = \frac{1}{2} \) again, one has Equation 13,

\[ \frac{N_{\frac{1}{2}}}{N_{-\frac{1}{2}}} = 1 + \frac{2\mu H}{kT} \]

Since one knows \( N_{\frac{1}{2}}/N_{-\frac{1}{2}} = 1 \) to about 3 parts in \( 10^{11} \), then \( 2\mu H/kT \approx 3 \times 10^{-10} \), and since \( H_0 \) is 10,000 gauss, this must mean that \( T \) is very large. One now defines \( T_s \), the spin temperature, as the number necessary to satisfy this equation. So, for nuclei with spin \( \frac{1}{2} \),

\[ T_s = \frac{2\mu H}{(N_{\frac{1}{2}}/N_{-\frac{1}{2}} - 1)} \]

This concept of a spin temperature (4) is reasonable, because, if as in this case, the populations are going to adjust so that some of the nuclear spins move into lower energy states, the moving spins must give up some of their energy to the lattice. Thus, there is an energy exchange or heat flow from the spins at temperature \( T_s \) to the lattice at temperature \( T \).

In order for the spin system to give up energy to the lattice there must be a net downward transfer of spins from the higher energy state. From Einstein's theory of proba-
bility coefficients, we know that the probability of transi-
tions upward by absorption is equal to the probability down-
ward by stimulated emission. Thus it appears as though there
can be no net downward transitions. However, the equality
of probabilities mentioned here refers to transition stimu-
lated by interactions with a radio-frequency field. We are
now considering only the interactions between the spins and
the lattice.

Let \( N_i \) and \( N_j \) be the equilibrium populations of two ad-
jacent magnetic energy levels \( i \) and \( j \) which differ in energy
by \( U_j - U_i \). If a detailed balance is to be maintained at a
lattice temperature \( T \), the number of upward and downward
transitions must be equal, hence

\[
N_i W(i \rightarrow j) = N_j W(j \rightarrow i),
\]

where \( W(i \rightarrow j) \) is the total probability per unit time of a
single transition between the \( i \) and \( j \) states. At equilibrium

\[
\frac{W(i \rightarrow j)}{W(j \rightarrow i)} = \frac{N_j}{N_i} = \exp \left( \frac{U_i - U_j}{kT} \right).
\]

Since a single transition from \( i \) to \( j \) cannot depend up-
on the population of \( j \), the total probabilities \( W \) must be re-
lated to the quantum-mechanical probabilities \( P \) through the
Boltzmann factor of the final state even before equilibrium
is obtained:
Again consider the case of the proton. Since \( P(\frac{1}{2} \rightarrow -\frac{1}{2}) = P(-\frac{1}{2} \rightarrow \frac{1}{2}) \), one has

\[
W (\frac{1}{2} \rightarrow -\frac{1}{2}) = P \exp (-\mu H_0/kT) \\
W (-\frac{1}{2} \rightarrow \frac{1}{2}) = P \exp (\mu H_0/kT)
\]

If the spin system is at a temperature \( T_s \) different from the lattice temperature \( T \) and the excess number of spins in the lower spin state \( n \) changes by 2 after each transition, then the rate of change of \( n \) is

\[
\frac{dn}{dt} = 2N_{-\frac{1}{2}} W (\frac{1}{2} \rightarrow -\frac{1}{2}) - 2N_{\frac{1}{2}} W (\frac{1}{2} \rightarrow -\frac{1}{2}).
\]

Now \( n \ll N = N_{\frac{1}{2}} + N_{-\frac{1}{2}} \), and substitute

\[
W (\frac{1}{2} \rightarrow -\frac{1}{2}) = P \cdot (1 - \mu H_0/kT) \\
W (-\frac{1}{2} \rightarrow \frac{1}{2}) = P \cdot (1 + \mu H_0/kT)
\]

into Equation 40

\[
\frac{dn}{dt} = 2P (n_0 - n)
\]

where \( n_0 = N \mu H_0/kT \) is the value of \( n \) at equilibrium between lattice and spin. Integrating Equation 42 one has

\[
n_0 - n = (n_0 - n_a) \exp (-2 PT)
\]

where \( n_a \) is the initial value of \( n \). Equilibrium is thus approached exponentially with a characteristic time.
and $T_1$ is called the spin-lattice relaxation time.

E. Spin-Spin Interactions

Nuclear spins interact with their lattice as we have just seen but nuclear spins also interact with other neighboring spins through their magnetic fields. Classically, each nucleus sees the large externally-applied field $H_0$ and a small local magnetic field $H_{\text{local}}$ which is produced by neighboring nuclear dipoles. Depending upon the vector orientations of the neighboring magnetic moments in the possible $(2I + 1)$ states, a given nucleus sees a slightly greater or smaller magnetic field than the large field $H_0$.

The magnetic field of a magnetic dipole $\mu$ decreases as a function of $1/r^3$. For protons, when $r = 1\text{Å}$, then $H_{\text{local}} = 5$ gauss. In general, the energy levels are broadened by an amount of about $\mu H_{\text{local}}/I$, or in terms of frequency, by $\delta \omega = \gamma H_{\text{local}}$ which is $10^4$/seconds for protons. This could mean that two protons precessing in phase at time $t = 0$ can be expected to be out of phase in a time of the order of $1/\delta \omega = 10^{-4}$ seconds. Thus, one introduces a general spin-spin interaction time $T_2$ to represent the lifetime or phase memory time of the nuclear spin state.
F. Saturation

In the absence of the radiation field, the populations are as described before. In the presence of the radio-frequency radiation and upon absorption of energy, the equilibrium populations tend to be equalized. The new dynamic state, i.e., in the presence of the radiation field, represents a balance between the energy absorption mechanism of the spins and the transfer of energy to the lattice by any and all internal degrees of freedom of the sample.

From Equation 42 and 44 one finds the differential equation for \( n \) to be

\[
\frac{dn}{dt} = \frac{n_0 - n}{T_1}.
\]

When radiation is present another term is added to account for the upward transitions due to energy absorption

\[
\frac{dn}{dt} = \frac{n_0 - n}{T_1} - 2nC,
\]

where \( C \) is the probability per unit time of a transition by a nucleus in a radiation field.

The steady state is reached when \( \frac{dn}{dt} = 0 \), and Equation 46 can be written using \( n_s \) for the steady state value for \( n \).
Quantum-mechanical calculations show that for spin \( \frac{1}{2} \),
\[
C = \frac{1}{2} \gamma^2 H^2 T^2_1 T^2_2,
\]
thus Equation 47 becomes
\[
\frac{n_s}{n_o} = \frac{1}{1 + \gamma^2 H^2 T^2_1 T^2_2} = \frac{1}{1 + S},
\]
where \( S = \gamma^2 H^2 T^1 T^2 \) is called the saturation factor.

If the amplitude of the applied radio-frequency field \( H_1 \) is large, then \( n_s/n_o \) becomes very small. The populations are nearly equal in all levels, the spin temperature \( T_s \) becomes very large, and the spin system is said to become saturated.

G. Bloch Equations

Recall Equation 23:
\[
dM/dt = \gamma M \times H.
\]

As we now realize the right side of this equation is incomplete because it ignores several of the mechanisms by which \( M \) changes. If the spin system and the lattice are described by two different temperatures \( T_s > T \) in the absence of a magnetic radiation field, \( M_z \) approaches \( M_o \) exponentially with a characteristic time \( T_1 \) so that
\[
dM_z/dt = (M_o - M_z)/T_1.
\]
Figure 3. Schematic representation of the resonance recording process in terms of the y component of the polarization and the modulation field.
Transverse components \( M_x \) and \( M_y \) are the rotating components of the precessing \( M \). As we have seen, in the absence of the radio-frequency field, local inhomogeneities of the large magnetic field inside the sample cause individual nuclei to lose their phase coherence in a time of the order \( T_2 \), thus bringing \( M_x \) and \( M_y \) to zero.

Bloch (3) has assumed that \( M_x \) and \( M_y \) approach zero exponentially with characteristic times \( T_2 \) giving

\[
\frac{dM_x}{dt} = -\frac{M_x}{T_2} \quad \text{and} \quad \frac{dM_y}{dt} = -\frac{M_y}{T_2}.
\]

Thus \( T_2 \) is often called the transverse relaxation time.

Bloch obtained the differential equations of the three components of \( M \) by combining Equations 49 and 50 with 23:

\[
\begin{align*}
\dot{M}_x - \gamma(M_y H_0 - M_z H_y) + \frac{M_x}{T_2} &= 0 \\
\dot{M}_y - \gamma(M_z H_x - M_x H_0) + \frac{M_y}{T_2} &= 0 \\
\dot{M}_z - \gamma(M_x H_y - M_y H_x) + \frac{M_z}{T_1} &= \frac{M_0}{T_1}
\end{align*}
\]

where \( H_x \) and \( H_y \) are given by Equation 26.

Upon integration of the Bloch equations, the general shape of \( M_y \) in arbitrary units as a function of \( H \) is that shown in Figure 3.
The shape of $M_y$ as a function of $H$ gives an idea of the relative number of nuclei that are precessing at a given field value $\omega/\gamma = H$. All the nuclei do not precess at the same field value because of the local magnetic field differences in the sample due to neighboring magnetic moments, etc.

The present physical interest in magnetic resonance lies not merely in finding resonances, but for the investigation of the resonance shape and width as a source of information for a clearer understanding of the relaxation processes, nuclear electric quadrupole interactions, magnetic interactions, saturation processes, thermal effects, etc.

H. Recording a Nuclear Magnetic Resonance

In the experimental recording of a nuclear magnetic resonance the frequency $\omega$ of the r.f. magnetic field is maintained constant and the field $H_0$ is slowly and uniformly increased or decreased through the resonance. In the $z$ or $H_0$ direction a low frequency ($\sim 40$ cps) magnetic modulating field is produced by a set of Helmholtz coils driven by an audio amplifier. The instantaneous value of the $z$ component of the magnetic field is then

$$H = H_0(t) + H_m \cos \omega_m t,$$

where $H_0(t)$ is understood to be a very slowly varying function
of time. $H_m$ is the amplitude of the modulation field with $\Omega_m$ its angular frequency. For normal operation, $\Omega_m$ is adjusted such that $T_2 << 1/\Omega_m$.

Figure 3 shows the variation of $H$ by the modulation field schematically represented by a sinusoidal curve of amplitude $2H_m$ with its axis vertical. When a portion of the $M_y$ curve experiences a given field value, resonance for those nuclei occurs, whereupon the nuclei change magnetic orientation and induce a voltage in the receiver coil. After a time $1/2\Omega_m$ other nuclei a magnetic distance $2H_m$ away are in resonance. After time $T_2$ the first group of nuclei have relaxed through spin-spin interactions. After another $1/2\Omega_m$ units of time, the originally excited nuclei are again resonated.

With the help of Figure 3, one can see that the induced voltage in the receiver coils (proportional to the peak-to-peak amplitude of the curve on the right hand side of Figure 3) is a measure of the difference in the number of nuclei at the two field values at the ends of the peak-to-peak modulation amplitude. It becomes apparent that if $H_m$ is small enough, the received signal is the derivative of $M_y$. A practical rule for $2H_m$ is that it be one-fifth of the resonance width.
II. Résumé of the Properties of Lithium

Lithium is found (5) in two isotopic states, \( \text{Li}^6 \) which is 7.43% abundant and \( \text{Li}^7 \) which is 92.57% abundant. \( \text{Li}^6 \) has a spin of 1 with a NMR frequency of 6.265 Mc in 10,000 gauss while \( \text{Li}^7 \) has a spin of 3/2 with a NMR frequency of 16.547 Mc in 10,000 gauss. \( \text{Li}^6 \) and \( \text{Li}^7 \) have nuclear electric quadrupole moments of \( 4.6 \times 10^{-28} \text{ cm}^2 \) and \( -4.2 \times 10^{-26} \text{ cm}^2 \) respectively. \( \text{Li}^6 \) has one of the smallest quadrupole moments measured while the quadrupole moment of \( \text{Li}^7 \) is still considered to be small.

Lithium metal has a body-centered cubic crystalline structure (6) between 75°K and 186°C at which temperature it melts. Below 75°K lithium metal has a hexagonal close-packed crystalline structure. At 25°C, the temperature at which the experiments to be described in this report were performed, the cubic structure of lithium insures that electric quadrupole interactions can be ignored. No mention of the quadrupole interactions in lithium or in general will be made in this report.

Lithium metal is the lightest metal known, with a density of 0.534 gm/cm³. Since lithium is a metal and an electrical conductor, it has a radio-frequency skin depth. In order that any NMR spectrometer "see" a resonance in lithium metal, the sample must be chopped up into fine particles. To eliminate cohesion the lithium particles are mixed with mineral
oil. Since the surface area of a given quantity of sample is much larger when chopped up into fine particles than when left in a single chunk, more nuclei per unit volume experience the effect of the radio-frequency magnetic field, etc., and thus the output signal can be quite large.

In a very general way the NMR lines in gases and liquids are very narrow, whereas solids characteristically have quite broad resonance lines. The ratio of these widths can be as large as 100,000 to 1. It is found that the line width is in general proportional to $1/T_2$, where $T_2$ is the spin-spin relaxation time. It is because of the lower density of liquids and gases that, compared to solids, the spins are separated by a larger distance so that it takes considerably longer for the spin system to relax for liquids and gases than for solids. For the same reason the local magnetic field inhomogenities are much smaller in liquids and gases than in solids.

Also, in a very general way, rigid solids have Gaussian resonance shapes with an absorption derivative amplitude of $-2X \exp(-X^2)$ where $X$ is the dimensionless abscissa parameter. Liquids characteristically have a Lorentaian resonance shape with an absorption derivative amplitude of $-2XS^{1/2}/(1+S+X^2)$, where $S$ is the saturation factor. Depending upon the tem-
perature of the sample, lithium can exhibit either of these two resonance shapes while it is in the solid form.

Below 230°K lithium (7) has a nearly Gaussian resonance shape with a line width of 6.2 gauss. With increasing temperature the resonance becomes quite narrow. Near room temperature it has a width of 0.13 gauss and has the Lorentzian line shape. Solid lithium near room temperature "looks like" a liquid in the sense of the NMR signal.

The reason that the NMR line in lithium is narrower at room temperature is that at this temperature there is self-diffusion occurring within the sample. Lithium atoms move from one lattice site to an unoccupied adjacent lattice site, overcoming in this movement a free energy barrier. The lattice of the metal is then not rigid in the microscopic sense at room temperature, and the resonance line is said to undergo motional narrowing. Because of this diffusional motion, nuclei "see" a more averaged local magnetic field inhomogeneity than in the rigid lattice case, and this results in a narrower line.

Considerable work has been done in studying the phenomenon of self diffusion in lithium by NMR methods. It has been found that lithium has an activation energy for self diffusion of 12.1 Kcal/mole, both by induction NMR spectroscopic methods and spin-echo spectroscopic methods.\(^1\)

III. DESCRIPTION OF THE VARIAN WIDE LINE SPECTROMETER

The experiments to be described in this report were performed using a Varian Associates Wide Line NMR Spectrometer, model number V-4200B.

The major components of the spectrometer system and the functions that each component performs are as follows: (8, p. 9) (see Figure 4 for the block diagram)

Variable Frequency RF Unit (Model V 4210)

1. Tunable oscillator and RF amplifier for driving the transmitter coil in the probe.
2. Receiver, which tracks with the transmitter, for amplifying and demodulating the NMR signal.

Probe (Model V 4230)

1. A sample holder.
2. A transmitter coil which generates the $H_1$ rotating field.
3. A receiver coil which picks up the NMR signal.
4. A pair of sweep coils which introduce periodic variations onto the $H_0$ field.

Sweep Unit (Model V 4250)

Generates a sine wave sweep voltage at selectable periods which is delivered to:
1. X-axis of an oscilloscope.
2. Sweep amplifier input terminals.
Sweep Amplifier Unit (Model V 4240)

1. Amplifies sweep unit output and drives the sweep coils in the probe.

2. Drives the synchroverter (phase detector) in the output control unit.

Output Control Unit (Model V 4270)

1. A phase detector which demodulates the NMR signal from the sweep carrier.

2. A controllable filter limits the band width and reduces higher harmonics of the sweep carrier.

3. Performs auxiliary control functions.

Selector Unit

1. Selects the scope presentation.

2. A filter which limits the band width of the signal presented to the scope.

Oscilloscope (Hewlett Packard Model 120A)

Presents a visual display of NMR signals.

Graphic Recorder (Model G-10)

Records strong or weak NMR signals.

Regulated Power Supplies (Models V 4260 and V 4261)

Supply power to spectrometer system.

Procession Field Scanning Unit (Model V 4280)

Controls the current output of the electromagnet
Figure 4. Block diagram of the wide-line spectrometer and regulated electromagnet.
power supply for producing wide range and slow variations in the polarizing field $H_0$.

The Varian spectrometer and most other nuclear induction spectrometers employ a set of flux-steering paddles (9) which are metal plates or plugs that can be moved with respect to the transmitter coils in the probe. By proper adjustment of these paddles it is possible to record the resonance signal that is in phase, or 90 degrees out of phase, with respect to the radio-frequency exciting signal. In this way variations of $M_y$ (absorption mode), variations of $M_x$ (dispersion mode), or combinations of these can be obtained as desired.
IV. RESULTS AND COMPARISON WITH THEORY

Because lithium metal resembles a liquid in the sense of the nuclear magnetic resonance, it has a spin-spin relaxation time at 25°C that is very small compared with most metals, but yet large compared with most liquids. In the recording of nuclear magnetic resonances of liquids by the conventional high resolution methods it is not necessary to modulate the large magnetic field $H_0$ with a low frequency magnetic field. To get resonances of liquids by high resolution techniques, it is only necessary to scan the resonance repeatedly with a slow linearly varying field. In the case of lithium metal at 25°C, however, it is necessary to modulate the large magnetic field $H_0$ as is done to obtain resonances in solids.

As was stated in the introduction, for general recording of nuclear magnetic resonances of solids the modulation frequency $\omega_m$ is adjusted such that $T_2 < \frac{1}{\omega_m}$. It is apparent from Figure 3 that for sufficiently small $H_m$, the amplitude of the modulation field, the signal amplitude is given by $H_m \frac{dM_y(H)}{dH}$. If, however, $T_2$ is comparable to but smaller than $\frac{1}{\omega_m}$, then, because of the "nuclear memory capacity" of the sample, the signal can no longer be a simple function of the modulation amplitude or of the magnetic field $H$. In this case a hysteresis effect occurs and there is a signal com-
ponent displaced 90 degrees with respect to the modulation field.

K. Halbach (10) has proposed a theory whereby no restriction is made upon the modulation frequency $\Omega_m$. In the theoretical development, Halbach begins by modifying the Bloch equations by replacing $H_0$ in these equations with $H_0 + H_m \cos \Omega_m t$. In order to solve these modified Bloch equations, he expands the dimensionless components of the magnetic polarization, $U = M_x/M$, $V = M_y/M$, and $W = M_z/M$ as Fourier series in terms of the modulation frequency. In order to further resolve these modified equations, the Fourier coefficients $U_n$, $V_n$, and $W_n$ are developed in power series in terms of the amplitude of the modulation field $H_m$. By eliminating the component $W_n$, Halbach obtains a system of equations for the coefficients $U_{n, \nu}$ and $V_{n, \nu}$ which appear in this power series. He shows that all the coefficients $U_{n, \nu}$ and $V_{n, \nu}$, for which $\nu < |n|$, vanish. Halbach also shows that $U_{0, 0}(X)$ and $V_{0, 0}(X)$ are the familiar Bloch slow passage solutions to Equations 53,

$$U_{0, 0}(X) = \frac{b^t X S^{\frac{3}{2}}}{1 + S + X^2},$$

$$V_{0, 0}(X) = \frac{b^t S^{\frac{3}{2}}}{1 + S + X^2}.$$

By using these values, $U_{0, 0}(X)$ and $V_{0, 0}(X)$, Halbach has obtained the first order solutions shown in Figure 5. These are called the first order approximations because they repre-
sent the second coefficient in the power series expansion in terms of \( H_m \). One can use these equations validly only when \( H_m \) is small so that higher order terms of \( H_m \) can be considered negligible. Note in Figure 5 the definitions of the terms used in the Halbach equations. \( V_{11}(X) \) and \( U_{11}(X) \), as they are called, are dimensionless functions of the dimensionless parameter \( X = (\omega - \omega_0)T_2 \).

In order to more clearly understand the Halbach solutions, which are complex functions, they have been separated into their real and imaginary (quadrature) components. The separated Halbach solutions are displayed in Figure 6.

Lithium metal at 25°C has a spin-spin relaxation time \( T_2 = 0.87 \) milliseconds. Using a modulation frequency \( f_m = 42.0 \) cps, this means that \( 1/\Omega_m = 3.79 \) milliseconds which is greater than \( T_2 \) but of the same order of magnitude. It is thereby apparent that the Halbach solutions should apply to the NMR properties of lithium at 25°C.

The separated Halbach solutions were calculated numerically for large ranges of the values of \( h_1 \) and \( X \) using the IBM 650 electronic digital computer. In order that this machine calculation could be made, the constants \( \beta \) and \( \Omega \) were evaluated using the best known values (11) of \( T_1 \) and \( T_2 \) for lithium metal at 25°C, and are \( T_1 = 0.140 \) seconds and
Figure 5. The Halbach equations for the complex absorption (V) mode and the dispersion (U) mode derivatives as functions of X. Several symbols used in the equations are defined.
HALBACH EQUATIONS

\[ V_{\|}(x) = \frac{h_1}{1 + x^2 + \frac{h_1^2}{\beta}} \frac{x(2-j\Omega)}{x^2 + (1-j\Omega) \left( 1 - j\Omega + \frac{h_1^2}{\beta - j\Omega} \right)} \]

\[ U_{\|}(x) = \frac{h_1}{1 + x^2 + \frac{h_1^2}{\beta}} \frac{1 - j\Omega + \frac{h_1^2}{(\beta - j\Omega)} - x^2}{x^2 + (1-j\Omega) \left( 1 - j\Omega + \frac{h_1^2}{\beta - j\Omega} \right)} \]

WHERE \( h_1 = \gamma H_1 T_2, \beta = T_2 / T_1, x = (\omega - \omega_0) T_2 \)

\( \Omega = \Omega_m T_2, \Omega_m = 2 \pi f_m, \) and \( j = \sqrt{-1}. \)

NOTE THAT \( \frac{h_1^2}{\beta} = \gamma^2 H_2^2 T_2^2 \frac{T_1}{T_2} = \gamma^2 H_1^2 T_1 T_2 = S \)

THE SATURATION FACTOR.
Figure 6. The Halbach real and imaginary (quadrature) solutions for the absorption (V) mode and the dispersion (U) mode derivatives as functions of the dimensionless abscissa parameter X.
\[
\text{Re } V_{II}(X) = \frac{h_i X}{(1 + X^2 + S)} \left\{ \frac{h_i^2 (2\beta + \Omega^2 + \Omega^2 \beta) + 2 X^2 (\beta^2 + \Omega^2) + 2 (\beta^2 + \Omega^2)}{(1 + \Omega^2) [h_i^4 + 2 h_i^2 (\beta - \Omega^2) + (\beta^2 + \Omega^2)(1 + \Omega^2)] + X^4 (\beta^2 + \Omega^2) + 2 X^2 [h_i^2 (\beta + \Omega^2) + (\beta^2 + \Omega^2)(1 - \Omega^2)]} \right\}
\]

\[
\text{Im } V_{II}(X) = \frac{\Omega h_i X}{(1 + X^2 + S)} \left\{ \frac{h_i^2 (\beta - \Omega^2 - 2) - X^2 (\Omega^2 \beta^2) + (\Omega^2 + 3)(\Omega^2 \beta^2)}{(1 + \Omega^2) [h_i^4 + 2 h_i^2 (\beta - \Omega^2) + (\beta^2 + \Omega^2)(1 + \Omega^2)] + X^4 (\beta^2 + \Omega^2) + 2 X^2 [h_i^2 (\beta + \Omega^2) + (\beta^2 + \Omega^2)(1 - \Omega^2)]} \right\}
\]

\[
\text{Re } U_{II}(X) = \frac{h_i}{(1 + X^2 + S)} \left\{ \frac{h_i^4 + 2 h_i^2 (\beta - \Omega^2) + (\beta^2 + \Omega^2)(1 + \Omega^2) - X^4 (\beta^2 + \Omega^2) + \Omega^2 X^2 (\beta^2 + \Omega^2 - h_i^2)}{(1 + \Omega^2) [h_i^4 + 2 h_i^2 (\beta - \Omega^2) + (\beta^2 + \Omega^2)(1 + \Omega^2)] + X^4 (\beta^2 + \Omega^2) + 2 X^2 [h_i^2 (\beta + \Omega^2) + (\beta^2 + \Omega^2)(1 - \Omega^2)]} \right\}
\]

\[
\text{Im } U_{II}(X) = \frac{\Omega h_i}{(1 + X^2 + S)} \left\{ \frac{h_i^4 + 2 h_i^2 (\beta - \Omega^2) + (\beta^2 + \Omega^2)(1 + \Omega^2) + X^2 (2 h_i^2 - h_i^2 \beta - 3 \beta^2 - 3 \Omega^2)}{(1 + \Omega^2) [h_i^4 + 2 h_i^2 (\beta - \Omega^2) + (\beta^2 + \Omega^2)(1 + \Omega^2)] + X^4 (\beta^2 + \Omega^2) + 2 X^2 [h_i^2 (\beta + \Omega^2) + (\beta^2 + \Omega^2)(1 - \Omega^2)]} \right\}
\]
and $T_2 = 0.87$ milliseconds. The modulation frequency $f_m$ was maintained at 42.0 cps. The value of $\gamma$, the gyromagnetic ratio, used was $1.040 \times 10^4$ sec$^{-1}$ gauss$^{-1}$. The equations used in the machine calculation are displayed in Figure 7.

These four equations were calculated for approximately 20 selected values of $h_1$ while increasing $X$ from 0 to 10 in 0.1 steps in the absorption mode case and from 0 to 20 in 0.2 steps in the dispersion mode case. It is expected (10) that the absorption mode derivative line shape be antisymmetric with respect to $X$ and that the dispersion mode derivative line shape be symmetric with respect to $X$. Therefore it was only necessary to calculate one half of the line shape in each case. In all cases the values of $h_1$ and $X$ were sufficient to adequately determine the theoretical line shapes.

To obtain the desired information from these calculations, the results of the line shape calculations for selected values of $h_1$ were plotted in large scale and the desired information, such as amplitudes and widths, were carefully read from these drawings. The various theoretical curves such as those in Figures 8, 10, 14, 19, 21, and 22 were obtained in this way.

The sample of lithium metal chosen for the experimental work was purchased from the Lithium Corporation of America. The lithium metal was in the form of fine particles dispersed
in mineral oil. The approximately spherically shaped particles were such that 90% of them were less than 20 microns in diameter.

At the temperature and radio frequency at which the experiments to be discussed in this report were performed, the ratio-frequency skin depth is about 50 microns. These particles were small enough so that no problems connected with the finite skin depths are expected.

In the following discussions the term "saturation study" will be used repeatedly. A saturation study is an experimental determination of the effects of the radio-frequency field amplitude $H_1$ on the shape and intensity of the resonance signal. We have seen in section F of the introduction that when the amplitude of the applied radio-frequency field becomes sufficiently large the level populations become equalized with an accompanying decrease in resonance signal. Experimentally, the resonance shape is recorded at each of a series of selected values of $H_1$, the entire sequence forming the saturation study.

The term "at saturation" is conventionally used to refer to various properties of the signal when the signal amplitude is at its maximum value with respect to the radio-frequency field $H_1$. 
Figure 7. The Halbach real and imaginary (quadrature) solutions for the absorption (V) mode and the dispersion (U) mode derivatives as functions of X and h_1, with the constants evaluated for lithium metal at 250°C and a modulation frequency of 42.0 cps.
\[ \text{Re } V_{\|}(x, h) = \frac{h x}{(1 + 161 h^2 + x^2)} \left\{ \frac{0.06546 h^2 + 0.1055 x^2 + 0.1055}{1.0527 h^4 - 0.09791 h^2 + 0.05275 x^4 + 0.09994 x^2 + 0.1178 h^2 x^2 + 0.05846} \right\} \]

\[ \text{Im } V_{\|}(x, h) = \frac{0.22959 h x}{(1 + 161 h^2 + x^2)} \left\{ \frac{-2.0465 h^2 - 0.05275 x^2 + 0.16103}{1.0527 h^4 - 0.09791 h^2 + 0.05275 x^4 + 0.09994 x^2 + 0.1178 h^2 x^2 + 0.05846} \right\} \]

\[ \text{Re } U_{\|}(x, h) = \frac{h}{(1 + 161 h^2 + x^2)} \left\{ \frac{h^4 - 0.09300 h^2 - 0.05275 x^4 + 0.00278 x^2 - 0.05271 x^2 h^2 + 0.05553}{1.0527 h^4 - 0.09791 h^2 + 0.05275 x^4 + 0.09994 x^2 + 0.1178 h^2 x^2 + 0.05846} \right\} \]

\[ \text{Im } U_{\|}(x, h) = \frac{0.22959 h}{(1 + 161 h^2 + x^2)} \left\{ \frac{h^4 - 0.09300 h^2 + 1.9938 h^2 x^2 - 0.15825 x^2 + 0.05553}{1.0527 h^4 - 0.09791 h^2 + 0.05275 x^4 + 0.09994 x^2 + 0.1178 h^2 x^2 + 0.05846} \right\} \]
A. Real Absorption Mode

The first interesting result of a saturation study of the absorption mode peak amplitude signal of Li$^7$ in lithium metal at 25°C is that, after applying the data to the classical (Bloch) theoretical curve, it is evident that the Bloch theory does not describe or follow the experimental data. The classical absorption mode peak amplitude as a function of the saturation factor $S$ is proportional to $S^{1/2}/(1+S)$ and has its peak value at $S = \frac{1}{2}$. The experimental data in Figure 8 have been normalized to the curve at its maximum. In Figure 8 the Halbach theoretical peak amplitude of the absorption mode derivative is also plotted. The same experimental data are normalized to the Halbach curve at its maximum which occurs at $S = 1.5$. It is apparent that within the limits of experimental error, the data do follow the Halbach curve. This means that for lithium metal at 25°C and a modulation frequency of 42.0 cps, the absorption mode peak derivative amplitude has its maximum at $S = 1.5$.

In order to determine the experimental $S$ scale the assumption was made that, at a fixed frequency of the radio-frequency oscillator of the Varian spectrometer, the amplitude of the radio-frequency magnetic field $H_1$ is directly proportional to the current in the transmitter coils. In order to have some idea of the magnitude of the current in
the transmitter coils, the voltage applied to these coils is rectified by a series combination of 3 crystal diodes. The direct current $i_{dc}$ that flows through the crystal diodes is displayed by a 100 $\mu$A ammeter.

It is possible to find the proportionality constant between $H_1$ and the metered current $i_{dc}$ experimentally. Since one can find the current, $(i_{dc})_{\text{max}}$, at which the maximum in the peak amplitude of the absorption mode derivative occurs, assuming that $S = 1.5$ at this maximum together with the fact that $S = \gamma^2 H_1^2 T_1 T_2$ and that $\gamma, T_1, \text{and } T_2$ are known, one can obtain the following equation:

$$H_1 = \frac{1}{\gamma (i_{dc})_{\text{max}}} \sqrt{\frac{1.5}{T_1 T_2}} i_{dc}.$$  \hspace{1cm} (54)

To verify this equation, an experimental run was made at about 14 Mc, and a maximum in the experimental absorption mode derivative peak amplitude was found at $i_{dc} = 120$ microamperes. Using this value of the metered current at the maximum, $(i_{dc})_{\text{max}}$, it was found that $H_1 = 90 i_{dc}$. A plot of this equation can be seen in Figure 9 together with a best-fit line through experimental data that were obtained with a calibrated search coil. Within the limit of experimental error these two methods of determining $H_1$ as a function of $i_{dc}$ are equally valid.
Figure 8. Graph of the classical (Bloch) and the Halbach theoretical absorption mode derivative peak amplitude in arbitrary units as functions of the saturation factor $S$. The circles and triangles represent one set of data of the experimental absorption mode derivative peak amplitude as a function of $S$, normalized to the two theoretical curves. The circles are normalized to the classical (Bloch) curves at its maximum which occurs at $S = 0.5$. The triangles are normalized to the Halbach curve at its maximum which occurs at $S = 1.5$. 
Figure 9. Graph of the amplitude of the radio-frequency magnetic field $H_1$ in gauss as a function of the metered current $i_{dc}$ in micro-amperes. The solid line with slope 90 gauss/ampere was experimentally derived from absorption saturation data using the Halbach theory, whereas the line with slope 81 gauss/ampere is a best-fit line through data obtained with a calibrated search coil.
AMPLITUDE IN GAUSS OF THE RADIO-FREQUENCY MAGNETIC FIELD $H_1$

DIRECT CURRENT IN MICRO-AMPERES - $i_{dc}$

90 GAUSS/AMPERE

81 GAUSS/AMPERE
Figure 10. Graph of the theoretical and experimental half peak amplitude $\alpha$ and the half width $\delta X_a/2$ of the absorption mode derivative as a function of the saturation factor $S$. The boxed insert contains a typical absorption mode derivative trace. $\alpha$ and $\delta X_a$ are defined in the insert. The experimental data are normalized to the theoretical curves at $S = 1.5$. The data points represent four different experimental runs. The four different runs are distinguishable by the use of the circle, square, triangle, and the inverted triangle. The data for $\alpha$ as a function of $S$ are represented by open circles, squares, etc., and the data for $\delta X_a/2$ as a function of $S$ by the solid data points.
Figure 11. Four graphs of one half of the real absorption mode derivative line shape at selected values of the saturation factor $S$. The solid curves are the averaged experimental line shapes and the points are the Halbach theory points. The theoretical points are normalized to the experimental curves at their maxima. The ordinate scales are in arbitrary units.
In establishing the validity of Equation 54 it has also been proven that indeed $S = 1.5$ at the maximum of the experimental absorption mode derivative peak amplitude.

In Figure 10, the Halbach theoretical half peak amplitude $\alpha$ and the half width $S_{X_a}/2$ are plotted as functions of $S$ over a range of $S$-values from about 0.1 to over 100. Also in Figure 10, the experimental data from 4 different saturation studies of the half peak amplitude and half width are plotted as functions of $S$. The experimental data are fitted to the curves at $S = 1.5$.

At $25^\circ C$ lithium metal is unusual both in the sense that its nuclear magnetic resonance line is very narrow and also in that the resonance saturates at such a small value of $H_1$ compared to most other metals. The first effect arises from the relatively small value of the activation energy for self-diffusion, and the second from the relatively large value of the spin-lattice relaxation time $T_1$. Because the resonance saturates so readily, the linear range of $S$-values obtainable with lithium with a typical induction spectrometer is much greater than that obtainable with most other materials.

In the saturation study of the real absorption mode derivative, four line shape studies were made at $S$-values of 0.1, 1.45, 10.1, and 103. Figure 11 displays four averaged
experimental line shapes drawn as solid curves onto which the theoretical points are superimposed. Averaged experimental line shapes were used to remove minor fluctuations resulting from magnetic field and radio-frequency drift during the time of recording. The theoretical points are fitted to the experimental curves at the point of maximum amplitude.

B. Complex Absorption Mode

From the calculations of the Halbach theoretical real and imaginary (quadrature) absorption mode derivative line shapes it is found that the intensity of the imaginary component is much less than that of the real part. As will be seen in the following discussion, the actual recorded signal is consequently a sensitive function of the phase angle between the in-phase (real) signal and the actual or complex signal.

The NMR signal recorded by the graphic recorder enters the output control unit of the spectrometer as time-varying amplitude signal having the frequency $\Omega_m$ of the modulation field. In the normal operation of the Varian spectrometer it is necessary to frequently readjust a phasing control resistor in the output control unit, so that with proper adjustment the signal amplitude at the chopper contacts of the synchroverter is zero when switching occurs. In this way, the signal recorded by the graphic recorder is in phase with the
Figure 12. Vector diagram of the complex absorption mode derivative amplitude $A$ at a given instant. $	heta$ is the phase angle between the complex absorption mode derivative and the real absorption mode derivative.
\[ A = \text{Re} V_{II}(X) \cos \theta + \text{Im} V_{II}(X) \sin \theta \]
modulation field. If, however, it is desired to record the signal that is 90 deg out of phase with respect to the modulation field phase, more precise and reproducible control of the relative phase is required, because of the considerable disparity in amplitude of the real and imaginary components of the signal.

For this purpose the single turn 470,000 ohm variable resistor used in the modulation phasing control was replaced by a variable series resistance network which contained a 30,000 ohm ten-turn helipot so that the resistance could be reset with precision.

With the advent of the use of this precision phasing control, several peculiarly shaped signals were recorded in the vicinity of the out of phase position. In order to understand these unusual shapes, complex derivative line shapes were calculated from the real and imaginary signal shapes derived from the Halbach theoretical expressions. Figure 12 displays a vector diagram for the calculation of the theoretical complex absorption mode derivative line shape. The angle \( \Theta \) is defined as the phase angle between the modulation field and the recorded signal. The intensity of the complex line shape for a given value of \( \Theta \) is evaluated for each X point using the equation displayed in Figure 12.
Figure 13 contains several of the theoretical complex absorption mode derivative line shapes for values of the phase angle $\Theta$ near 90 deg. Note that as $\Theta$ increases from about 90 deg, the resonance tails cross the X axis and at the same time the peak intensity diminishes. At values of $\Theta$ between roughly 93 and 105 deg there are two sets of peaks in the line shape. For the last shape in Figure 13, $\Theta = 110$ deg, and the inner peak is no longer visible.

A plot of the theoretical inner and outer peak amplitudes as a function of the phase angle $\Theta$ for $S = 1.5$ is shown in Figure 14. The curves for the inner and outer peak amplitudes intersect at 98.1 deg. This intersection of the two amplitude curves provides a very sensitive method for adjusting the experimental modulation phase in the Varian spectrometer. In Figure 14, the amplitude of the inner and outer peaks at the point where they are equal is 24.5 arbitrary units, whereas the amplitude of the inner peak at 90 deg is 59.5 units. Thus, the amplitude of the inner peak at 90 deg is $59.5/24.5 = 2.41$ times its amplitude at 98.1 deg where the inner and outer peak amplitudes are equal. This relation can be used in determining the correct experimental 90 deg and zero degree phase positions of the phasing control resistor.

In carrying out the experimental determination of the proper setting of the phasing control resistor a sequence of
Figure 13. Graph of the theoretical complex absorption mode derivative at a saturation factor value $S = 1.5$ and at several selected values of the phase angle $\theta$. The insert at the lower center of the figure defines the amplitude $A$ and the dimensionless parameter $X$. 
Figure 14. Graph of the so-called inner and outer peak amplitudes of the complex absorption mode derivative as a function of the phase angle $\theta$ for one value of the saturation factor, $S = 1.5$. 
INNER PEAK AMPLITUDE

OUTER PEAK AMPLITUDE

(90.0°, 59.5)

(98.1°, 24.5)
Figure 15. Circuit diagram of the 90 degree electronic phase shifter and associated cathode follower circuit.
Figure 16. A typical complex absorption mode derivative recording sequence used to determine the $0^\circ$ or $90^\circ$ phase positions. The numbers 0, 25, 50, 75, etc., to the right of the traces indicate the respective helipot setting of the phasing control resistor. During $0^\circ$ and $90^\circ$ phase angle position determinations of this type, the experiment is performed at a saturation factor value of $S = 1.5$. 
Figure 17. Graph of the experimental inner and outer peak amplitudes of the complex absorption mode derivative data shown in the preceding figure.
NMR signals resembling the shapes of those in Figure 13 are recorded. A typical sequence of such experimental recordings is shown in Figure 16. The experimental inner and outer peak amplitudes in arbitrary units of the traces seen in Figure 16 are shown in Figure 17 as functions of the helipot setting of the phasing control resistor. One may note in Figure 17 that the experimental inner and outer peak amplitude curves intersect at an amplitude of 19.3 arbitrary units. Moving along the experimental inner peak amplitude curve to an amplitude which is $2.41 \times 19.3 = 46.5$ units shows that the $\theta = 90$ deg position should occur at a helipot setting of 56.8.

In the Varian spectrometer, the demodulated resonance signal is normally directed from the radio-frequency amplifier to the synchroverter. In order to precisely determine the phasing control setting corresponding to $\theta = 0$ deg, the signal is interrupted between the radio-frequency amplifier and the synchroverter and sent into a 90 deg phase shifter and cathode follower circuit (see Figure 15). The output signal from this circuit is then sent to the synchroverter. By the same procedure used to determine the $\theta = 90$ deg phasing control position, an apparent 90 deg helipot setting can be obtained. By-passing the 90 deg phase shifter circuit, the signal is now in phase with the modulation field.

The phase shifter shown in Figure 15 was constructed such
that it could be set to provide an exact 90 deg shift for 20, 40, 80, 200, and 400 cps, as well as for any other audio-frequency which might be used as a modulation frequency with the Varian spectrometer.

C. Imaginary (Quadrature) Absorption Mode

Figure 18 contains five selected theoretical imaginary (quadrature) absorption mode derivative line shapes. Note that for very low values of $S$ the tails of the curves cross the X-axis. As $S$ is increased the same qualitative change in the line shape occurs that occurred in the complex absorption line shape as the phase angle $\theta$ was changed. At large $S$-values, the curve has turned over and the tails no longer cross the X-axis.

The theoretical inner and outer peak amplitudes of the imaginary derivative as functions of the square-root of the saturation factor, $S^{\frac{1}{2}}$, are displayed in Figure 19. Note that the inner and outer peak amplitude curves intersect at $S^{\frac{1}{2}} = 3.02$. This corresponds to an $S$-value of 9.12.

A saturation study was performed on the imaginary absorption mode. The data of this study in the form of the experimental inner and outer peak amplitudes in arbitrary units as functions of the metered current $i_{dc}$ is displayed in Figure 20. For higher values of $i_{dc}$ a straight line is drawn through
Figure 18. Graph of several theoretical imaginary (quadrature) absorption mode derivatives at selected values of the saturation factor $S$. The insert at the lower center of the figure defines the ordinate and the dimensionless parameter $X$. 
Figure 19. Graph of the theoretical inner and outer peak amplitude of the imaginary (quadrature) absorption mode derivative as functions of the square root of the saturation factor, $S^\theta$. 
Figure 20. Graph of the experimental inner and outer peak amplitudes of the imaginary (quadrature) absorption mode derivative as functions of the current \( i_{dc} \).
IMAGINARY ABSORPTION PEAK AMPLITUDES IN ARBITRARY UNITS

DIRECT CURRENT IN MICRO-AMPERES - \( i_{dc} \)

INNER PEAK AMPLITUDE

OUTER PEAK AMPLITUDE

(286, 14.6)
the inner peak amplitude data and a smooth curve is drawn through the outer peak amplitude data. These experimental curves intersect at a current value of 286 μA. For this particular run the maximum in the real absorption mode derivative peak amplitude occurred at \((i_{dc})_{\text{max}} = 115 \, \mu A\). Using this number an \(S\)-value of 9.28 is calculated for the current of 286 μA from the relation

\[ S = 1.5 \frac{i_{dc}}{((i_{dc})_{\text{max}})^2}. \]

This result indicates an alternate method of phasing the Varian spectrometer. By adjusting the current to correspond to an \(S\)-value of 9.12 and recording the inner and outer peak amplitudes for various settings of the phasing control resistor, one can find the setting of the phasing control resistor corresponding to equal inner and outer peak amplitudes of the experimental signal. At this setting \( \Theta = 90 \, \text{deg} \).

Although no data is provided in this report with respect to this method of 90 deg or zero deg phase determination, one must realize that the signal-to-noise ratio of the experimental traces is not nearly as good as it is at a power level corresponding to \(S = 1.5\). For that reason, the phasing method based on the complex absorption mode signal is to be preferred in practice.
D. Real Dispersion Mode

A typical real dispersion mode derivative line is pictured in the boxed insert in Figure 21. The central peak of the dispersion mode derivative has an amplitude designated by a. The outer side peaks have an absolute amplitude called b. The overall amplitude of the dispersion derivative line is a+b.

Figure 21 is a graph of the theoretical amplitudes a, b, and a+b; the ratio of the inner and outer amplitudes a/b; and the half width $\delta X_d/2$ of the real dispersion mode derivative as functions of the saturation factors.

A saturation study of the dispersion mode for Li$^7$ in lithium metal at 25°C was made. The data for the various parameters as functions of S can be seen in Figure 22. The S-values were determined from the real absorption mode saturation data in the manner previously described and are related to the metered current $i_{dc}$ in the manner shown in Figure 9.

One should note in Figure 22 that no data were obtained below $S = 1$. It is characteristic of the Varian spectrometer that at the low currents corresponding to $S = 1$ for lithium metal at 25°C the spectrometer can not be adjusted properly.
Figure 21. Graph of the theoretical inner amplitude \(a\), outer amplitude \(b\), maximum amplitude \(a+b\), ratio of the inner and the outer amplitudes \(a/b\), and the half width \(\delta x_d/2\) of the dispersion mode derivative as a function of the saturation factor \(S\). The boxed insert of the typical dispersion mode derivative in the upper right hand corner of this graph defines \(a\), \(b\), and \(\delta x_d\).
SATURATION FACTOR $S = \gamma^2 H_1^2 T_1 T_2$

$a, b$, and $a+b$ in ARBITRARY UNITS

$\frac{\eta}{a+b}$ and $\frac{a}{b}$ in DIMENSIONLESS UNITS

$Bx_d$
Figure 22. Graph of the experimental inner amplitude $a$ represented by open circles, outer amplitude $b$ represented by open squares, maximum amplitude $a+b$ represented by open triangles, and the half width $\Delta X_d/2$ by inverted triangles, and the ratio of inner and outer amplitudes $a/b$ represented by solid circles, of the real dispersion mode derivatives as functions of $S$. The data of $a$ vs. $S$ were normalized to the theoretical curve at $S = 1.0$, $b$ vs. $S$ at $S = 5$, $a+b$ vs. $S$ at $S = 1$, and $\Delta X_d/2$ at $S = 1.5$. 
a, b, and a+b in arbitrary units

\[
\frac{3X_{d}}{2} \quad \text{and} \quad \frac{a+b}{2}
\] in dimensionless units
Figure 23. Three graphs of one half of the real dispersion mode derivative line shape at selected values of the saturation factor $S$. The solid curves are the averaged experimental line shapes and the points are the Halbach theory points. The theoretical points are normalized to the experimental curves at their minima.
Figure 24. Three graphs of the theoretical imaginary (quadrature) dispersion mode derivatives as functions of the dimensionless parameter $X$, at several values of the saturation factor $S$. 
by means of the flux-steering paddles to obtain the required flux leakage from the transmitter coils to the receiver coils. This, however, is not true in the case of the absorption mode. For the absorption mode the required leakage can be obtained at relatively low current values.

Figure 23 contains the graphs of one half of an averaged experimental real dispersion mode derivative line shape at three values of the saturation factor, 5.8, 10.1, and 103. The amplitudes and X scales of the theoretical Halbach line shape points for these S-values are normalized to the averaged experimental curves at their minima.

E. Imaginary (Quadrature) Dispersion Mode

From the machine calculations of the imaginary dispersion mode line shape it was apparent that the signal undergoes three typical shapes with increasing values of the saturation factor S. Figure 24 contains three graphs of these typical imaginary dispersion mode line shapes. Figure 24 shows that at an S-value of 1.95 the imaginary dispersion line has the shape, qualitatively, of the real dispersion derivative line. The imaginary dispersion shape at $S = 19.7$ resembles the shape of the real absorption mode signal $M_y$ seen as a function of $H$ in Figure 3. The final shape at $S = 48.7$ is an unusual resonance shape that has a peculiar
relative minimum at its center.

Actually, the range of S-values within which the quadrature dispersion mode derivative shape approximates that of the real absorption mode signal is quite narrow, beginning at $S = 12.6$ and ending at approximately $S = 30$ at which value the onset of the indented line shape occurs.

Figure 25 contains three pairs of experimental imaginary (quadrature) dispersion mode line shapes that were recorded at currents which have corresponding S-values very near those of the theoretical line shapes in Figure 24.
Figure 25. Three pairs of experimental imaginary (quadrature) dispersion mode derivative line shapes at selected values of the saturation factor $S$. The amplitudes of these curves are not to be compared.
V. CONCLUSIONS

The experimental work reported herein has demonstrated that the behavior of the Li\(^7\) NMR in lithium metal at 25°C is very closely described by the original Bloch equations as modified by Halbach. This means that within the temperature range in which, from the nuclear resonance standpoint, significant self-diffusion occurs, the environment of the nuclei is effectively in the liquid state. All of the assorted types and shapes of resonance signals observed in this work are accounted for within the context of this theory.

The existence of the four types of signals predicted by the Halbach theory has been convincingly shown. These are the real, or in-phase, and imaginary, or out-of-phase absorption and dispersion mode signals. In addition, the existence of a complex absorption mode signal has been demonstrated, and its behavior as a function of the phase \(\Theta\) has been used to determine accurately the \(\Theta = 90\) deg setting. This determination was cross-checked by using the behavior of the imaginary (quadrature) absorption mode signal as a function of the radio-frequency amplitude \(H_1\).

With respect to saturation effects, the Bloch-Halbach theory is found again to describe very satisfactorily the behavior of the nuclear resonance signals, both absorption and
dispersion modes. This agreement has been found to hold over a wide range of the radio-frequency amplitudes $H_1$, including quite large values.

In summary, the behavior of the Li$^7$ NMR in lithium metal at a temperature within the range in which motional narrowing of the resonance occurs has been shown to be satisfactorily described by the Bloch-Halbach theory involving only two parameters characteristic of the material, namely the relaxation times $T_1$ and $T_2$. 
VI. REFERENCES


