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AN INVESTIGATION OF THE DIRECT SPIN-LATTICE INTERACTION
IN PARAMAGNETIC CRYSTALS BY THE
METHOD OF ULTRASONIC PARAMAGNETIC RESONANCE

by

Grover C. Wetsel, Jr.

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Thesis Director’s signature:

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I. INTRODUCTION

The interaction between the system of electron spins of a paramagnetic ion and the crystalline lattice which contains the ion is an important phenomenon in the physics of paramagnetic solids. From the viewpoints of both theoreticians and experimentalists, the subject of spin-lattice interactions has been of interest for some time. The principal problem has been to determine the nature of the interaction for a particular type of ion, and several processes have been suggested (See review by Pake in *Paramagnetic Resonance*¹). It is the purpose of the investigation described in this thesis to obtain information about one process, the "direct process," in several types of paramagnetic solid.

Phenomenologically, the exchange of energy between the spin system and the lattice has been described by a rate equation²,

\[
(1-1) \quad \frac{d}{dt} (\Delta n - \Delta n_0) = - \frac{(\Delta n - \Delta n_0)}{T_1}
\]

where \( \Delta n \) is the population difference between two spin energy levels, \( \Delta n_0 \) is the difference at thermal equilibrium, and \( T_1 \) is the "spin-lattice relaxation time." Much effort has been expended toward measuring \( T_1 \) for various ions in solids. However, it turns out, as might be expected, that \( T_1 \) is the result of all processes that contribute to relaxation, so that a measurement of \( T_1 \) does not in general give a direct measure-
ment of the effect of a particular one of the various processes.

The direct, or "one-phonon" process of spin-lattice relaxation involves the exchange of a single quantum of energy between the spin and lattice; the spin system of the paramagnetic ion emits a quantum of energy $\hbar \nu$, and a phonon of lattice energy is created ($\nu = \text{frequency of phonon}$). The direct process is a first-order process and is expected to dominate over other relaxation processes at low temperatures; hence, it is worthy of investigation.

In a reformulation and extension of earlier theories, Mattuck and Strandberg$^3$ have presented a theory of the direct process for certain iron-group ions in such a form that it can be compared with experiment. The result of their calculation is presented in the form of an effective "spin-lattice Hamiltonian" which is analogous in its utilization to the more common "spin Hamiltonian" used by experimentalists in electron paramagnetic resonance (EPR) studies. This spin-lattice Hamiltonian is treated as a perturbation on the eigenstates of the spin Hamiltonian. It contains unknown parameters which would be very difficult, if not impossible, to calculate accurately, but which can be measured experimentally. This work has thus inspired investigations at Rice which have as their purpose the experimental determination of the nature of spin-lattice Hamiltonians for various ions, not
only those ions explicitly covered by the theory of Mattuck and Strandberg, but also some "rare-earth-type" ions.

Two types of experiment were suggested by Mattuck and Strandberg as possible means of verifying their theoretical arguments: (1) ultrasonic paramagnetic resonance and (2) ultrasonic saturation of the EPR signal. The essentials of these two methods plus those of a third utilizing the application of a steady strain to the paramagnetic crystal are described below.

Ultrasonic paramagnetic resonance (UPR) involves the measurement of the attenuation of high-frequency elastic waves in a paramagnetic crystal when the crystal is placed in an external magnetic field of magnitude equal to that necessary for electron paramagnetic resonance. Under these conditions, the system of paramagnetic ions absorbs energy from the elastic wave in a resonant manner quite similar to EPR. In essence, this process is spin-lattice relaxation in reverse. This method has been used by several investigators\(^4,5,6,7,8\) and a review by Russian authors has been published\(^9\).

The saturation method also involves the interaction of high frequency elastic waves with the spin system\(^10,11,12,13\). In this method, with the frequency of the elastic waves at a given value, the paramagnetic resonance frequency is varied. It is found that there is a resonant decrease in the EPR signal as the EPR frequency is varied through the frequency of the
elastic waves. This effect is a result of saturation by the elastic waves, and thus is a measure of the spin-lattice interaction.

A third technique, the steady-strain method, has been used here at Rice\textsuperscript{14} and elsewhere. This method utilizes the measurement of the change in the EPR frequency when the paramagnetic sample is subjected to a steady strain. This change in resonant frequency is related to the spin-lattice interaction (direct process). Thus, the nature of the spin-lattice Hamiltonian can also be deduced from such a measurement.

The advantages and disadvantages of each of the three methods seemed clearly defined at the beginning of this investigation. However, it now appears that the selection of the experimental method must be made for each type of ion of interest, and a combination of methods may be necessary. In fact, if a comprehensive program of spin-lattice interaction studies is to be maintained, it would be appropriate to have available the apparatus for each method. The advantages and disadvantages of each method are discussed in Section VII.

The method of ultrasonic paramagnetic resonance is used in this investigation. As discussed above briefly, and in detail in Section IV, this method consists of measuring the attenuation of high frequency (9.3 Gc) elastic waves in a paramagnetic sample when the magnitude of an external magnetic field is varied through the value for electron paramagnetic
resonance. The attenuation is proportional to the square of the absolute value of the matrix element of the spin-lattice Hamiltonian between eigenstates of the spin Hamiltonian. Measurement of the attenuation for various types of elastic waves thus allows the evaluation of the spin-lattice Hamiltonian.

The samples considered in this investigation are tetra-valent uranium in calcium fluoride (\(\text{U}^{4+}\):CaF\(_2\)), trivalent uranium in calcium fluoride (\(\text{U}^{3+}\):CaF\(_2\)), and trivalent chromium in aluminum oxide (\(\text{Cr}^{3+}\):Al\(_2\)O\(_3\)). It was originally planned to study only \(\text{U}^{3+}\):CaF\(_2\) because its properties are suitable for spin-lattice investigations, because the rare-earth-type ions had not been studied, and because "laser quality" crystals of U\(^{3+}\):CaF\(_2\) were available, supposedly in a relatively short delivery time. When the crystal was obtained and the UPR measurements were made, it was found that no attenuation could be observed which could be attributed to U\(^{3+}\) ions. However, attenuation of significant amplitude was observed. The absorption lines were broad and extremely asymmetric. About this time, reports\(^{15,16}\) appeared describing the EPR absorption of U\(^{4+}\) ions in CaF\(_2\). A subsequent EPR analysis on the sample and comparison with these reports revealed that the crystal did indeed contain significant amounts of U\(^{4+}\). Although the samples on hand were not sufficient for a complete analysis of the spin-lattice interaction, certain observations could be made, and the results were reported\(^{17}\).

When it was learned that the crystal had an insufficient
quantity of $U^{3+}$, a new crystal of $U^{3+}:CaF_2$ was ordered from a different supplier. When the latter crystal was received, it was found to contain $U^{3+}$. However, time has not permitted a complete analysis of this ion, and only preliminary results have been obtained.

The third type of sample, $Cr^{3+}:Al_2O_3$ (ruby), was one on hand on which some work had already been done. Since it would be beneficial to complete this work, and compare the results with those from strain measurements, ruby was studied by the UPR method.

The three types of ion are really quite different in terms of their spin-lattice Hamiltonians, and the theory of each will be presented separately.
II. THEORY

2.1 The Spin-Lattice Hamiltonian

The spin-lattice Hamiltonian is an effective Hamiltonian containing unknown parameters and effective spin operators which can be used to describe the effect of lattice vibrations or lattice strain on the ground-state energy levels of a paramagnetic ion in a crystalline solid. When treated as a perturbation on the eigenstates of the more familiar spin Hamiltonian, the spin-lattice Hamiltonian can be used to explain the attenuation of elastic waves in ultrasonic paramagnetic resonance or the change in the ion energy levels in a steady-strain experiment.

One may assume that lattice vibrations or lattice strain produces a term which is proportional to strain in the total Hamiltonian for the ion (A term proportional to displacement of the atoms would produce no change in electric field at the ion.):

\[ V = \sum_{i,j} U_{ij} u_{ij} \]

where \( U_{ij} \) is a function of the electron coordinates and \( u_{ij} \) is a strain component. This term leads to the spin-lattice Hamiltonian.

The case discussed by Mattuck and Strandberg\textsuperscript{20}, that of certain non-S state iron-group ions, yields a spin-lattice Hamiltonian which can be written in the form,
\[ (2-2) \quad H_{SL} = \sum_i A_i S_i + \sum_{ij} F_{ij} B_i S_j + \sum_{ij} D_{ij} S_i S_j. \]

The quantities \( A_i, F_{ij}, \) and \( D_{ij} \) are dependent upon the crystalline electric field at the site of the ion, and are assumed to vanish with strain; the \( S_i \) are effective spin operators; and \( B_i \) is a component of the external magnetic field. It might seem reasonable for the spin-lattice Hamiltonian of eq. (2-2) to be more general than implied by the theory of Mattuck and Strandberg. One might expect that one or more of the terms would dominate for a given type of ion, but otherwise that the form is applicable to ions such as \( U^{4+} \) and \( U^{3+} \). The validity of this surmise is discussed separately for each type of ion.

2.2 - \( U^{4+}:CaF_2 \)

A. Description of \( U^{4+}:CaF_2 \)

Tetravalent uranium \( (U^{4+}) \) as found in a crystal of calcium fluoride \( (CaF_2) \) has interesting if experimentally frustrating properties. The ground state of the \( U^{4+} \) ion in the crystalline field of \( CaF_2 \) is what is known as a "non-Kr"amers doublet"; that is, its degeneracy can be removed by local deviations in the crystalline electric field from the primary symmetry at the site of the ion. This is to be contrasted with the behavior of a "Kramers doublet" whose degeneracy can be removed only by the application of an external magnetic
field. As will be explained below, the non-Kramers behavior of $U^{4+}$ leads to broad, asymmetric, absorption line-shapes which make the measurement of attenuation difficult.

Tetravalent uranium has two 5f electrons, which are responsible for its paramagnetic properties. The electrostatic interaction produces a ground-state term of $^3H$. If L-S coupling is assumed to hold, and apparently it does for $U^{4+}$, the ground state of the free ion is a term of the form $^3H_4$, which is nine-fold degenerate. This is depicted by the energy schematic diagram in Figure 1.

The crystal structure of CaF$_2$ is illustrated in Figure 2. The space lattice is face-centered-cubic$^{21}$. Each calcium ion is surrounded by eight fluorine ions on the corners of a cube centered at the calcium ion. Each fluorine ion is surrounded by four calcium ions on the corners of a tetrahedron centered at the fluorine ion. The $U^{4+}$ ion substitutes for a Ca$^{2+}$ ion in $U^{4+}$:CaF$_2$. For charge compensation, two F$^-$ ions replace the F$^-$ ions at opposite corners of the body diagonal through the $U^{4+}$ ion, according to the model proposed by Title, et al.$^{22}$. This is illustrated in Figure 2. This arrangement defines an axis of symmetry for the crystalline field at the $U^{4+}$ ion. The symmetry of the crystalline field is $C_{3v}$, which means that the axis is one of three-fold rotational symmetry to which three planes of symmetry are parallel. It should be noticed that the $C_{3v}$
ENERGY SCHEMATIC DIAGRAM FOR $U^{4+}: \text{CaF}_2$

FIGURE 1
Figure 2: Diagram of CAF₂-U⁴⁺ and U⁴⁺ and nearest neighbors.
axis of the paramagnetic ion is along a (111) direction of the \( \text{CaF}_2 \) lattice. Since there are four possible (111) type directions - (111), (1̅1̅1), (11̅1), and (1̅1̅1) - there are four equally probable possibilities for the axis of the \( \text{U}^{4+} \) ion. This manifests itself in the paramagnetic resonance spectrum of the crystal, where, in general, four lines appear corresponding to the four "types of magnetic ion."

The ground state of the free ion, the \( ^3H_4 \) level, is split into three singlets and three non-Kramers doublets by the \( \text{C}_{3v} \) crystalline field. A doublet lies lowest in energy and is responsible for the EPR spectrum observed at 4.2°K.

B. The Spin Hamiltonian

The spin Hamiltonian is an effective Hamiltonian operator which can be used to describe the behavior of the ground state of a paramagnetic ion in a crystalline lattice when the crystal is placed in an external magnetic field. It contains effective spin operators and unknown parameters which are related to the crystalline electric field at the site of the ion. These parameters are determined experimentally by electron paramagnetic resonance (EPR) measurements. The spin Hamiltonian is therefore a mathematical device used by experimentalists to describe the observed EPR spectrum.

The theory of electron paramagnetic resonance in ions with a non-Kramers-doublet ground state has been discussed by
Baker and Bleaney\textsuperscript{23}. The EPR spectrum of U\textsuperscript{4+} in CaF\textsubscript{2} was reported by Title\textsuperscript{24}, et al., and by Yariv\textsuperscript{25}.

The ground state of the free U\textsuperscript{4+} ion is $3\text{H}_4$, which is nine-fold degenerate, corresponding to values of $M_J = 4, 3, \ldots, 0, \ldots, -4$. If one assumes that the set of nine wavefunctions characteristic of $M_J$ form a basis for the ground state of the ion, the total Hamiltonian consisting of that for the free ion plus the crystalline field can be diagonalized. The results show that, for a perfect $C_{3v}$ crystalline field, the $3\text{H}_4$ level splits into three singlets and three doublets. According to Judd\textsuperscript{26}, who has made the crystalline field calculations for $4f^2$ electrons, the ground state is a doublet described by wave functions of the type:

\begin{equation}
|\alpha\rangle = a|4\rangle + b|1\rangle + c|-2\rangle.
\end{equation}

\begin{equation}
|\beta\rangle = a|-4\rangle - b|-1\rangle + c|2\rangle.
\end{equation}

These are eigenfunctions of the square of the total angular momentum ($J = 4$). The numbers in the kets refer to values of $M_J$.

When the crystal is placed in a magnetic field, the degeneracy is lifted by the additional term in the Hamiltonian,

\begin{equation}
H^{(z)} = \beta \mathbf{E} \cdot (\mathbf{I} + 2\mathbf{S}),
\end{equation}

where $\mathbf{E}$ is the magnetic field, $\mathbf{I}$ is the total orbital angular
momentum, $\mathbf{S}$ is the total spin angular momentum for the ion, and $\beta$ is the Bohr magneton. If the energy of the first excited state (\( S \) in Figure 1) is much greater than the Zeeman energy, the total Hamiltonian consisting of that for the free ion plus crystalline field and $H'$ can be diagonalized, using $|\alpha\rangle$ and $|\beta\rangle$, to obtain the Zeeman energy. The result of this calculation can be put in the form of an effective Hamiltonian. The off-diagonal elements, $\langle \alpha | H' | \beta \rangle$, are zero, and the spin Hamiltonian is

\begin{equation}
H_s = g_{||} \beta B_z S_z,
\end{equation}

where

\begin{equation}
g_{||} = 2 \langle \alpha | L_z + 2S_z | \alpha \rangle = \frac{8}{5} \left[ \frac{4 |a|^2 + |b|^2 - 2 |c|^2}{2} \right]
\end{equation}

and $S_z$ is an effective operator of spin 1/2. Since the coefficients $a$, $b$, and $c$ are unknown, $g_{||}$ is obtained by experiment. (It must be remembered that the $z$ axis referred to here is the symmetry axis of the ion in the $C_{3v}$ crystalline field.)

The Hamiltonian of equation (2-6) does not include all the effects of the crystalline field, however. It has been derived with the assumption of perfect $C_{3v}$ symmetry. Since the doublet is non-Kramers, small local departures from the $C_{3v}$ electric field at the site of the ion as a result of random strains can remove the degeneracy. To include this possibility, the spin Hamiltonian is finally written (neglecting hyperfine.

-12-
terms) as \(27\)

\[
H_S = g_{||} \beta B_z S_z + \Delta_x S_x + \Delta_y S_y
\]

where \(\Delta_x\) and \(\Delta_y\) represent the effects of local strain. These values vary from site to site, and thus lead to an asymmetric line shape, as will be discussed below.

The spin Hamiltonian of eq. (2-8) is taken as the unperturbed Hamiltonian for the problem of the interaction between the elastic waves in the lattice and the spin system of the ion. The spin-lattice Hamiltonian will then be treated as the perturbation on the eigenfunctions of \(H_S\). With this viewpoint, one must solve the spin Hamiltonian for its eigenvalues and eigenfunctions. This calculation is performed in Appendix 8.1. The energy eigenvalues of \(H_S\) are

\[
E_{\pm} = \pm 1/2 \sqrt{(g_{||} \beta B_z)^2 + \Delta^2},
\]

where \(\Delta^2 = \Delta_x^2 + \Delta_y^2\).

The value of \(g_{||}\) has been measured by Yariv \(28\) to be 3.238 \(\pm\) .005 at 4.2°K. Yariv also found that the rms value of \(\Delta\) was on the order of 0.1 cm\(^{-1}\). The parameter \(\Delta\) is the zero-field splitting for a particular ion. From equation (2-9), the resonant magnetic field can be obtained. If the energy of transition between the levels is \(h\nu\), then

\[
B_z = B \cos \alpha = \frac{\sqrt{(h\nu)^2 - \Delta^2}}{g_{||} \beta}
\]
where \( \alpha \) is the angle \( \beta \) makes with the ion axis.

As Baker and Bleaney pointed out, the most probable value of \( \Delta \) is zero. For UPR, the peak absorption will therefore occur at a value of \( B \) corresponding to \( \Delta = 0 \). Since this value of \( B \) is the maximal value for resonance, the absorption versus magnetic field will increase slowly from zero, peak, and then decrease very rapidly to zero on the high field side. For \( \Delta = 0 \), the value of \( B \) for resonance is then

\[
(2-11) \quad B = \frac{\hbar \nu}{\gamma_i B \cos \alpha}.
\]

The curves of Figure 4 were drawn through points calculated from eq. (2-11). The value of \( B \) for resonance is understood to be that measured at peak absorption in the UPR experiment in the discussion that follows.

The situation for an EPR measurement is slightly different. The absorption line in this case has the same general shape but the peak does not occur for a value of \( B \) corresponding to \( \Delta = 0 \). This can be understood by referring to Appendix 8.1 where the transition probability for EPR is calculated. It is shown there that the absorption depends upon \( \Delta \) and vanishes when \( \Delta = 0 \). It follows that the peak in an EPR absorption-line occurs at a lower value of \( B \) than that for UPR.
C. The Spin-Lattice Hamiltonian

The spin-lattice Hamiltonian for U\(^{4+}\):CaF\(_2\) will be derived assuming that the lattice strain creates a term, \(V\), in the total Hamiltonian for the ion which represents a deviation from perfect \(C\(_{3v}\) crystalline potential energy. This potential, \(V\), plus the Zeeman energy will be treated as a perturbation on the Hamiltonian for the free ion plus \(C\(_{3v}\) potential.

Let the energy of the ground state doublet in the \(C\(_{3v}\) potential be \(E_0\) and the doublet wave functions be those of eqs. (2-3) and (2-4). Then,

\[
(2-12) \quad H_o |\alpha\rangle = E_0 |\alpha\rangle \\
(2-13) \quad H_o |\beta\rangle = E_0 |\beta\rangle 
\]

where \(H_o\) is the total Hamiltonian for the free ion in the \(C\(_{3v}\) crystalline field. The perturbing Hamiltonian is

\[
(2-14) \quad H' = H^{(z)} + V ,
\]

where \(H^{(z)}\) is given by eq. (2-5).

Assume that \(|\alpha\rangle\) and \(|\beta\rangle\) form a sufficient set of wave functions for the problem in the first approximation. Expand the eigenfunctions, \(\Psi\), of the total Hamiltonian, \(H\), as a linear combination of \(|\alpha\rangle\) and \(|\beta\rangle\).

\[
(2-15) \quad H = H_o + H' \\
(2-16) \quad H\Psi = E\Psi
\]
Substitution of $\psi$ in terms of $|\alpha\rangle$ and $|\beta\rangle$ into (2-16) leads to the secular determinant, the solution of which yields the energy eigenvalues of $H$:

\begin{equation}
\begin{vmatrix}
H'_{\alpha,\alpha} - (E - E_0) & H'_{\alpha,\beta} \\
H'_{\beta,\alpha} & H'_{\beta,\beta} - (E - E_0)
\end{vmatrix} = 0
\end{equation}

where $H'_{\alpha,\beta}$ is the matrix element of $H'$ between $|\alpha\rangle$ and $|\beta\rangle$, etc.

In order to calculate matrix elements of $H^{(z)}$, one can use the following relation, which is valid between states of the same $J$:

\begin{equation}
\langle J, \cdots | (L + 2S) | J, \cdots \rangle = \langle J | \Lambda | J \rangle \langle J, \cdots | J | J, \cdots \rangle,
\end{equation}

where

\begin{equation}
\langle J | \Lambda | J \rangle = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}.
\end{equation}

For $U^{4+}$, $J = 4$, $L = 5$, and $S = 1$. Therefore

\begin{equation}
\langle J | \Lambda | J \rangle = \Lambda = 4/5.
\end{equation}

Then, the matrix elements for $H^{(z)}$ can be written:

\begin{equation}
\langle 1 | H^{(z)} | 1 \rangle = \Lambda \langle 1 | \mathbf{E} \cdot J | 1 \rangle,
\end{equation}

\begin{equation}
\langle \alpha | J_z | \alpha \rangle = 4|a|^2 + |b|^2 - 2|c|^2,
\end{equation}

\begin{equation}
\langle \beta | J_z | \beta \rangle = -4|a|^2 - |b|^2 + 2|c|^2 = -\langle \alpha | J_z | \alpha \rangle.
\end{equation}
(2-24) \[ \langle \alpha | J_x | \alpha \rangle = \langle \beta | J_x | \beta \rangle = 0, \]
(2-25) \[ \langle \alpha | J_y | \alpha \rangle = \langle \beta | J_y | \beta \rangle = 0. \]

If \( c \) and \( b \) are real, as indicated by Judd\textsuperscript{30},

(2-26) \[ \langle \alpha | J_x | \beta \rangle = \langle \alpha | J_y | \beta \rangle = \langle \alpha | J_z | \beta \rangle = 0. \]

Therefore:

(2-27) \[ \langle \alpha | H^{(z)} | \alpha \rangle = \Lambda \beta B_z \langle \alpha | J_z | \alpha \rangle, \]
(2-28) \[ \langle \beta | H^{(z)} | \beta \rangle = -\Lambda \beta B_z \langle \alpha | J_z | \alpha \rangle, \]
(2-29) \[ \langle \beta | H^{(z)} | \beta \rangle = 0. \]

With the use of eq. (2-7), the secular determinant becomes:

(2-30) \[
\begin{vmatrix}
V_{\alpha,\alpha} & \frac{1}{2} g_{ij} \beta B_z - (E - E_o) \\
V_{\beta,\alpha} & [V_{\beta,\beta} - \frac{1}{2} g_{ij} \beta B_z - (E - E_o)]
\end{vmatrix}
= 0.
\]

An equivalent Hamiltonian operator, \( H_{eq} \), can now be constructed.

(2-31) \[
H_{eq} = \begin{pmatrix}
\frac{1}{2} g_{ij} \beta B_z + V_{\alpha,\alpha} & V_{\alpha,\beta} \\
V_{\beta,\alpha} & -\frac{1}{2} g_{ij} \beta B_z + V_{\beta,\beta}
\end{pmatrix}
\]
The trace of this matrix is invariant and is equal to the sum of the roots of the secular equation. This sum represents the sum of the energy shifts of each state from $E_0$, and is arbitrary within some constant. For purposes of this experiment, the trace can be chosen to be zero, and the following requirement can be imposed:

\[(2-32) \quad V_{\rho \rho} = - V_{\varsigma \varsigma} \quad \]

Then,

\[(2-33) \quad H_{eq} = \begin{pmatrix}
(\frac{1}{2} g_{\parallel} \beta B_z + V_{\varsigma \varsigma}) & V_{\varsigma \rho} \\
V_{\rho \varsigma} & - (\frac{1}{2} g_{\parallel} \beta B_z + V_{\varsigma \varsigma})
\end{pmatrix} \]

This can be written as the sum of two equivalent operators, $H_S$ and $H_{SL}$, where

\[(2-34) \quad H_S = g_{\parallel} \beta B_z S_z \]

is recognized as the first-order spin Hamiltonian, and

\[(2-35) \quad H_{SL} = A_1 S_x + A_2 S_y + A_3 S_z \]

is the first-order spin-lattice Hamiltonian. The spin operators are those for spin 1/2, and
\begin{align}
\begin{cases}
A_1 &= \text{Re } V_{\alpha \rho}, \\
A_2 &= \text{Im } V_{\alpha \rho}, \\
A_3 &= V_{\alpha \alpha}.
\end{cases}
\end{align}

This argument indicates that an effective Hamiltonian term linear in spin operators should dominate for \( U^{4+} \). If a second-order perturbation calculation including the effects of the excited states were considered, a term of the form \( B_i S_j \) might be added to the effective Hamiltonian. Such a term will be considered so that when adequate experimental evidence is available, the data can be examined for the existence of both terms in the spin-lattice Hamiltonian.

Assume, then, that the spin-lattice Hamiltonian for \( U^{4+}:\text{CaF}_2 \) is of the form

\begin{equation}
H_{\text{SL}} = \sum_{i=1}^{3} A_i S_i + \sum_{i,j=1}^{3} F_{ij} (B_i S_j + B_j S_i)
\end{equation}

where \( F_{ij} \) is a symmetrical tensor because \( H_{\text{SL}} \) must be a Hermitian operator. Assume further that \( A_i \) and \( F_{ij} \) are linearly proportional to strain:

\begin{align}
(2-38) \quad A_i &= \sum_{k=1}^{3} B_{ijk} u_{jk}, \\
(2-39) \quad F_{ij} &= \sum_{k,l=1}^{3} E_{ijkl} u_{kl},
\end{align}

where \( u_{kl} \) is a component of the strain tensor. The quantities
$B_{ijkl}$ and $E_{ijkl}$ are the "magnetoelastic coupling tensors" which must be experimentally evaluated.

The strain is computed by considering the crystal as an elastic continuum for the purposes of expressing the effect of macroscopic strain on the energy levels of the ion. The elastic strain is defined by

$$u_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

where $u_i$ is the $i$th component of the displacement vector and $x_i$ is a coordinate, $x, y, or z$.

It is convenient to express the various tensors in the Voigt notation. Since the strain tensor is symmetric, there are in general only six independent components; thus in Voigt notation the nine double-subscript components are replaced by six single-subscript components as follows.

$$xx = 11 = 1 \quad yz = 23 = 4$$
$$yy = 22 = 2 \quad zx = 31 = 5$$
$$zz = 33 = 3 \quad xy = 12 = 6$$

$$u_{11} = e_1 \quad u_{23} = u_{32} = 1/2e_4$$
$$u_{22} = e_2 \quad u_{31} = u_{13} = 1/2e_5$$
$$u_{33} = e_3 \quad u_{12} = u_{21} = 1/2e_6$$

Since $u_{ijk}$ is symmetric, it follows that $B_{ijkl}$ is symmetric.
with respect to an interchange of \( j \) and \( k \). In Voigt notation,

\[
\begin{align*}
B_{111} &= B_{11} & B_{123} &= B_{14} \\
B_{122} &= B_{12} & B_{131} &= B_{15} \\
B_{133} &= B_{13} & B_{112} &= B_{16}
\end{align*}
\]

where \( i = 1, 2, 3 \). The magnetoelastic coupling tensors are assumed to have the same symmetry as the crystalline electric field at the \( U^4^+ \) site, i.e., \( C_{3v} \). The \( B_{ijk} \) tensor for \( C_{3v} \) symmetry in Voigt notation is

\[
(2-44) \\
(\mathbf{B}_{ij}) = \begin{pmatrix}
0 & 0 & 0 & 0 & B_{15} & -B_{22} \\
-B_{22} & B_{22} & 0 & B_{15} & 0 & 0 \\
B_{31} & B_{31} & B_{33} & 0 & 0 & 0
\end{pmatrix}
\]

Consider now the fourth rank tensor \( E_{ijkl} \). Since \( F_{ij} \) and \( u_{kl} \) are symmetric, \( E_{ijkl} \) is symmetric with respect to interchange of \( i \) and \( j \), and symmetric with respect to interchange of \( k \) and \( l \). The fourth rank tensor with 81 components can thus be reduced to a 6 x 6 array with 36 independent components in Voigt notation, each component being of the form \( E_{ij} \), where \( i \) and \( j \) range from 1 to 6. It will furthermore be assumed that \( E_{ij} \) is symmetric (in analogy to the elastic-constant tensor) with respect to an interchange of \( i \) and \( j \). This being the case, \( E_{ij} \) becomes a symmetric array with at most 21 independent.
components. For \( C_{3v} \) symmetry \( E_{ijkl} \) reduces, in Voigt notation, to

\[
(2-45) \quad (E_{ij}) = \begin{pmatrix}
E_{11} & E_{12} & E_{13} & E_{14} & 0 & 0 \\
E_{12} & E_{11} & E_{13} & -E_{14} & 0 & 0 \\
E_{13} & E_{13} & E_{33} & 0 & 0 & 0 \\
E_{14} & -E_{14} & 0 & E_{33} & 0 & 0 \\
0 & 0 & 0 & 0 & E_{44} & E_{14} \\
0 & 0 & 0 & 0 & E_{14} & 1/2(E_{11} - E_{12})
\end{pmatrix}
\]

Equations (2-38) and (2-39) are written in Voigt notation as:

\[
(2-46) \quad A_i = \sum_{j=1}^{6} B_{ij} e_j, \quad i = 1, 2, 3.
\]

\[
(2-47) \quad F_i = \sum_{j=1}^{6} E_{ij} e_j, \quad i = 1, 2, \ldots, 6.
\]

The preceding tensors are valid in a coordinate system with the \( z \)-axis (3-axis) along the symmetry axis of the ion.

For each type of magnetic ion, a spin-lattice Hamiltonian must be determined for the particular type of elastic wave excited in the crystal. The elastic strain is first expressed in the coordinate system of the \( \text{CaF}_2 \) crystal; then, that tensor is transformed to the coordinate system of each of the four types of ion.

The experimental work has been done with longitudinal (111) waves, therefore, only that type of wave will be
discussed. The expression for the displacement from equilibrium of a point in the crystal (considered as an elastic continuum) is

\[
(2-48) \quad \overline{u} = \frac{u}{\sqrt{3}} \left( \hat{x} + \hat{y} + \hat{z} \right) \cos \left[ \frac{k_0}{\sqrt{3}} (X + Y + Z) - \omega t \right],
\]

where \( \omega \) is the angular frequency of the elastic wave, \( k_0 \) is the magnitude of the propagation vector, the XYZ coordinate system is that illustrated in Figure 3a, and \( \hat{x}, \hat{y}, \hat{z} \) are unit vectors.

The strain tensor corresponding to the elastic wave of eq. (2-48) is calculated from

\[
(2-49) \quad U_{ij} = \frac{1}{2} \left( \frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right), \quad i, j = 1, 2, 3,
\]

where \( U_{ij} \) is the \( ij \)th component of the strain tensor, \( U_i \) is the \( i \)th component of the displacement vector, and \( x_i \) is a coordinate \( X, Y, \) or \( Z \). The result is

\[
(2-50) \quad (U_{ij}) = e \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix},
\]

where

\[
(2-51) \quad e = -\frac{u_o k_0}{3} \sin \left[ \frac{k_0}{\sqrt{3}} (X + Y + Z) - \omega t \right].
\]

The strain tensor must be transformed to the coordinate system of each type of ion before its \( H_{SL} \) can be calculated.
(a) LABORATORY \((x'y'z')\) AND CRYSTALLINE \((XYZ)\) COORDINATE SYSTEMS FOR \(\text{U}^{4+}\text{CaF}_2\)

(b) LABORATORY SYSTEM

FIGURE 3
The transformations are described in Appendix 8.1 for the two types of ion of primary interest. The results are listed below:

\[
(2-52) \quad H^{(l)}_{SL} = 3e \left[ B_{33} S_z + 2 E_{13} (B_x S_x + B_y S_y) + 2 E_{33} B_z S_z \right],
\]

\[
(2-53) \quad H^{(l)}_{SL} = \varepsilon \left\{ -8 \sqrt{\frac{1}{8}} B_{15} S_x - \frac{1}{3} B_{22} S_y + \left( \frac{8}{3} B_{13} + \frac{1}{3} B_{33} \right) S_z \\
+ 2 \left[ \left( \frac{1}{3} E_{13} + \frac{1}{3} E_{13} \right) B_x - 4 \sqrt{\frac{1}{8}} \left( E_{1\alpha} B_{1\alpha} + E_{1\alpha} B_{1\alpha} \right) \right] S_x \\
+ 2 \left[ \left( \frac{1}{3} E_{12} + \frac{1}{3} E_{13} \right) B_y + 4 E_{14} \left( \frac{1}{3} B_{1z} - \sqrt{\frac{1}{8}} B_{1x} \right) \right] S_y \\
+ 2 \left[ \left( \frac{1}{3} E_{13} + \frac{1}{3} E_{33} \right) B_z + 4 \frac{1}{3} E_{14} B_y - 4 \sqrt{\frac{1}{8}} E_{1\alpha} B_{1\alpha} \right] S_z \right\},
\]

where the x, y, z subscripts refer to the coordinate system chosen for the particular type of ion (See Appendix 8.1).

2.3 \(U^{3+}:\text{CaF}_2\)

A. Description of \(U^{3+}:\text{CaF}_2\)

Trivalent uranium has three 5f electrons, which are responsible for its paramagnetic properties. For L-S coupling, the spin-orbit interaction produces a ground-state term for the free ion of the form \(^4I_{9/2}\). A schematic diagram of the ground-state energy levels is shown in Figure 5 (q.v. Sorokin and Stevenson\textsuperscript{35}).

The model for the substitution of \(U^{3+}\) into the \(\text{CaF}_2\) lattice has been proposed by Bleaney, \textit{et al.}\textsuperscript{36}. A \(U^{3+}\) ion is
assumed to substitute for a Ca\(^{2+}\) ion, and an extra F\(^{-}\) ion to occupy an interstitial site in the center of the adjacent cubic array of F\(^{-}\) ions. This model is illustrated in Figure 6. The extra fluorine ion and the U\(^{3+}\) ion define an axis of fourfold rotational symmetry which is parallel to one of the CaF\(_2\) cubic axes. Since the extra F\(^{-}\) can equally probably occupy sites in any one of six possible adjacent positions, three mutually perpendicular tetragonal axes of symmetry for the ion are possible. Therefore, there are three types of magnetic ion, each type having an axis of tetragonal symmetry along one of the three cubic axes of CaF\(_2\).

B. The Spin and Spin-Lattice Hamiltonians

The \(^{4}\text{I}_{9/2}\) level splits into five Kramers doublets in the tetragonal crystalline electric field\(^{37}\). The spin Hamiltonian, neglecting hyperfine terms, is of the form\(^{38}\).

\[
H_S = \bar{g}_\parallel \beta B_z S_z + \bar{g}_\perp \beta (B_x S_x + B_y S_y)
\]

for each type of magnetic ion, where the z-axis must be the axis of symmetry for the ion, and the effective spin is 1/2. The \(g\) values have been measured by Yariv\(^{39}\) to be:

\[
\bar{g}_\parallel = 3.528 \pm 0.005 \quad \text{and} \quad \bar{g}_\perp = 1.875 \pm 0.005 \quad \text{at} \quad 4.2^\circ\text{K}.
\]

The spin Hamiltonian is solved for its eigenvalues and eigenfunctions for each type of magnetic ion in Section 8.2. The value of magnetic field for electron paramagnetic resonance at 9.31 Gc
is plotted in Figure 8 for each type of ion as a function of the angle the field makes with a CaF$_2$ cubic axis (See Figure 7).

Since the ground state of the U$^{3+}$ ion in the crystalline field is a Kramers doublet, no lattice strain, even if it removes all symmetry at the site of the ion, can remove the degeneracy. For this reason, it can be assumed that a first-order spin-lattice Hamiltonian linear in effective spin operators will not exist for U$^{3+}$. One must go to second order to find the spin-lattice Hamiltonian. Thus, it is reasonable to expect that the spin-lattice Hamiltonian will be dominated by a term of the form

$$H_{SL} = \sum_{i,j=1}^{3} F_{ij} (B_i S_j + B_j S_i)$$

for each type of ion, where the quantities involved have the same definitions as in eq. (2-37). Again,

$$F_{ij} = \sum_{k,l=1}^{3} E_{ijkl} u_{kl}$$

The $C_{4v}$ tetragonal symmetry requires that the coupling tensors have the form, in Voigt notation,

$$E_{ij} = \begin{pmatrix} E_{11} & E_{12} & E_{13} & 0 & 0 & 0 \\ E_{12} & E_{11} & E_{12} & 0 & 0 & 0 \\ E_{13} & E_{13} & E_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & E_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & E_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & E_{66} \end{pmatrix}.$$
(a) "z" IONS

(b) "x" IONS

(c) "y" IONS

COORDINATE SYSTEMS FOR $U^{3+}:CaF_2$

FIGURE 7
RESONANT B VS. $\theta$ FOR U3+CAF2, $v = 9.31$ Gc

$\theta =$ ANGLE BETWEEN $\bar{B}$ AND (001) ROD AXIS

FIGURE 8
This can be shown by performing the symmetry operations on eq. (2-56) and requiring \(E_{ij}\) to be unchanged (cf. Landau and Lifshitz\(^{40}\)).

The particular form of the spin-lattice Hamiltonian for each type of magnetic ion when longitudinal (001) waves are present in the \(\text{CaF}_2\) crystal is calculated in Section 8.2. These Hamiltonians are used to obtain the attenuation of the elastic waves in Sections 3.3.

2.4 \(\text{Cr}^{3+}:\text{Al}_2\text{O}_3\)

Trivalent chromium has three 3d electrons, which are responsible for its paramagnetic properties. In the crystalline electric field of \(\text{Al}_2\text{O}_3\) the ground-state levels of \(\text{Cr}^{3+}\) consist of two Kramers doublets, and the spin and spin-lattice Hamiltonians are of a different nature than those discussed in the preceding sections. This difference is mainly the result of the fact that the spin-orbit interaction is weaker than the crystalline field for the iron-group ions.

The \(\text{Cr}^{3+}\) ion in \(\text{Al}_2\text{O}_3\) and the theory of its spin-lattice Hamiltonian have been discussed in previous work by Hemphill\(^{41}\).

The purpose of the investigations on ruby discussed in this thesis is to compare the results of ultrasonic paramagnetic resonance with those obtained by the steady-strain technique.

The spin Hamiltonian for ruby is
(2-58) \[ H_S = g \, \mathbf{B} \cdot \mathbf{S} + D(S_z^2 - 5/4), \]

where the effective spin is 3/2. The spin-lattice Hamiltonian is of the form

(2-59) \[ H_{SL} = \sum_{i,j=1}^{3} D_{ij} \, S_i \, S_j \]

where

(2-60) \[ D_{ij} = \sum_{k,l=1}^{3} G_{ijkl} \, u_{kl}. \]

Again, \( u_{kl} \) is the strain tensor, \( D_{ij} \) is a symmetric tensor, and \( G_{ijkl} \) is the magnetoelastic coupling tensor ("G" tensor). In Voigt notation,

(2-61) \[ D_i = \sum_{j=1}^{6} G_{ij} \, e_j, \quad i = 1, 2, \ldots, 6. \]

For agreement with experimental results obtained in this investigation, it has been found necessary to modify the form of the G tensor used by Hemphill. First, the G tensor is assumed to have \( C_3 \) symmetry (three-fold rotational symmetry) to conform with the point symmetry at the site of the \( \text{Cr}^{3+} \) ion. The G tensor for \( C_3 \) symmetry is then \(^{42}\)

(2-62) \[ (G_{ij}) = \begin{pmatrix} G_{11} & G_{12} & G_{13} & G_{14} & -G_{25} & 0 \\ G_{12} & G_{11} & G_{13} & -G_{14} & 0 & G_{25} \\ G_{13} & G_{13} & G_{33} & 0 & 0 & 0 \\ G_{14} & -G_{14} & 0 & G_{44} & 0 & G_{25} \\ -G_{25} & G_{25} & 0 & 0 & G_{44} & G_{14} \\ 0 & 0 & 0 & G_{25} & G_{14} & 1/2(G_{11} - G_{12}) \end{pmatrix} \]
Now, any tensor can be written as the sum of a traceless tensor and a diagonal tensor. Therefore the tensor, $D_{ij}$, is so written. However, since the diagonal tensor does not lead to terms which contribute to the absorption, it can be neglected as unobservable. Therefore, the tensor, $D_{ij}$, can be assumed to be traceless. In Voigt notation,

\[(2-63) \quad \sum_{i=1}^{3} D_i = 0\]

The traceless condition places the following requirement on $G_{ij}$:

\[(2-64) \quad \sum_{j=1}^{3} G_{ij} = 0 \quad , \quad i = 1,2,\cdots 6,\]

which yields

\[(2-65) \quad \begin{cases} 
G_{12} = (1/2 \ G_{33}-G_{11}) \\
G_{13} = -1/2 \ G_{33}
\end{cases}\]

Furthermore, there are two types of sites available to the $\text{Cr}^{3+}$ ion in $\text{Al}_2\text{O}_3$ which are equivalent in an EPR measurement and have the same spin Hamiltonian\textsuperscript{43}. The two types of sites have different $G$ tensors, ($G_{ij}$) and ($G_{ij}'$), of the form described by eqs. (2-62) and (2-65). A symmetry operation of the $\overline{3}m \ \text{Al}_2\text{O}_3$ lattice, namely a 180° rotation about the crystalline $x$-axis, brings one type of site into coincidence with the other, however. This symmetry operation yields the following relation between the $G$ tensors for the two sites:
\begin{equation}
\begin{cases}
G_{ij} = G_{ij}', \\ G_{25} = -G_{25}'
\end{cases}
\end{equation}

The final form of the tensors for the two types of sites is therefore:

\begin{equation}
(G_{ij}) = \begin{pmatrix}
G_{11} (\frac{1}{2} G_{33} - G_{11}) - \frac{1}{2} G_{33} & G_{14} & \mp G_{25} & 0 \\
(\frac{1}{2} G_{33} - G_{11}) G_{11} & -\frac{1}{2} G_{33} & -G_{14} & \mp G_{25} \\
-\frac{1}{2} G_{33} & -\frac{1}{2} G_{33} & G_{33} & 0 & 0 & 0 \\
G_{14} & -G_{14} & 0 & G_{44} & 0 & \mp G_{25} \\
\mp G_{25} & \mp G_{25} & 0 & 0 & G_{44} & G_{14} \\
0 & 0 & 0 & \mp G_{25} & G_{14} & (G_{11} - \frac{1}{4} G_{33})
\end{pmatrix}
\end{equation}

The z-axis (3-axis) is, as usual, chosen as the symmetry axis for the spin and spin-lattice Hamiltonians. The ruby sample used in this investigation is cut in the form of a circular cylinder with its axis along the crystalline z-axis. Both longitudinal and transverse waves have been used, and the spin-lattice Hamiltonians corresponding to these types of waves must be determined.

For longitudinal waves along the z-axis, the spin-lattice Hamiltonian for both types of ions is (See Appendix 8.3.)

\begin{equation}
H_{SL} = \frac{3}{2} e \ G_{33} \left[ S_z^2 - \frac{5}{4} \right].
\end{equation}
For transverse waves along the z-axis, the spin-lattice Hamiltonians for the two types of ion are

\[
H_{SL} = e^{i \left( G_{14} \sin \phi + G_{25} \cos \phi \right) \left( S_x^2 - S_y^2 \right)} + G_{44} \left( S_y S_z + S_z S_y \right) \sin \phi + G_{44} \left( S_z S_x + S_x S_z \right) \cos \phi + \left( \pm G_{25} \sin \phi + G_{14} \cos \phi \right) \left( S_x S_y + S_y S_x \right),
\]

where the angle of polarization, \( \phi \), is defined in Figure 16.

The attenuation corresponding to these Hamiltonians is derived in Section 3.4.
III. RELATION OF THEORY TO EXPERIMENT

Verification of the forms assumed for the spin-lattice Hamiltonians and the determination of their unknown parameters by the method of ultrasonic paramagnetic resonance depends upon the measurement of the attenuation of the elastic waves. In this section, the expressions for attenuation for each of the samples studied will be presented.

3.1 Definition of Attenuation

Define:

(3-1) \[ P = \text{the energy per unit time per unit volume absorbed from the elastic waves by the paramagnetic ions}, \]

(3-2) \[ I = Uv = \text{the intensity of the elastic wave}, \]

where \( U \) is the elastic energy density and \( v \) is the velocity of the elastic wave in the crystal containing the paramagnetic ions.

The attenuation in nepers per unit length is then defined as

(3-3) \[ \alpha \equiv \frac{P}{I}. \]

The intensity of the wave is

(3-4) \[ I = I_o e^{-\alpha x}, \]

where \( x \) is the distance the wave travels through the crystal and \( I_o \) is the incident intensity. Then,
\[ (3-5) \quad \frac{1}{I} \frac{dI}{dx} = -\alpha = -\frac{P}{I}. \]

The power density is related to the transition probability per unit time for the interaction, \( W \), by

\[ (3-6) \quad P = \frac{(\Delta n) \hbar \omega}{V} W, \]

where:  \( \Delta n \) = population difference between levels involved,
\( \omega \) = angular frequency of elastic waves,
\( V \) = volume of sample = \( m/\rho \),
\( m \) = mass of sample,
\( \rho \) = density of sample,
\( \hbar \) = Planck's constant divided by 2\( \pi \).

The attenuation is therefore

\[ (3-7) \quad \alpha = \frac{(\Delta n) \hbar \omega}{VU\nu} \quad W. \]

The time-averaged elastic energy density, in Voigt notation, is given by

\[ (3-8) \quad U = \frac{1}{2} \sum_{i,j=1}^{6} c_{ij} e_i e_j, \]

where the \( c_{ij} \) are the elastic constants of the crystal and the \( e_i \) are the amplitudes of the components of strain.

The transition probability per unit time for a perturbation term of the form \( A \cos (kx - \omega t) \) is found to be

\[ (3-9) \quad W = \frac{1}{4\hbar^2} |\langle i | A | j \rangle|^2 g(\nu), \]

-33-
where \( g(\nu) \) is the normalized line-shape function, and \( i, j \) refer to eigenstates of the spin Hamiltonian.

A described in Section IV, the measured quantity is the number of decibels (db) of attenuation of the echo power in the waveguide. The electromagnetic power, \( P_{EM} \), is related to the power of the elastic wave, \( P_E \), by some constant, \( C \),

\[
(3-10) \quad P_{EM} = CP_E.
\]

The measured attenuation in number of db, \( N \), is then

\[
(3-11) \quad N = -10 \log_{10} \frac{P_{EM}}{P_{EM_0}} = -10 \log_{10} \frac{P_E}{P_{E_0}}.
\]

But,

\[
(3-12) \quad P_E = A I,
\]

where \( A \) is the cross-sectional area of the sample; therefore,

\[
(3-13) \quad N = -10 \log_{10} \frac{I}{I_0} = -10 \log_{10} e^{-\alpha x} = 10 \alpha x \log_{10} e.
\]

The distance the elastic wave has traveled is related to the echo number, \( n \), by

\[
(3-14) \quad x = 2nL,
\]

where \( L \) is the length of the sample. The attenuation of the \( n \)th echo is thus

\[
(3-15) \quad \alpha_n = \frac{N}{20nL \log_{10} e} = \frac{N}{8.686nL}.
\]
3.2 Attenuation in \( \text{U}^{4+}:\text{CaF}_2 \)

The spin-lattice Hamiltonians for the two types of ion under consideration are given in eqs. (2-52) and (2-53). Matrix elements of \( H_{\text{SL}} \) between the two eigenstates of the spin Hamiltonian must be calculated.

The wave functions are given by eqs. (8.1-5) and (8.1-6) in Section 8.1. However, as is discussed in Section 2.2, \( \Delta^2 \) is small compared to \( (g_{\|} \beta B_z)^2 \). If the peak attenuation is measured, it will correspond approximately to the absorption by ions with \( \Delta = 0 \). Therefore, the wave functions with \( \Delta = 0 \) will be used:

\[
\psi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \psi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
\]

A. (111) Ions

The geometry of the experiment is such that \( B_y = 0 \). The spin-lattice Hamiltonian becomes

\[
H_{\text{SL}}^{(111)} = 3\varepsilon \left[ 3g_{33} S_z + 2E_{13} B_x S_x + 2E_{33} B_z S_z \right].
\]

The matrix elements of \( S_x \) and \( S_z \) between \( \psi_- \) and \( \psi_+ \) are required.

\[
\left\langle -|S_z| + \right| \right. = 0
\]

\[
\left\langle -|S_x| + \right| \right. = 1/2 \hbar.
\]

Therefore,
(3-20) \( \langle - | H_{SL} | + \rangle = 3e \hbar E_{13} B_x \).

The experimental data have revealed no absorption by the (111) ions in the presence of (111) longitudinal elastic waves. Therefore it can be concluded that \( E_{13} \) is approximately zero, and it will be neglected in the following equations.

B. (111) Ions

Again the experimental geometry is such that \( B_y = 0 \).

Also \( \langle - | S_z | + \rangle = 0 \), so that the terms in \( S_z \) can be neglected. The spin-lattice Hamiltonian then becomes (neglecting \( E_{13} \) as small):

\[
(3-21) \quad H_{SL}^{(111)} = e \left[ -8 \sqrt{\frac{\alpha}{16}} B_{15} S_x - \frac{8}{3} B_{zz} S_y + 2 \left( \frac{8}{3} E_{11} B_x \right. \right.

\[
\left. \left. - 4 \sqrt{\frac{\alpha}{18}} E_{zz} B_z \right) S_x + 8 E_{14} \left( \frac{1}{3} B_z - \sqrt{\frac{\alpha}{16}} B_x \right) S_y \right] \]

(3-22) \( \langle - | S_y | + \rangle = \frac{\hbar}{2} \)

Therefore:

\[
(3-23) \quad \langle - | H_{SL}^{(111)} | + \rangle = e \hbar \left[ \left( - 4 \sqrt{\frac{\alpha}{16}} B_{15} - i \frac{8}{3} B_{zz} \right) + \left( \frac{8}{3} E_{11} B_x \right. \right. \right.

\[
\left. \left. - 4 \sqrt{\frac{\alpha}{18}} E_{zz} B_z \right) + i \left( 8 E_{14} \left( \frac{1}{3} B_z - \sqrt{\frac{\alpha}{16}} B_x \right) \right) \right] .
\]
The elastic energy density for longitudinal (111) waves is

\[ U = \frac{1}{2} \sum_{i,j=1}^{6} c_{ij} e_i e_j = \frac{3}{2} e^2 (c_{11} + 2c_{12} + 4c_{44}). \]

The velocity of (111) longitudinal waves in CaF\(_2\) is

\[ V_{(111)} = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3 \rho}}. \]

where the \(c_{ij}\) are the elastic constants for CaF\(_2\) and \(\rho\) is the density. The energy density can thus be written:

\[ U = \frac{9}{2} \rho e^2 V_{(111)}^2. \]

The attenuation is

\[ \alpha^{(111)} = \frac{(\Delta n) \omega g(\nu_0)}{18m V_{(111)}^3 \hbar e^2} \left| \left< H_{SL}^{(111)} \right| + \right|^2. \]

3.3 Attenuation in U\(^{3+}\):CaF\(_2\)

The spin-lattice Hamiltonians for each type of magnetic ion for the case of longitudinal (001) waves are derived in Section 8.2. The matrix elements and attenuation are calculated in this section.

A. "z" Ions

The spin-lattice Hamiltonian is

\[ H_{SL}^{(z)} = 2eB \left[ E_{13} \sin \Theta S_x + E_{33} \cos \Theta S_z \right]. \]

The matrix elements can be calculated with the use of...
eqs. (8.2-3) and (8.2-4) in Section 8.2:

\[ (3-29) \quad \langle -|S_x|+ \rangle = - \frac{\hbar g_{||} \cos \theta}{2g(\theta)} , \]

\[ (3-30) \quad \langle -|S_z|+ \rangle = \frac{\hbar g_\perp \sin \theta}{2g(\theta)} , \]

where

\[ (3-31) \quad g(\theta) = \sqrt{g_{||}^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta} , \]

and \( \theta \) is defined by Figure 7a. Therefore,

\[ (3-32) \quad \langle -|H_{SL}^{(z)}|+ \rangle = \frac{\hbar}{2g} \sin 2\theta \left(-g_{||} E_{13} + g_\perp E_{33} \right). \]

The elastic energy density is

\[ (3-33) \quad U = \frac{1}{2} \sum_{ij=1}^{6} c_{ij} e_i e_j = \frac{1}{2} c_{33} e_3^2 = \frac{1}{2} c_{11} e^2 . \]

The velocity of longitudinal waves along a cubic axis in CaF\(_2\) is

\[ (3-34) \quad \sqrt{(001)} = \sqrt{\frac{c_{11}}{\rho}} , \]

therefore,

\[ (3-35) \quad U = \frac{1}{2} \rho \sqrt{(001)} e^2 . \]

The attenuation is

\[ (3-36) \quad \alpha^{(z)} = \frac{(\Delta n) t}{8m} \sqrt{(001)} \frac{\omega E^2 g(\nu)}{8m \sqrt{(001)}} \left(-g_{||} E_{13} + g_\perp E_{33} \right)^2 \frac{\sin^2 2\theta}{(g_{||} \cos^2 \theta + g_\perp^2 \sin^2 \theta)} . \]
where the quantities are as previously defined.

B. "x" Ions

The spin-lattice Hamiltonian is

\( H_{\text{SL}}^{(x)} = 2eB \left[ E_{11} \sin \theta' S_x' + E_{13} \cos \theta' S_z' \right] \),

where \( \theta' \) is defined in Figure 7b. The relation between \( \theta' \) and the laboratory angle, \( \theta \), is

\[
\begin{align*}
\cos \theta' &= \sin \theta \\
\sin \theta' &= -\cos \theta
\end{align*}
\]

\( \langle -|S_x'|+ \rangle = -\frac{\hbar g_{11} \cos \theta'}{2g(\theta')} = -\frac{\hbar g_{11} \sin \theta}{2g(\theta)} \)

\( \langle -|S_z'|+ \rangle = \frac{\hbar g_{13} \sin \theta'}{2g(\theta')} = -\frac{\hbar g_{13} \cos \theta}{2g(\theta)} \)

\[
G(\theta) = \sqrt{\frac{g_{11}^2 \sin^2 \theta + g_{13}^2 \cos^2 \theta}{}}
\]

Therefore,

\( \langle -|H_{\text{SL}}^{(x)}|+ \rangle = \frac{eBh}{2g(\theta)} \sin 2\theta \left( g_{11} E_{11} - g_{13} E_{13} \right) \),

and the attenuation is

\( \alpha^{(x)} = \frac{(\Delta n) \hbar \omega B^2 g(\nu) \left( g_{11} E_{11} - g_{13} E_{13} \right)^2 \sin^2 2\theta}{3m \sqrt{3}_0(001)} \cdot \frac{G(\theta)^2}{G(\theta)^2} \).
C. "y" Ions

The spin-lattice Hamiltonian is

\[
(3-44) \quad H_{SL}^{(y)} = 2\varepsilon E_1 \cos \phi' S_x' + E_2 \sin \phi' S_y',
\]

where $\phi'$ is defined in Figure 7c. The relation between $\phi'$ and the laboratory angle, $\theta$, is

\[
(3-45) \quad \begin{cases} 
\cos \phi' = \cos \theta \\
\sin \phi' = \sin \theta 
\end{cases}
\]

\[
(3-46) \quad \langle -|S_x'|+ \rangle = \frac{\mu}{4} (1-e^{-12 \phi'}) = \frac{\mu}{4} (1-e^{-12 \theta})
\]

\[
(3-47) \quad \langle -|S_y'|+ \rangle = -\frac{\mu}{4} (1+e^{-12 \phi'}) = -\frac{\mu}{4} (1+e^{-12 \theta})
\]

Therefore,

\[
(3-48) \quad \langle -|H_{SL}^{(y)}|+ \rangle = \frac{\varepsilon B \hbar}{2} (E_{11} - E_{12}) \sin 2\theta \left( \sin \theta + \frac{1}{2} \cos \theta \right),
\]

and the attenuation is

\[
(3-49) \quad \alpha^{(y)} = \frac{(\Delta n) \hbar \omega B^2 \varepsilon(\nu) (E_{11} - E_{12})^2 \sin^2 2\theta}{8m \sqrt{3}} \quad (001)
\]
3.4 Attenuation in Cr$^{3+}$:Al$_2$O$_3$

A. Longitudinal Waves

The elastic energy density for longitudinal waves propagated along the z-axis (c-axis) of Al$_2$O$_3$ is (See Section 8.3 for strain.)

\[(3-50) \quad U = \frac{1}{2} \sum_{i,j=1}^{6} c_{ij} e_i^1 e_j^1 = \frac{1}{2} c_{33} e^2.\]

The velocity of longitudinal waves along the z-axis is

\[(3-51) \quad v_L = \sqrt{\frac{c_{33}}{\rho}},\]

therefore,

\[(3-52) \quad U = \frac{1}{2} \rho v_L^2 e^2.\]

The attenuation follows, using eqs. (2-68) and (3-6):

\[(3-53) \quad \alpha_L = \frac{(\Delta n) \omega g(\nu_0)}{2m v_L^3 \hbar e^2} \left| \left\langle 1 | H_{SL} | j \right\rangle \right|^2 = \frac{9 c_{33}^2 (\Delta n) \omega g(\nu_0)}{8m v_L^3 \hbar} \left| \left\langle 1 | s_z^2 | j \right\rangle \right|^2.\]

B. Transverse Waves

The elastic energy density for transverse waves propagated along the z-axis is (See Section 8.3)

\[(3-54) \quad U = \frac{1}{2} (c_{44} e_4^2 + c_{55} e_5^2) = \frac{1}{2} c_{44} e^2 (\sin^2 \phi + \cos^2 \phi) = \frac{1}{2} c_{44} e^2.\]
The velocity of the transverse waves is

\[(3-55) \quad v_T = \sqrt{\frac{c}{\rho}} e^2; \]

therefore,

\[(3-56) \quad U = \frac{1}{2} \rho v_T^2 e^2. \]

The attenuation is, using eqs. (3-6) and (8.3-10),

\[(3-57) \quad \alpha_T = \frac{\omega g(\nu_c)}{2m v^3} \left[ \frac{(\Delta n)}{2} \left| \langle 1 | H_{SL} | J \rangle \right|^2 + \frac{(\Delta n)}{2} \left| \langle 1 | H'_{SL} | J \rangle \right|^2 \right] \]

In this expression, \(H_{SL}\) and \(H'_{SL}\) refer to the Hamiltonians for the two different types of ion (nonequivalent sites). One-half the total number of \(Cr^{3+}\) ions is assumed to occupy each type of site. Taking into account the implicit imaginary factor in terms involving the first power of \(S^y\), one finds

\[(3-58) \quad \left| \langle 1 | H_{SL} | J \rangle \right|^2 = e^2 \left\{ \left( G_{14} \sin \psi + G_{25} \cos \psi \right) \left| \langle 1 | S_{2x}^A | J \rangle \right|^2 + \left( G_{44} \cos (\phi - \gamma) \right) \left| \langle 1 | S_{xy}^A | J \rangle \right|^2 + \left( G_{14} \cos \psi - G_{25} \sin \psi \right) \left| S_{xy}^A \right| J \right\}, \]

where \(S_{xy}^A\) is the anti-commutator of \(S_x^A\) and \(S_y\), etc. The total attenuation is finally

\[(3-59) \quad \alpha_T = \frac{(\Delta n)\omega g(\nu_c)}{4mv^3} \left( M^2 \right)_{ij} \]

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where $M_{1j}^2$ is defined to be

\begin{equation}
M_{1j}^2 = \left\{ \left( G_{14} \sin \psi - G_{25} \cos \psi \right) \left\langle 1 \left| S_{zx}^A \right| j \right\rangle^2 + \left| G_{44} \sin (\phi - \gamma) \left\langle 1 \left| S_{yz}^A \right| j \right\rangle \right|^2 \right\} + \left\{ \left( G_{14} \cos \psi + G_{25} \sin \psi \right) \left\langle 1 \left| S_{xy}^A \right| j \right\rangle \right\}^2 + \left\{ \left( G_{14} \sin \psi + G_{25} \cos \psi \right) \left\langle 1 \left| S_{xx}^A \right| j \right\rangle \right\}^2 + \left| G_{44} \sin (\phi - \gamma) \left\langle 1 \left| S_{yz}^A \right| j \right\rangle \right|^2 \right\} + \left\{ \left( G_{14} \cos \psi - G_{25} \sin \psi \right) \left\langle 1 \left| S_{xy}^A \right| j \right\rangle \right\}^2 .
\end{equation}
IV. EXPERIMENTAL TECHNIQUES

4.1 The UPR Spectrometer

A. General Description

The apparatus used in ultrasonic paramagnetic resonance measurements is outlined in Figure 9. The quantities that must be measured are: (1) number of decibels (db) of attenuation, (2) magnitude of magnetic field for electron paramagnetic resonance, (3) line widths, (4) temperature of sample, (5) frequency and velocity of the elastic wave. A description of the block diagram and the method of measurement follows.

The sample, in the form of a cylindrical rod, is bonded to a piezoelectric quartz transducer and placed in a tunable, reentrant, resonant cavity. The cavity is immersed in a liquid helium bath in the inner dewar of a double-dewar cryostat which is placed between the pole pieces of an electromagnet.

Pulses of electromagnetic energy at about 9.3 Gc (9.3 x 10^9 c.p.s.) and a duration of 0.4 microsecond are transmitted from the QK 299 tunable magnetron at a repetition rate of approximately 1000 pulses per second. The output from the magnetron passes through a variable attenuator and a circulator to the sample cavity. The sample is positioned such that the transducer is located in a region of high electric field in the cavity but such that the sample itself does not appreciably extend into the cavity. By means of the piezoelectric effect, the pulses of electromagnetic energy are con-
verted into pulses of elastic energy by the transducer. The elastic waves propagate through the bonding material to the sample. Since the pulses have a shorter duration than the time necessary for the elastic waves to travel from one end of the sample to the other, the initial disturbance is reflected back and forth from the end faces of the sample in the form of echoes. The temporal spacing of the echoes is equal to twice the length of the sample divided by the velocity of the elastic wave. As each echo returns to the transducer-end of the sample, part of the elastic energy is converted back into electromagnetic energy. The echoes so created propagate through the circulator, T-R tube, and precision variable attenuator to a standard superheterodyne receiver where they are detected. The output of the I.F. amplifier, which is in the form of a pulse-echo pattern (See Figure 13.), is connected to the gated integrator. The gated integrator is a modified, more stable version of that previously used in this laboratory. It produces a DC output which is dependent upon the amplitude of the signal appearing at its input terminals when its amplifier is gated "on" by the control pulser. That is, a short gating pulse (of the order of 0.1 microsecond) determines the sampling time of the integrator, and the time delay of the gate after the transmitter pulse is variable. Therefore, any echo can be sampled, and the output of the integrator is a function of the amplitude.
of the sampled echo.

The integrator output is connected to a strip recorder. The magnetic field is varied linearly with time through the value necessary for paramagnetic resonance. By observing a voltmeter which monitors a reference voltage in the magnet power supply, one can mark the recorder chart to calibrate the time scale in voltage. A calibration chart can then be consulted to determine the corresponding magnetic field within 15 gauss. The ordinate of the strip recorder chart, which depends upon echo amplitude, can be calibrated in db by inserting known amounts of attenuation with the precision attenuator. This has the advantage of making the calibration independent of the response law of the detection system. The record thus appears as decibels of attenuation versus magnetic field for the particular echo of interest. Equation (3-15) can then be used to calculate the attenuation.

The line shapes and widths can be determined from the records if one is careful to make calibration marks at close intervals such that one can interpolate without appreciable error.

The frequency of the elastic waves are read from the calibrated dial of the magnetron. The velocity of the waves is obtained by observing the time between echoes on the oscilloscope and knowing the length of the sample. The velocity can also be calculated from known data on the
elastic constants.

The temperature of the sample must be known so that the difference in population between the energy levels, \((\Delta n)\), can be calculated. If the sample is in a liquid helium bath at atmospheric pressure, the temperature is 4.2\(^\circ\)K. At lower temperatures (obtained by pumping on the helium), the pressure is measured with a Wallace and Tiernan absolute pressure gauge to an accuracy of 0.1mm. The temperature is then obtained from vapor pressure-temperature tables for liquid helium.

B. Components

The sample cavity is the reentrant type\(^{47}\), constructed of brass and silver-plated. The resonant frequency and coupling of such a cavity are very sensitive to perturbations. In general, a slightly different cavity must be used for each type of sample. The resonant frequency of the cavity is varied by inserting a 0.1" diameter dielectric rod containing a small brass slug. Since fine tuning is necessary, a brass spur-gear arrangement with a 1:2 ratio is used to control the dielectric travel. This arrangement is illustrated in Figure 10. A CW rotation of the drive shaft moves the larger gear attached to the tuning rod CCW, and the gears can be rotated in either direction. The driven gear is fixed to a threaded rod screwed into the cavity housing such that as it is rotated,
[Diagram showing various components of a scientific apparatus, labeled as follows:

- Pressure Window
- "Stuffing Boxes"
- Dewar Top-Plate
- Low-Temperature Sample Holder
- Stainless Steel Tubing and Waveguide
- Slide-Screw Tuner
- Sample Cavity
- Spur-Gear-Driven Tuner

Scale: 1/4]

Figure 10
it translates toward or away from the cavity. The gears will track over translation distances of the order of 1/4", which is more than adequate for the fine tuning. The choice of tuning dielectric is also important. It was found that teflon, though normally possessing excellent properties, caused drift in the cavity resonant frequency at low temperatures (apparently as a result of its flexibility). When the tuner was constructed of polystyrene, the drift became negligible, although the polystyrene did have a tendency to crack at low temperatures, which causes the tuner lifetime to be limited.

The magnetron pulser design is similar to that described by an application note published by the manufacturers of Shockley diodes, which are used in it. The pulser provides a 0.4 microsecond pulse at 4 KV and 0.5 amperes for the magnetron. The repetition rate is controlled by an external triggering signal and can be any value up to about 1200 pulses per second.

C. Technique of Measurement

In order to obtain echoes, one must first tune the magnetron and sample cavity to the resonant frequency of the transducer (See following section). Next the local oscillator is tuned for maximum output from the I.F. amplifier. Once echoes are detected, one must adjust the system such that the signal-to-noise ratio (S/N) is optimized. The magnetron power is increased to a level a few db below that which will cause high
field breakdown in the cavity. Finally, the slide-screw
tuner which matches the mixer to the transmission line and
the local oscillator power are adjusted for optimum S/N.

Since the absorption signal is proportional to the echo
number and the echoes decrease in amplitude with increasing
echo number, the echo is selected to optimize these effects.
The selection of the echo is accomplished with the use of
the "delay trigger" feature of the Tektronik 545A oscilloscope.

4.2 Generation of the Elastic Waves

A. Elastic Waves in Crystals

The classical theory of elasticity is adequate to describe
the elastic waves used in this experiment\(^{49}\). Solution of
the equations of motion yields the velocity as a function of
elastic constants and density of the crystal for each type of
wave.

The elastic constants and density of CaF\(_2\) as a function of
temperature have been measured with the use of radio frequency
elastic waves by Huffman and Norwood\(^{50}\). The long-wavelength
limit is assumed to be above 10 Gc, therefore their results
can be used to calculate the velocities. (The elastic wave-
length is about 1000 lattice spacings for CaF\(_2\) at 10 Gc.).
Their results for two temperatures, \(T = 300^\circ\text{K}\) and \(T = 4.2^\circ\text{K}\)
are presented in Table 4-1. The units of density, \(\rho\), are
grams per cubic centimeter and the elastic constants are in


units of $10^{11}$ dynes per square centimeter.

<table>
<thead>
<tr>
<th>T</th>
<th>$c_{11}$ ± 8%</th>
<th>$c_{44}$ ± 2%</th>
<th>$c_{12}$ ± 4%</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>16.4</td>
<td>3.370</td>
<td>5.3</td>
<td>3.1795</td>
</tr>
<tr>
<td>4.2</td>
<td>17.4</td>
<td>3.593</td>
<td>5.6</td>
<td>3.2107</td>
</tr>
</tbody>
</table>

Table 4-1

The velocities of three types of waves, calculated from the above quantities, are given in Table (4-2) for CaF$_2$ in units of $10^5$ cm/sec.

<table>
<thead>
<tr>
<th>Wave Type</th>
<th>Equation for Velocity</th>
<th>Velocity at 300°K</th>
<th>Velocity at 4.2°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long. (001)</td>
<td>$\sqrt{\frac{c_{11}}{\rho}}$</td>
<td>7.19</td>
<td>7.36</td>
</tr>
<tr>
<td>Long. (110)</td>
<td>$\sqrt{\frac{c_{11} + c_{12} + 2c_{44}}{2\rho}}$</td>
<td>6.69</td>
<td>6.86</td>
</tr>
<tr>
<td>Long. (111)</td>
<td>$\sqrt{\frac{c_{11} + 2c_{12} + 4c_{44}}{3\rho}}$</td>
<td>6.52</td>
<td>6.69</td>
</tr>
</tbody>
</table>

Table 4-2

The velocities of longitudinal and transverse waves along the c-axis of Al$_2$O$_3$ (ruby) have been measured by Wachtmann, et al. at low frequencies and room temperature to be, respectively: $V_L = 1.10 \times 10^6$ cm/sec. and $V_T = 5.94 \times 10^5$ cm/sec.

The results at higher frequencies are presented in Section V along with a comparison with the above values.
B. The Piezoelectric Transducers

The piezoelectric transducers used to excite the elastic waves are quartz. Longitudinal waves are generated by x-cut crystals and transverse waves by y-cut crystals. The transducers are 0.1" in diameter and approximately 0.01" in thickness. They were cut and polished to optical tolerances by the Valpey Crystal Corporation\textsuperscript{52}. The transducers have a fundamental resonant frequency of about 10 mc. They are used as resonant transducers\textsuperscript{53} at about 9.3 Gc, that is, at a high-order harmonic of the fundamental frequency.

An electric field perpendicular to the faces of the x-cut transducer produces longitudinal waves in the direction of the surface normal\textsuperscript{54}. Thus, longitudinal waves are excited along the axis of a sample bonded to the transducer.

A y-cut quartz transducer in the same arrangement excites transverse waves along the sample axis\textsuperscript{55}. The polarization of the waves is along the x-axis of quartz. Since it is necessary to know the direction of polarization of the elastic waves in the paramagnetic sample, the x-axis of the transducer must be located and marked. The method used for determining the x-axis is a combination of optical and X-ray techniques.

An illustration of the various types of common crystal cuts for quartz can be found in the book by Heising\textsuperscript{56}. The optical axis, an axis of threefold (D\textsubscript{3}) rotational symmetry, is designated as the z-axis. There are three twofold axes
perpendicular to the optical axis. One of the twofold axes is chosen as the x-axis, and the y-axis is chosen to form a right-handed coordinate system. The faces of an x-cut transducer are perpendicular to the x-axis, and those of a y-cut transducer are perpendicular to the y-axis.

The x-axis can be determined by X-ray analysis. For a y-cut crystal, the x and z axes will be in the plane of the crystal face. A back-reflection Laue photograph with the X-ray beam along the y-axis will reveal a prominent axis with no rotational symmetry (the y-axis). Also, if one draws the hyperbolas through the prominent spots, one finds that two of these curves intersect at right angles at the spot corresponding to the y-axis pole. As might be expected these two curves represent the x and z axes. A complete analysis of the X-ray photograph reveals which one is the x-axis. (See Heising for X-ray reflection angles.)

Although the x-axis can be located within a degree or so by X-ray analysis, it is very difficult to mark the small transducers with accuracy. However, one can make use of the optical properties of quartz to facilitate the marking. Since light incident on the y-cut crystals will be broken into two linearly polarized components in the quartz, the light leaving the crystal can be analyzed for the directions of polarization. A simple way to accomplish this is as follows.

The light incident along the y-axis will generally be
resolved into a component polarized along the z-axis and a component polarized along the x-axis. These components propagate at different velocities in the crystal and recombine at the exit surface as elliptically polarized light. However, suppose that linearly polarized light is incident on the transducer with its polarization vector parallel to either the x-axis or the z-axis. The light leaving the crystal will then have the same polarization as the incident light. Therefore by shining polarized light on the crystal, and varying the direction of polarization, one can locate the x and z axes.

A simple arrangement for determining the required axes in y-cut quartz is depicted in Figure 11a. Light from the source is polarized by a Nicol prism so that its polarization vector is vertical. The second Nicol prism is adjusted so that no light is transmitted through it, i.e., so that its direction of polarization is horizontal. The y-cut quartz transducer is placed in the rotating sample holder (Figure 11b) with its faces perpendicular to the light beam. For an arbitrary orientation of the transducer about its y-axis, light now appears at the output side of the analyzing Nicol prism since the incident light is converted into elliptically polarized light by the quartz. However, if the x-axis or the z-axis is vertical, the light leaving the quartz will still be linearly polarized in the vertical plane, and no light will be transmitted by the second prism. (Notice that one cannot
(a) OPTICAL ANALYSIS APPARATUS

(b) ROTATING HOLDER FOR TRANSDUCER

FIGURE II
distinguish between the two axes by this method.)

The transducer is placed on the adhering side of a strip of Scotch brand "Magic Tape" before the tape is placed in the sample holder such that the transducer is in the light channel. When the crystal is correctly oriented, one can place a vertical pencil mark on the tape through the hole in the sample holder, using the scribe marks as a guide. Since the accuracy of this mark can be checked (and the mark redrawn if necessary) by simply observing the orientation on the optical bench, it can be made with good accuracy (probably within 2°). Once one is satisfied with the accuracy of the pencil mark, he can remove the taped transducer for permanent marking. This is accomplished with the aid of a special holder which clamps the small transducer while a permanent mark is made on the thin edge of the crystal with a diamond scribing tool.

The method for finding the direction of polarization (the x-axis) for the transverse waves then consists of: (1) finding (and marking on the tape) the x and z axes using the optical method, (2) determining which is the x-axis by X-ray analysis, and (3) marking the crystal permanently with a diamond scribing tool.

C. The Transducer-Sample Bond

One of the major problems in an ultrasonic experiment is the bonding of the transducer to the sample. The bond must
uniformly transmit the elastic waves to the sample with low losses at low temperatures. A number of bonding materials have been tried with varying amounts of success. The "perfect" bond has not been found for all applications, but several materials are adequate for some applications.

For longitudinal waves, Dow Corning DC-200 silicone fluid with a viscosity of $10^6$ centistokes has proved to be adequate since only the change in the amplitude of the echo with magnetic field is important in this work. Although it has the disadvantage of non-permanency, a large number of bonds can be made and tested in a relatively short time (See below). Also, the silicone fluid does not attack the surface of the samples and can easily be removed. This latter feature is particularly important in the case of CaF$_2$.

Since transverse waves are more strongly attenuated in the silicone fluid than the longitudinal waves, the DC-200 fluid is not used for transverse waves. Armstrong C-7 epoxy resin$^{61}$ has been used successively as a bond material transmitting transverse waves to ruby. One end of the sample is coated with a thin film of the epoxy and the transducer and sample are placed in a spring-loaded press overnight so that the epoxy can harden.

Although the intrinsic attenuation of 9.3 Gc elastic waves is too high at room temperature to allow the testing of bonds, the attenuation at 1 Gc is not. Therefore a 1 Gc
apparatus is used for testing of bonds. This test system consists of a tunable reentrant cavity, a pulsed transmitting tube, and a superheterodyne receiver. The block diagram is shown in Figure 12. The echo pattern is observed on the oscilloscope.

Preparation of the bonds requires some amount of patience. The sample and transducer are cleaned and wiped with optical lens tissue. A small amount of silicone fluid is placed between the transducer and sample and they are placed in a spring-loaded press under a small amount of pressure. The bonded sample is then placed in the 1 Gc test cavity. The procedure for aligning transducer resonance, cavity resonance, and superheterodyne receiver is the same as described in Section 4.1. If no echoes are obtained, the silicone film is made thinner and the process is repeated. If the film becomes too thin, the echoes will ring as a result of spaces between transducer and sample not covered by the fluid. It is sometimes difficult to know when one has a "good" bond, because there is no guarantee that a bond which is sufficient at 1 Gc and room temperatures will still be so at 9.3 Gc and 4.2°K. It has been found by experience, however, that an echo pattern showing several sharp echoes in the test system has a good probability of being usable in the experimental system.

The Armstrong epoxy bonds are tested with the same procedure. However, if the bond is not good, the transducer must
FIGURE 12

PULSED TRANSMITTER

T-R SWITCH

MIXER-DETECTOR

I.F AMPLIFIER

OSCILLOSCOPE

TUNABLE CAVITY

LOCAL OSCILLATOR

1 Gc BOND-TESTING EQUIPMENT
be removed from the sample and the epoxy cleaned off both crystals. Heating the sample to about 200°C with a heat gun is usually sufficient to "break" the bond. The residual epoxy can be removed by acid and carbon tetrachloride. The process of applying and curing the epoxy and testing the bond is repeated until a suitable one is found.

It was indicated above that the epoxy, though adequate for ruby, is not desirable for CaF₂. The reasons are that ruby is hard to scratch, strong, and resistant to acids and other cleaning solutions. However, the polished surfaces of the CaF₂ samples are easily marred and they are attacked slightly by acids and water. A further problem is that CaF₂ cleaves very easily along a (111) plane. Heating the crystal to remove the bond may cleave it, and the difference in thermal contraction between the epoxy and CaF₂ when they are cooled to 4.2°K has fractured a CaF₂ sample.

Both the silicone fluid and epoxy bonds can only be used for one experiment at low temperatures because the thermal expansion breaks the bonds. A material that could be used for more permanent and possibly less lossy bonds is indium. This has been used with success elsewhere and with some success here. The development of the techniques for such a bond would probably be worthwhile.

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4.3 The Paramagnetic Samples

Samples which are to be used for ultrasonic paramagnetic resonance at 9.3 Gc must be fabricated with great care. The axis of the rod must be parallel to a pure-mode axis of the crystal to prevent off-axis propagation, and end faces of the rod must be polished flat and parallel to very close tolerances. The final polishing has thus been done by commercial firms.

The U\textsuperscript{4+}:Ca\textsubscript{2} samples were ordered from the Adolf Meller Company, ostensibly doped with 0.1\% U\textsuperscript{3+} (Subsequent investigation revealed that they were found to contain mostly U\textsuperscript{4+} ions.). Two unoriented crystals about 3/8" in diameter and 1" in length were obtained such that one sample with its axis along a (111) direction could be fabricated from each. The crystals were aligned in this laboratory with the use of a back-reflection Laue X-ray camera and a reference cut was made along a (111) plane using a diamond saw. The oriented crystals were then shipped back to the Adolf Meller Company for fabrication into circular cylindrical rods 3.0 mm in diameter and 0.72 inches in length. The alignment and cutting were such that the reference cut was parallel to a (111) plane within 0.5°. The end faces were polished flat to 1/4 wavelength of light and parallel within 6" of arc.

When the Meller samples were found not to contain U\textsuperscript{3+} in sufficient quantity for UPR, a second order was placed
with the Harshaw Chemical Company for a large boule of 0.1% $U^{3+}:CaF_2$. After much delay, an unoriented boule about 2" in diameter and 1 1/2" in length was obtained. Its deeper red color indicated that it was more properly doped with $U^{3+}$ than the Meller crystals. An EPR analysis revealed that this was the case. The Harshaw boule was large enough for samples in any orientation to be obtained from it. The boule was analyzed by X-ray techniques as before. Two samples were cut in the form of rectangular cylinders. One was cut such that its axis was along a (001) direction and the side faces were parallel to (100) and (010) planes, respectively. The second was cut such that its axis was along a (101) direction and its sides were parallel to (010) and (101) planes, respectively. The rods were then shipped to the Adolf Meller Company where their end faces were polished flat within 1/20 wavelength of light and parallel to 2" of arc.

The ruby sample was obtained from the Linde Company in the form of a circular cylindrical rod containing 1.2% $Cr^{3+}$. The end faces were polished parallel within 10" of arc and flat to 1/4 wavelength of light by the Valpey Crystal Corporation. The final dimensions of the sample were: diameter = 0.10" and length = 0.496".
V. EXPERIMENTAL RESULTS

5.1 $^{4+}\text{U}:\text{CaF}_2$

The first UPR measurements were made using one of the (111)-cut crystals obtained from Adolf Meller Company (ostensibly containing 0.1% $^{3+}\text{U}$). A very small absorption was observed at 4.2°K; however, the absorption lines were broad and asymmetric, and did not correspond to $^{3+}\text{U}$ resonances. During later attempts, the temperature was decreased to about 1.5°K in order to increase the signal, and records showing several different lines with the asymmetric line-shape were obtained. The optical and EPR spectra of $^{4+}\text{U}:\text{CaF}_2$ were published about this time and the indications were that the observed UPR lines could be attributed to $^{4+}\text{U}$. This was verified by an EPR analysis of the sample which revealed that it contained both $^{3+}\text{U}$ and $^{4+}\text{U}$ as well as other impurities. By this time the end faces of the sample had been damaged by use and all subsequent measurements were made on the remaining (111)-cut sample. These measurements could not be completed because of damage to the second sample (See below.) and the results presented in Figure 14 are not conclusive.

Measurements on the (111)-cut $^{4+}\text{U}:\text{CaF}_2$ samples were especially difficult for two major reasons: (1) the small, unknown number of $^{4+}\text{U}$ ions in the crystal, and (2) the broad asymmetric line-shapes.
The growing conditions of the crystals are apparently quite important in determining the distribution of the uranium placed in the melt. The possibilities known to be available to the uranium impurity in CaF$_2$ are U$^{4+}$ in a site of trigonal symmetry, U$^{3+}$ in a site of tetragonal symmetry, and U$^{3+}$ in a site of cubic symmetry. There are four types of magnetic ion for the U$^{4+}$ ions and three types for the U$^{3+}$ ions in tetragonal symmetry which are, in general, not degenerate in a magnetic field. Therefore, the number of ions contributing to a given absorption line can be small. When the temperature of the sample was lowered by pumping on the helium in order to increase the difference in population of the energy levels, the lifetime of the liquid helium in the dewar was reduced by about 75%. The time available for taking data was correspondingly reduced. The time element is important because, if one is to measure the line-shape accurately, he must vary the magnetic field slowly. A greater number of U$^{4+}$ ions might remove the necessity of pumping.

The line-shape affects the measurement adversely in two ways. The local strain spreads the line out and reduces the peak absorption. Also, the broad lines (of the order of hundreds of gauss) overlap sufficiently to prevent accurate attenuation measurements at many angles of the magnetic field. One must be careful in analyzing the absorption lines to make sure that there is no interference. Since the absorption
decreases sharply on the high field side of the line (See Figure 15.), the peak absorption can usually be measured accurately only for the line at highest field near angles where interference occurs.

The peak attenuation of (111) longitudinal elastic waves in U$^{4+}$:CaF$_2$ was measured for three types of ion: (111), (111), and (111). No absorption by (111) ions was observed at any angle of the magnetic field.

Absorption by the (111) ions was observed. The attenuation is given by eq. (3-27). This is related to the measured attenuation of the nth echo in db by eq. (3-15). Combining these two equations,

\[
\frac{N}{8.686 \, nL} = \frac{(\Delta n) \omega g(\nu_c)}{18m \sqrt{3} \frac{\hbar^3}{ne^2}} \left| \langle -H_{SL}^{(111)} \rangle + \rangle \right|^2.
\]

The population difference as a function of temperature, $T$, is (by Boltzmann statistics):

\[
(\Delta n) = \frac{n_0 (1 - e^{-\hbar \nu/kT})}{(1 + e^{-\hbar \nu/kT})},
\]

where $k$ is Boltzmann's constant, $\hbar \nu$ is the difference in energy of the levels, $n_0$ is the number of U$^{4+}$ ions contributing to the absorption, and the other symbols are as previously defined. Since $n_0$ is not known and insufficient data has been taken to determine $g(\nu_c)$ accurately, the magnitude of the matrix element cannot be determined from the data. The angular dependence of
the matrix element can give information about the nature of
the spin-lattice Hamiltonian, however. Therefore the quantity

\[
\frac{N n_e}{(\Delta n)n} = \frac{8.686 n_o \omega_g(\nu_g)}{18m \nu_{(\text{Hi})}^3 \kappa e^2} \left| \left\langle - \left| H_{SL}^{(1\text{II})} \right| + \right\rangle \right|^2
\]

\[
= \text{(number)} \left| \left\langle - \left| H_{SL}^{(1\text{II})} \right| + \right\rangle \right|^2
\]

which is independent of echo number and temperature, represents
the angular dependence of the attenuation. This quantity is
plotted in Figure 14.

Absorption by (1\text{II}) ions also was observed. The spin-
lattice Hamiltonian for (1\text{II}) ions is even more complicated than
that for (1\text{III}) ions. Again, insufficient data is available
for complete analysis, therefore the data points are not in-
cluded in this thesis.

After the preliminary data on the (1\text{III}) and (1\text{II}) ions were
obtained, attempts were made to complete the analysis. It was
found on two different occasions that the attenuation had de-
creased considerably from previous measurements. This is
illustrated in Figure 15. A possible explanation of this is
that the crystal may have received additional strains which
broadened the lines and thus reduced the peak attenuation.

A photograph of the echo pattern for longitudinal (1\text{III})
waves at 9.4 Gc in U^{4+}:\text{CaF}_2 is shown in Figure 13. The bottom
trace illustrates the amplitude of the echoes with the magnetic
field off and the top trace illustrates the situation with the field at resonance.

It is interesting to note that no dispersion in the velocity of the (111) longitudinal elastic waves in CaF$_2$ at 1 Gc and 9.3 Gc has been observed. Assuming that the change in length of the sample at 4.2°K is negligible$^{68}$, the room temperature length and the time interval between echoes measured on the photographs of oscilloscope traces were used to calculate the velocity. Within experimental error, the values agreed with the values given in Table 4-2.

5.2 Cr$^{3+}$:Al$_{2}$O$_{3}$

A. Longitudinal Waves

The photograph in Figure 18a illustrates a typical echo pattern for 9.31 Gc longitudinal elastic waves in the 1.2% Cr$^{3+}$ ruby sample at 4.2°K. The velocity of the waves was found to be $1.17 \times 10^6$ cm/sec, $\pm 5\%$, assuming that the sample's change in length due to thermal contraction is negligible. This compares favorably with the value of $1.10 \times 10^6$ cm/sec obtained by Wachtmann, et al., at room temperature and low frequencies.

The attenuation of the 9th echo in db is plotted in Figure 19 as a function of $\theta$ (the angle between the magnetic field and the z-axis) for data taken on the 2-3 high-field
transition. The error in attenuation is shown by the error bars; the error in \( \Theta \) is estimated to be \( \pm 1^\circ \) for \( \Theta > 15^\circ \). The crystalline z-axis is not exactly parallel to the rod axis. This misalignment, plus the error in placing the sample such that its axis is in the plane of rotation of the magnet, means that the error in \( \Theta \) can be several degrees for small values of \( \Theta \); and it is estimated to be \( \pm 3^\circ \) for \( \Theta < 15^\circ \).

The line-width of the absorption at half-maximum in gauss is presented in Figure 20 as a function of \( \Theta \). The error in line-width is estimated to be less than 15 gauss, and the error in \( \Theta \) is as above.

B. Transverse Waves

The photograph in Figure 24 illustrates the echo pattern for 9.15 Gc transverse waves along the z-axis of the 1.2\% Cr\(^{3+}\) ruby sample at 4.2\(^\circ\)K. The echoes are broad and show signs of a mixture of waves. This makes a measurement of the velocity difficult, but an estimate yields \( V_T = 5.7 \times 10^5 \) cm/sec, \( \pm 10\% \). The value of \( 5.94 \times 10^5 \) cm/sec given in Section 4.2A is probably more accurate, and it will be used in the calculations.

The attenuation, \( N \), of the 4th echo in db is presented in Figure 25 as a function of \( \Theta \) for data taken on the 1-2 high-field transition. The error in the measurement of \( N \) is estimated to be less than 0.2 db at all angles. Data was taken on the 4th and 5th echoes; the data on the 5th echo was
multiplied by 4/5 and averaged with that on the 4th echo.

The line-width of the absorption at half-maximum in gauss is presented in Figure 26 as a function of $\Theta$. Again, it is estimated that the error in line-width is less than 15 gauss and that the error in $\Theta$ is $\pm 1^\circ$. No data was taken for values of $\Theta$ between 23$^\circ$ and 32$^\circ$ because of interference between absorption lines of the 1-2 and 2-3 high-field transitions.

5.3 $U^{3+}$:CaF$_2$

The two $U^{3+}$:CaF$_2$ samples with axes along (001) and (101) respectively, were received too late for meaningful data to be obtained. Time was available for only one data "run" on the (001) sample.

The photograph in Figure 30 illustrates the echo pattern for 9.31 Gc longitudinal waves along the (001) direction of CaF$_2$ at 4.2$^\circ$K. The velocity was found to be $7.40 \times 10^5$ cm/sec, $\pm 5\%$, which is in good agreement with the value of $7.36 \times 10^5$ cm/sec given in Table 4-2.

Absorption was observed at 4.2$^\circ$K, but the signal-to-noise ratio was so poor that the lines were almost obscured. The signal was much weaker than for the $U^{4+}$:CaF$_2$ samples. There was evidence of saturation, and a different technique will probably be necessary for measuring attenuation in the $U^{3+}$:CaF$_2$ samples.
FIGURE 13

(III) LONGITUDINAL ELASTIC WAVES AT 9.4 Gc IN $^{4+}\text{CaF}_2$
FIGURE 14

$\phi = \text{ANGLE BETWEEN } \overline{B} \text{ AND (111) ROD AXIS}$

ANGULAR DEPENDENCE OF ATTENUATION OF (111) LONGITUDINAL WAVES
BY (111) IONS IN $U^{4+}:CAF_{2}$
AFTER HANDLING

INITIALLY

COMPARISON OF UPR ABSORPTION LINES IN $U^{234,CaF_2}$

FIGURE 15

RELATIVE ATTENUATION

B IN KG

1.9
1.8
2.0
2.1
2.2
COORDINATE SYSTEMS FOR Cr\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3}

FIGURE 16
RESONANT MAGNETIC FIELD B, VS. θ FOR RUBY

$\nu = 9.3 \, g_c$

$[0, 90]$

$[0, 90]$

FIGURE 17
LONGITUDINAL WAVES ALONG THE C-AXIS OF RUBY

ν = 9.31 GHz

FIGURE 18
ATTENUATION OF 9th ECHO VS. $\theta$ FOR LONGITUDINAL WAVES ALONG THE C-AXIS OF RUBY, $\nu = 9.31$ Gc, 2-3 HIGH-FIELD TRANSITION
$\left( \frac{\partial \mu}{\partial B} \right)_c$ vs. $\theta$ for ruby, 2-3 transition, $\nu = 931 \text{ Gc}$.
ENERGY HALF-WIDTH, $\delta$, VS. $\theta$ FOR RUBY, 2-3 TRANSITION, $\nu = 9.31$ Gc
ANGULAR DEPENDENCE OF ATTENUATION OF LONGITUDINAL WAVES IN RUBY.

2-3 TRANSITION

- EXPERIMENTAL
- THEORETICAL $\langle 2|S_z^2|3\rangle^2$
- RESULTS OF TUCKER

$\frac{\text{in} \sqrt{\text{N}}}{\text{in} \times 10^{-3}}$

Figure 23
\( \nu = 9.15 \text{ Gc} \)

TRANVERSE WAVES ALONG THE C-AXIS OF RUBY

FIGURE 24
ATTENUATION OF TRANSVERSE WAVES IN 1.2% RUBY, I-2 TRANSITION, VS. $\theta$. 

$\nu = 9.15 \text{ Gc}$ 

ERROR

ATTENUATION OF 4TH ECHO IN DB

$\theta$ IN DEGREES

FIGURE 25
LINE HALF-WIDTH VS. $\theta$ FOR RUBY, 1-2 TRANSITION, $v = 9.15$ Gc

$\Delta B_{1/2}$ in Gauss x $10^{-2}$

$\theta$

ERROR

FIGURE 26
ENERGY HALF-WIDTH, $\delta$, VS. $\theta$ FOR RUBY, 1-2 TRANSITION, $\nu = 9.15$ Gc

FIGURE 28
$M_2^* \text{ vs. } \theta$ for transverse waves along the c-axis of ruby, 1-2 transition.
(001) LONGITUDINAL WAVES IN $U^{3+}:CaF_2$

$\nu = 9.31$ Ge
VI. ANALYSIS OF RESULTS

6.1 $\text{U}^{4+}:\text{CaF}_2$

The results obtained from the measurement of attenuation of (111) longitudinal elastic waves in $\text{U}^{4+}:\text{CaF}_2$ are not conclusive. However, some observations can be made.

Consider first the (111) ions. The spin-lattice Hamiltonian for them is (from eq. 3-17)

$H^{(111)}_{\text{SL}} = 3e \left[ B_{33} S_z + 2E_{13} B x S_x + 2E_{33} B z S_z \right].$

The matrix element of $S_z$ between the two eigenstates of $H_S$ is zero; therefore, the attenuation is proportional to $E_{13}^2$. Since no absorption by the (111) ions has been observed, $E_{13}$ must be small, or zero.

No absorption by the (111) ions should be expected to first order. This can be shown by two simple arguments. First, consider the effect of strain along the symmetry axis of the ion. To first order this does not change the symmetry of the crystalline field at the site of the ion and thus does not remove the degeneracy of the doublet. Similarly, suppose that the perturbing potential, $V$, can be expanded in powers of $J_1$ with the use of operator equivalents. A longitudinal elastic wave along the symmetry axis could then be expressed in powers of $J_z$. The matrix elements of all powers of $J_z$ between $|\chi\rangle$ and $|\phi\rangle$ vanish (Refer to Section 2.2); therefore absorption by an ion from longitudinal waves along its symmetry axis should
be zero to first order.

The absorption by (\(1\overline{1}1\)) ions is illustrated in Figure 14. The data on the 6th echo was obtained first; then the data on the 7th echo was obtained after the transmission characteristics of the bond improved following a retransfer of liquid helium. The two sets of data do not fit smoothly (This may be evidence of saturation.). One can use these results and some observations on absorption by (1\(1\overline{1}\)) ions to make conjectures about the nature of the spin-lattice Hamiltonian.

It was shown in Section 2.2 that terms of the form \(A_1^I S^I_1\) should predominate in the spin-lattice Hamiltonian for \(U^{4+}:CaF_2\) (See eq. 2-35.). If the assumed second-order terms of the form \(S^I_1 B_j\) can be neglected as small, then the attenuation for (1\(1\overline{1}\)) ions is of the form (from eq. 3-27)

\[
(6-2) \alpha^{(1\overline{1}1)} = \frac{(\Delta n) \hbar \omega g(\nu_0)}{18m \sqrt{\nu_{(1)}^3}} \left| \frac{-4}{1/18} \sqrt{B_{15}} - 1(4/3 B_{22}) \right|^2.
\]

Notice that the only quantity in (6-2) that may have angular dependence is \(g(\nu_0)\), the normalized line-shape function, and its variation with angle should be small.

The second-order terms in the spin-lattice Hamiltonian introduce angular dependence into the attenuation through the presence of magnetic field components. According to the assumed form of the spin-lattice Hamiltonian, the peak attenuation should then have a small variation with angle about a
larger value independent of angle. The data on (111) ions
(and on (111) ions) do not show marked angular variation, and
this appears to justify the assumptions. However, certainly a
greater quantity of reliable data should be available before
conclusions are drawn.

6.2 Cr\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3}

The experimental attenuation in db, N, is related to the
theoretical value by eq. (3-15). Knowledge of the normalized
line-shape function is also required for verification of the
specific nature of the spin-lattice Hamiltonian. The line-
shape function, \(g(\nu)\) is assumed to be a normalized Gaussian
function,

\[
(6-3) \quad g(\nu) = \frac{a}{\sqrt{\pi}} e^{-a^2 (\nu - \nu_0)^2},
\]

where \(\nu_0\) is the resonant frequency. If the width at half-
maximum of \(g(\nu)\) is designated by \(\delta\), then

\[
(6-4) \quad \delta = 2(\nu_{1/2} - \nu_0),
\]

where \(\nu_{1/2}\) is the frequency at half-maximum; and

\[
(6-5) \quad a = 2 \frac{\sqrt{\ln 2}}{\delta}.
\]

Therefore, at resonance,

\[
(6-6) \quad g(\nu_0) = 2 \frac{\sqrt{\ln 2}}{\pi} \left(\frac{1}{\delta}\right).
\]
The half-width, $\delta$, cannot be measured directly since frequency is held constant and the magnetic field is varied in the experiment. Let $G(B)$ be the experimental line-shape function, which has a shape similar to $g(\nu)$. The width at half-maximum of $G(B)$, $\Delta B_{1/2}$, was measured. For small line-widths,

\begin{align}
(6-7) \quad \nu &= \nu_o + \left( \frac{\partial \nu}{\partial B} \right)_o (B - B_o), \\
(6-8) \quad \delta &= 2(\nu_{1/2} - \nu_o) = \left( \frac{\partial \nu}{\partial B} \right)_o 2(B_{1/2} - B_o) = \left( \frac{\partial \nu}{\partial B} \right)_o \Delta B_{1/2}
\end{align}

approximately. The slope, $(\partial \nu / \partial B)_o$, is obtained from the plot of resonant frequency versus magnetic field for the transition of interest at each angle, $\theta$. Figure 21 illustrates the slope as a function of $\theta$, for the 2-3 high field transition at $\nu_o = 9.31$ Gc; and Figure 27 illustrates the slope as a function of $\theta$ for the 1-2 transition at $\nu_o = 9.15$ Gc.

The difference in population of energy levels $i$ and $j$ for the four-level system of ruby is calculated from (by Boltzmann statistics)

\begin{align}
(5-9) \quad \Delta n &= n_o \left( e^{-E_i/kT} - e^{-E_j/kT} \right) / \sum_{i \in I} e^{-E_i/kT}
\end{align}

where $n_o$ is the total number of Cr$^{3+}$ ions in the sample. If the total mass of the crystal is $m$, the concentration of ions is 1.2%, $M$ is the molecular weight of Al$_2$O$_3$, and $N_o$ is
Avogadro's number, then

\[ n_0 = \frac{0.012}{1.012} \frac{m}{M} N_0. \]

Now, \( m = 0.2597 \) gram and \( M = 52.0 \) grams; therefore

\[ n_0 = 3.6 \times 10^{19} \text{ ions}. \]

A. Longitudinal Waves

The comparison of theory to experiment for longitudinal waves in ruby can be made by combining eqs. (3-15), (3-53), and (6-6). The data was obtained on the 9th echo for the 2-3 high-field transition; therefore the square of the product of \( G_{33} \) and the matrix element is

\[ G_{33}^2 \langle 2 | S_z^2 | 3 \rangle = \frac{4 m v_L^3 h}{8l(8.666)(1.73)\sqrt{\hbar^2 m^2 l^2}} \frac{N \delta}{(\Delta n \hbar_0)} \]

The length of the sample is 1.260 cm, \( v_L = 1.17 \times 10^5 \text{ cm/sec}, \)
\( \nu_0 = 9.31 \text{ Gc} \) and \( m = 0.2597 \) g; therefore

\[ G_{33}^2 \langle 2 | S_z^2 | 3 \rangle = 53.8 \frac{N \delta}{(\Delta n / \hbar_0)} \]

in units of \((\text{Gc})^2\), where \( \delta \) is in Gc and \( N \) in db. The attenuation, \( N \), is given in Figure 19 and \( \delta \) in Figure 22. The quantity \((\Delta n / \hbar_0)\) is obtained from eq. (6-9) for \( T = 4.2^\circ \text{K} \). The values of the energy and matrix elements were obtained from Dr. P.L. Donoho. 69

The right-hand side of eq. (6-13) is plotted in Figure 23.

-71-
It should have the same angular dependence as $\left| \langle \frac{2}{3} | S_z | \frac{2}{3} \rangle \right|^2$, which is shown for comparison (in arbitrary units). Although the experimentally-determined curve has the same general shape, the deviation—which is outside experimental error—indicates other effects.

First, the z-axis of the crystal is not exactly parallel to the sample axis, but makes an angle of $3^\circ - 4^\circ$ with it. The axis of the sample is therefore not a "pure-mode" axis, and it is possible that the residual attenuation as $\theta$ approaches zero is due to other waves mixed with the longitudinal waves of interest. Another possibility is that the crystalline z-axis was not in the plane of rotation of the magnet so that $\theta$ approached a small angle as the magnetic field was rotated toward the sample axis (This effect is not large enough to explain the total discrepancy.).

Also, it is possible that the paramagnetic-ion system was saturated by the elastic waves. Since the crystal was pulsed once every millisecond and $T_1$ is of the order of milliseconds, a steady state of partial saturation could have occurred.

The dashed curve in Figure 23 has been plotted in arbitrary units to illustrate the angular dependence of the transition probability obtained by Tucker$^{70}$ using the saturation technique. It illustrates the effect of the presence of transverse waves in addition to the longitudinal waves.
Since the angular dependences of the theoretical and experimental curves are not the same, the value of $G_{33}$ calculated from the results depends upon angle. For $\theta > 45^\circ$, the agreement of the two curves is good and the values of $G_{33}$ calculated are nearly independent of angle. These results indicate that $G_{33}$ is of the order of 100 Gc, which is the same order of magnitude as that obtained by other investigators. The accuracy of this value is limited by several factors. The possibilities of saturation and the presence of small-amplitude transverse waves have already been mentioned. Also, the assumption of the form of $g(\psi)$ may not be justified. A further uncertainty is in the number of ions, $n_0$. If the resonances of a large number of ions are sufficiently perturbed by exchange interactions, as they might well be in crystals of high concentration, then the value of $n_0$ used in the calculation would be too high.

B. Transverse Waves

The comparison of theory to experiment for transverse waves along the $z$-axis of ruby can be made by combining eqs. (3-15), (3-53), and (6-6). The attenuation of the 4th echo for the 1-2 transition is shown in Figure 25. Therefore, the quantity of interest, $M_{12}^2$, is:

\[ M_{12}^2 = \left[ \frac{m v_T^3 h}{8.686(8m^2) \sqrt{\frac{\ln 2}{\pi} \frac{\mu L}{\Delta n}}} \right] N \frac{s}{(\Delta n)}. \]
For the transverse waves; \( v_T = 5.94 \times 10^5 \text{ cm/sec} \) and \( \nu_0 = 9.15 \text{ Gc} \); therefore

\[
(6-15) \quad M_{12}^2 = 62 \frac{N S}{(\Delta n/n_0)}
\]

in units of \((\text{Gc})^2\), where \( S \) is in Gc and \( N \) in db. Again, the values of \((\Delta n/n_0)\) were obtained from eq. (6-9) for \( T = 4.2^\circ \text{K} \); and the values of the matrix elements were obtained from Dr. P. L. Donoho. The values of \( S \) are illustrated in Figure 28.

The right-hand side of eq. (6-15), corresponding to the experimental data, is plotted in Figure 29. The theoretical curve drawn through the points represents the fit minimizing the standard deviation. The ratios of \( G_{14}, G_{44}, \) and \( G_{25} \) obtained from this fit are: \( G_{25} = \mp 1.1 \) \( G_{44} \) and \( G_{14} = -0.13 \) \( G_{44} \). The magnitudes are then: \( G_{25} = \mp 29, G_{14} = -3.41, \) and \( G_{44} = 26 \), in units of Gc.

The results obtained from the attenuation of transverse waves are subject to the errors previously described for longitudinal waves. However, the general shape of the experimental curve (Figure 29) should be correct, and this curve could not be fitted at all without the assumption of the G tensors described in Section 2.4. Therefore, the existence of two G tensors with \( C_3 \) symmetry, differing in the sign of \( G_{25} \), appears to be verified. Although it was found that the shape of the theoretical curve depended markedly on the assumed ratios of the above components of the G tensor, no quantitative infor-
mation is yet available for the probable error in the ratio.

The values of \( G_{44} \) and \( G_{33} \) obtained by Hemphill are believed to be accurate. The ratio of \( G_{33} \) to \( G_{44} \) obtained by him is 4.0. The ratio of \( G_{33} \) and \( G_{44} \) obtained in this experiment is also 4, implying agreement of the UPR results with the strain results. Also, the result that \( G_{14} \) is much smaller than \( G_{44} \) is consistent with the results obtained by the strain method.

In conclusion, the ratios of the components of the \( G \) tensor observable on the sample studied are believed to be correct. The magnitudes are in doubt for the reasons previously discussed. The line-widths of the interactions for both longitudinal and transverse waves were found to be \( 3 \times 10^8 \) cps.
VII. DISCUSSION

It is clear from the discussions in the preceding sections of this thesis that the method of ultrasonic paramagnetic resonance involves difficult experimental techniques and requires knowledge of the line-shape function and actual concentration of ions for accurate determination of the parameters in the spin-lattice Hamiltonian. It is worthwhile to compare this method with the methods of steady strain and saturation, which were discussed in Section I.

The method utilizing steady strain applied to the crystal has several advantages. It is not necessary to know the line-shape function or the concentration. Although more samples (cut in different orientations) are required, the samples do not have to be polished to optical tolerances as in UPR. The UPR method is not always sensitive to the signs of the components of the magnetoelastic coupling tensors, whereas, the strain method is. There is, of course, no transducer-bond problem in the strain method; and while it is necessary to reduce the temperature of the sample to 4.2°K to decrease the intrinsic attenuation of elastic waves at 9.3 Gc to a reasonable value, strain experiments on some crystals (such as ruby) can be done at room temperature.

The method of saturation of the EPR signal by elastic waves at the resonant frequency is useful also; however, it requires the auxiliary measurement of $T_1$ for determination of the ultra-
sonic transition probability\textsuperscript{72}. Although the same specifications are required for the sample as in UPR, the bond problem may not be as severe because less ultrasonic power is required.

The three types of crystals studied in this investigation provide good examples of the applicability of the three methods. One can study samples such as ruby by all three techniques with success, and the methods complement each other. For rare-earth or actinide ions such as $\text{U}^{3+}\text{:CaF}_2$ with Kramers doublet ground-states, both the UPR signals and steady-strain effects have been found to be small; therefore a saturation experiment on $\text{U}^{3+}\text{:CaF}_2$ may provide the most information. For rare-earth or actinide ions such as $\text{U}^{4+}\text{:CaF}_2$ with non-Kramers-doublet ground states, the UPR method is probably the most useful. The reason is that the EPR signal vanishes to first order (See Section 8.1B.), and the observed line-shape is distorted by the $(\Delta/h\nu)^2$ dependence of the EPR transition probability. (To first order, the UPR signal is independent of $\Delta$, and should be much stronger for non-Kramers doublets than for Kramers doublets.)

In view of the evidence of saturation in the UPR results on longitudinal waves in ruby, an improvement on any UPR experiment would be the addition of a second cavity in which a portion of the paramagnetic sample could be inserted. The purpose of the additional cavity would be to provide a means of monitoring the sample with a small EPR signal to detect saturation. Such
a double-cavity arrangement is presently being constructed.

The spin and spin-lattice Hamiltonians developed in Section 2.3 for \( \text{U}^{3+}:\text{CaF}_2 \) should also be applicable to \( \text{Nd}^{3+}:\text{CaF}_2 \). The configuration of \( \text{Nd}^{3+} \) is \( 4f^3 \), the ground state of the free ion is \( ^4I_{9/2} \), and the ground state in the crystalline field of \( \text{CaF}_2 \) is a Kramers doublet. The EPR analysis of \( \text{Nd}^{3+}:\text{CaF}_2 \) has been reported\(^7\)\(^3\), and samples are available commercially. A comparison of the behavior of \( 4f^3 \) and \( 5f^3 \) electrons in \( \text{CaF}_2 \) could be made.

Similarly, \( 4f^2 \) ions such as \( \text{Pr}^{3+} \) in \( \text{CaF}_2 \) would provide a comparison with \( \text{U}^{4+}:\text{CaF}_2 \).

Theoretical calculations for rare-earth and actinide ions are needed to augment the experimental program now underway. An extension of the simple argument in Section 2.2 for \( \text{U}^{4+}:\text{CaF}_2 \) to include the effects of excited states would be useful as well as more rigorous calculations such as those indicated by the Russian authors\(^7\)\(^4\).
8.1 \textbf{U}^{4+}:\textbf{CaF}_2

A. Eigenvalues and Eigenfunctions of \(H_S\) for \(U^{4+}:\text{CaF}_2\)

The spin Hamiltonian for each type of ion is of the form

\begin{equation}
\label{eq:1}
H_S = g_{||} \beta B_z S_z + \Delta_x S_x + \Delta_y S_y = \frac{1}{2} \begin{pmatrix}
\gamma & \Delta \\
\Delta & -\gamma
\end{pmatrix}
\end{equation}

where

\begin{align}
\gamma & \equiv g_{||} \beta B_z, \\
\Delta & = \Delta_x \pm i \Delta_y.
\end{align}

The axis of the coordinate system which is proper for eq. (8.1-1) must be parallel to the symmetry axis of the type of ion being considered.

The diagonalization of \(H_S\) yields the energy,

\begin{equation}
\label{eq:2}
E_{\pm} = \pm \frac{1}{2} \sqrt{\gamma^2 + \Delta^2} \equiv \pm \varepsilon,
\end{equation}

where \(\Delta^2 = \Delta_x^2 + \Delta_y^2\).

The parameter \(\Delta\) is the zero field splitting for the ion, as shown in the illustration.

\begin{equation}
E_+ - E_- = 2\varepsilon = h\nu
\end{equation}
It must be remembered that $\Delta$ can vary from ion to ion, and may well be zero for some.

The eigenfunctions corresponding to $E^+$ and $E^-$ are, respectively:

\[
(8.1-5) \quad \psi_+ \equiv \begin{pmatrix} a_+ \\ b_+ \end{pmatrix} = \begin{pmatrix} (2E)^{-1/2} (E^+ + E^+ \gamma)^{1/2} \\ \frac{1}{2} \Delta \left[ 2E (E^+ + E^+ \gamma) \right]^{-1/2} \end{pmatrix}
\]

\[
(8.1-6) \quad \psi_- \equiv \begin{pmatrix} a_- \\ b_- \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} \Delta \left[ 2E (E^+ + E^+ \gamma) \right]^{-1/2} \\ (2E)^{-1/2} (E^+ + E^+ \gamma)^{1/2} \end{pmatrix}
\]

B. EPR Absorption

In an EPR experiment the sample is placed in a resonant cavity such that the paramagnetic ions are influenced by an alternating rf magnetic field, $B_0^i$, in addition to the dc magnetic field. The Hamiltonian for this interaction is

\[
(8.1-7) \quad H^i = \varepsilon_{\parallel} B_0^i S_z
\]

Time-dependent perturbation theory can be used to calculate the energy absorbed from the rf field by each ion. Since the absorption is proportional to the square of the absolute value of the matrix element of $H^i$ between the two eigenstates, one is interested in the quantity,

\[
(8.1-8) \quad \left\langle - \middle| H^i \right| + \right\rangle = \frac{\varepsilon_{\parallel} B_0^i}{2} (a^* a_+ - b^* b_+) = \frac{\varepsilon_{\parallel} B_0^i}{2} \left( -\frac{\Delta}{2E} \right)
\]
The absorption per ion $A$ is then proportional to:

\[ A \sim \left| \left\langle H' \right| + \right| \right|^2 g(\nu_0) = \left( \frac{\mu \phi B_z'}{4 \hbar \nu_0} \right)^2 (\Delta)^2 g(\nu_0), \]

where $\nu_0$ is the frequency of the rf field and $g(\nu_0)$ is the normalized line-shape function.

C. Resonant $B$ in Laboratory System

The magnitude of the magnetic field for resonance for each type of ion must be determined for each angle which $B$ makes with a reference direction in the laboratory so that the various absorption lines can be identified. This calculation can be made by relating the crystalline coordinate system to the laboratory coordinate system when the sample is oriented in a known direction in the laboratory. The coordinate systems are illustrated in Figure 3a.

The $XYZ$ system is chosen to coincide with the natural cubic axes of CaF$_2$. The $x'y'z'$ system is the laboratory system. The U$^{4+}$:CaF$_2$ sample is cut such that its axis lies along a (111) direction in the crystalline coordinate system. This axis is placed in the horizontal plane of the laboratory, and the $x'y'z'$ system is chosen such that the sample axis is parallel to the $x'$ axis. Furthermore, the sample is so oriented that its (100) direction lies in the horizontal plane ($x'-y'$ plane) of the laboratory. To relate the resonant value of $B$ for each type of ion to the angle $B$ makes with $x'$ (the
reference direction), one must find the relation between that angle and the angle $\mathbf{E}$ makes with each ion axis, i.e., each (111) type direction of the crystal.

The Eulerian angles can be used to find the relation between the description of a vector in the $\text{XYZ}$ system and the description of the same vector in the $x'y'z'$ system. This relation is necessary for finding the laboratory angular dependence of the resonant value of $B$. The definition and transformation matrices for the Eulerian angles $(\phi, \theta, \psi)$ are discussed in the book by Goldstein$^{75}$.

Choose $\phi = 0$. Since $x'$ has been chosen as the direction of the axis of the sample, it is the (111) direction in the $\text{XYZ}$ system. Therefore,

\begin{equation}
\psi = \cos^{-1}\sqrt{1/3}, \quad \sin \psi = \sqrt{2/3}.
\end{equation}

One must use the fact that the (100) direction of the crystal has been chosen to be in the $x'-y'$ plane to determine $\theta$.

Consider a vector, $\mathbf{r}'$, parallel to $x'$. Its description in the $x'y'z'$ system is

\begin{equation}
\mathbf{r}' = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.
\end{equation}

The description of the same vector in the $\text{XYZ}$ system can be obtained with the use of the inverse transformation matrix, $A^{-1}$, involving the Eulerian angles:
(8.1-12) \[ \mathbf{F} = \mathbf{A}^{-1} \mathbf{F}' \].

The matrix, from Goldstein, p. 109, is
\[
(8.1-13) \quad \mathbf{A}^{-1} = \begin{pmatrix}
\frac{1}{\sqrt[3]{3}} & -\frac{\sqrt{2}}{\sqrt[3]{3}} & 0 \\
\frac{2}{\sqrt[3]{3}} \cos \varphi & \frac{1}{\sqrt[3]{3}} \cos \varphi & -\sin \varphi \\
\frac{2}{\sqrt[3]{3}} \sin \varphi & \frac{1}{\sqrt[3]{3}} \sin \varphi & \cos \varphi
\end{pmatrix}.
\]

However, one also knows that \( \mathbf{F} \) in the XYZ system is given by
\[
(8.1-14) \quad \mathbf{F} = \frac{r}{\sqrt[3]{3}} \begin{pmatrix}
1 \\
1 \\
1
\end{pmatrix}.
\]

Therefore by substituting (8.1-11), (8.1-13), and (8.1-14) into (8.1-12), one obtains \( \varphi \).
\[
(8.1-15) \quad \frac{r}{\sqrt[3]{3}} \begin{pmatrix}
1 \\
1 \\
1
\end{pmatrix} = \begin{pmatrix}
\frac{1}{\sqrt[3]{3}} & -\frac{\sqrt{2}}{\sqrt[3]{3}} & 0 \\
\frac{2}{\sqrt[3]{3}} \cos \varphi & \frac{1}{\sqrt[3]{3}} \cos \varphi & -\sin \varphi \\
\frac{2}{\sqrt[3]{3}} \sin \varphi & \frac{1}{\sqrt[3]{3}} \sin \varphi & \cos \varphi
\end{pmatrix} \begin{pmatrix}
1 \\
r \\
0
\end{pmatrix}
\]
\[
= r \begin{pmatrix}
\frac{1}{\sqrt[3]{3}} \\
\frac{2}{\sqrt[3]{3}} \cos \varphi \\
\frac{2}{\sqrt[3]{3}} \sin \varphi
\end{pmatrix}
\]

(8.1-16) \[ \sin \varphi = \cos \varphi = \frac{1}{\sqrt[3]{2}}, \Rightarrow \varphi = 45^\circ \]

The transformation matrix is then
\[
(8.1-17) \quad \tilde{\mathbf{A}} = \begin{pmatrix}
\frac{1}{\sqrt[3]{3}} & \frac{1}{\sqrt[3]{3}} & \frac{1}{\sqrt[3]{3}} \\
\frac{2}{\sqrt[3]{3}} & \frac{1}{\sqrt[3]{6}} & \frac{1}{\sqrt[3]{6}} \\
0 & -\frac{1}{\sqrt[3]{2}} & \frac{1}{\sqrt[3]{2}}
\end{pmatrix}.
\]

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Equation (8.1-17) can be used to find the angular dependence of the resonant \( B \) in the laboratory system. First the description of each (\( 111 \)) type direction in the laboratory system must be found. This is done by using the equation,

\[(8.1-18)\]
\[\overline{F}' = \overline{A} \overline{F}\]

for each direction. As an example, the (\( 1\overline{1}1 \)) direction will be considered. For (\( 1\overline{1}1 \)):

\[(8.1-19)\]
\[\overline{F} = \frac{r}{\sqrt{3}} \begin{pmatrix} 1 \\ -1 \\ -1 \end{pmatrix},\]

\[(8.1-20)\]
\[\overline{F}' = \begin{pmatrix} \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \\ -\sqrt{2/3} & \sqrt{1/6} & \sqrt{1/6} \\ 0 & -\sqrt{1/2} & \sqrt{1/2} \end{pmatrix} \begin{pmatrix} 1 \\ -1 \\ -1 \end{pmatrix} \sqrt{3} = r \begin{pmatrix} -1/3 \\ -2/3 \sqrt{2} \\ 0 \end{pmatrix} .\]

By referring to Figure 3b, one can see that \( \overline{F} \), in the laboratory system, is

\[(8.1-21)\]
\[\overline{F} = \hat{\varphi}' \overline{B} \cos \varphi' + \hat{\varphi}' \overline{B} \sin \varphi',\]

where \( \varphi' \) is the azimuthal angle in a polar coordinate system.

To determine the value of \( \overline{B} \) for resonance, one must know the angle, \( \alpha \), between \( \overline{B} \) and the axis of the ion.

\[(8.1-22)\]
\[\overline{B} \cdot \overline{F}' = Br \cos \alpha = \left( -1/3 \cos \varphi' - 2/3 \sqrt{2} \sin \varphi' \right) \]

\[(8.1-23)\]
\[\cos \alpha = -1/3 \cos \varphi' - 2/3 \sqrt{2} \sin \varphi'\]

The values of \( \cos \alpha \) for the other three ion axes can be obtained.
similarly and are given in the following table.

<table>
<thead>
<tr>
<th>Ion Axis</th>
<th>( \cos \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>( \cos \phi' )</td>
</tr>
<tr>
<td>(1\overline{1}1)</td>
<td>(-\frac{1}{3} \cos \phi' + \frac{2}{3} \sqrt{2} \sin \phi')</td>
</tr>
<tr>
<td>(1\overline{1}1)</td>
<td>(\frac{1}{3} \cos \phi' - \frac{1}{3} \sqrt{2} \sin \phi')</td>
</tr>
<tr>
<td>(11\overline{1})</td>
<td>(\frac{1}{3} \cos \phi' - \frac{1}{3} \sqrt{2} \sin \phi')</td>
</tr>
</tbody>
</table>

D. The Spin-Lattice Hamiltonian

The spin-lattice Hamiltonian for each type of magnetic ion is assumed to be of the form

\[ H_{SL} = \sum_i A_i S_i + \sum_{i,j} F_{ij} (S_i B_j + S_j B_i), \]

where

\[ A_i = \sum_{j,k} B_{ijk} u_{jk}, \]

\[ F_{ij} = \sum_{k,l} E_{ijkl} u_{kl}. \]

The indices in the above equations each take on the values 1, 2, 3. Equations (8.1-25) and (8.1-26) can be expressed more succinctly in the Voigt notation:

\[ A_i = \sum_{j=1}^{6} B_{ij} e_j, \quad i = 1, 2, 3 \]
\[(8.1-28) \quad F_1 = \sum_{j=1}^{6} E_{1j} e_j, \quad 1 = 1, 2, \ldots, 6.\]

The magnetoelastic coupling tensors are given in Section 2.2 in the Voigt notation. All the above quantities are defined in Section 2.2.

The purpose of the calculations in this section is to determine the particular form of \(H_{SL}^{*}\) for each type of ion when longitudinal (111) waves are excited in the crystal.

From eq. (2-50) in Section 2.2, the strain tensor in the crystalline coordinate system is

\[\quad (U_{1j}^{\star}) = E \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}.\]

One must transform \(U_{1j}^{\star}\) to the coordinate system of each ion type in order to determine its \(H_{SL}^{*}\).

(a) (111) Ions

The coordinate system for the (111) ions is chosen such that its z axis is along the (111) direction of the crystal, its x axis along (211), and its y axis along (011). The transformation matrix for the Eulerian angles will again be used.

For this transformation,

\[\begin{align*}
\varphi &= \cos^{-1} \sqrt{1/3}, \quad \Rightarrow \sin \varphi = \sqrt{2/3} \\
\varphi &= 135^\circ, \quad \Rightarrow \sin \varphi = \sqrt{1/2}, \cos \varphi = -\sqrt{1/2} \\
\psi &= 30^\circ, \quad \Rightarrow \sin \psi = 1/2, \cos \psi = 1/2 \sqrt{3},
\end{align*}\]
\[ (8.1-31) \quad \bar{\mathbf{A}} = \begin{pmatrix} -\sqrt{2}/3 & \sqrt{1/6} & \sqrt{1/6} \\ 0 & -\sqrt{1/2} & \sqrt{1/2} \\ \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \end{pmatrix} \]

Now, in the ion coordinate system, xyz,

\[ (8.1-32) \quad \bar{\mathbf{u}} = \bar{\mathbf{A}} \cdot \bar{\mathbf{u}} \cdot \bar{\mathbf{A}}^{-1}, \]

thus:

\[ (8.1-33) \quad \bar{\mathbf{u}} = e \begin{pmatrix} -\sqrt{2}/3 & \sqrt{1/6} & \sqrt{1/6} \\ 0 & -\sqrt{1/2} & \sqrt{1/2} \\ \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \end{pmatrix} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -\sqrt{2}/3 & 0 & \sqrt{1/3} \\ \sqrt{1/6} & \sqrt{1/2} & \sqrt{1/3} \\ \sqrt{1/6} & \sqrt{1/2} & \sqrt{1/3} \end{pmatrix} \]

\[ = 3e \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

In Voigt notation,

\[ (8.1-34) \quad e_3 = 3e, \quad e_{13} = 0 \]

Using eqs. (8.1-27) and (8.1-28) and the tensors given in Section 2.2, one obtains:

\[ (8.1-35) \quad \begin{cases} A_3 = 3e B_{33} \\ A_1 = A_2 = 0 \end{cases} , \]

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(8.1-36) \[ \begin{align*}
F_1 &= 3e E_{13} \\
F_2 &= 3e E_{13} \\
F_3 &= 3e E_{33} \\
1_{13} &= 0
\end{align*} \]

One now obtains the spin-lattice Hamiltonian by substituting the results of eqs. (8.1-35) and (8.1-36) into eq. (8.1-24) being careful to convert from Voigt to regular notation.

(8.1-37) \[ H^{(iii)}_{SL} = 3e \left[ B_{33} S_z + 2E_{13} (S_x x + S_y y) + 2E_{33} S_z B_z \right] \]

(b) \((\bar{1}1\bar{1})\) Ions

The coordinate system for the \((\bar{1}1\bar{1})\) ions is chosen such that \(z\) is along \((\bar{1}1\bar{1})\), \(x\) along \((21\bar{1})\), and \(y\) along \((0\bar{1}1)\). The Eulerian angles are \(\theta = 109.47^\circ\), \(\phi = 45^\circ\), and \(\psi = 30^\circ\); the corresponding transformation matrix is

(8.1-38) \[ \bar{A} = \begin{pmatrix}
2 \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} \\
0 & -\sqrt{1/2} & \sqrt{1/2} \\
\sqrt{1/3} & -\sqrt{1/3} & -\sqrt{1/3}
\end{pmatrix} \]

and the strain tensor in the \((\bar{1}1\bar{1})\) system is

(8.1-39) \[ \bar{u} = e \begin{pmatrix}
8/3 & 0 & -4 \sqrt{1/18} \\
0 & 0 & 0 \\
-4 \sqrt{1/18} & 0 & 1/3
\end{pmatrix} \]
In Voigt notation:

\[(8.1-40)\]
\[
\begin{align*}
e_1 &= \frac{8}{3} e \\
e_3 &= \frac{1}{3} e \\
e_5 &= -8 \sqrt{\frac{1}{18}} e \\
e_2 &= e_4 = e_6 = 0
\end{align*}
\]

\[(8.1-41)\]
\[
\begin{align*}
A_1 &= -8 \sqrt{\frac{1}{18}} e B_{15} \\
A_2 &= -\frac{8}{3} e B_{22} \\
A_3 &= e \left( \frac{8}{3} B_{31} + \frac{1}{3} B_{33} \right)
\end{align*}
\]

\[(8.1-42)\]
\[
\begin{align*}
F_1 &= e \left( \frac{8}{3} E_{11} + \frac{1}{3} E_{13} \right) \\
F_2 &= e \left( \frac{8}{3} E_{12} + \frac{1}{3} E_{13} \right) \\
F_3 &= e \left( \frac{8}{3} E_{13} + \frac{1}{3} E_{33} \right) \\
F_4 &= \frac{8}{3} e E_{14} \\
F_5 &= -8 \sqrt{\frac{1}{18}} e E_{44} \\
F_6 &= -8 \sqrt{\frac{1}{18}} e E_{14}
\end{align*}
\]

The spin-lattice Hamiltonian for (111) ions is thus
(8.1-43)
\[ H_{\text{SL}}^{(\text{III})} = 2e \left\{ \left[ (8/3E_{11} + 1/3E_{13})B_x - 4\sqrt{1/18} (E_{14}B_y + E_{44}B_z) \right] S_x \right. \\
+ \left[ (8/3E_{12} + 1/3E_{13})B_y + 4/3E_{14}B_z - 4\sqrt{1/18} E_{14}B_x \right] S_y \\
+ \left[ (8/3E_{13} + 1/3E_{33})B_z + 4/3E_{14}B_y - 4\sqrt{1/18} E_{44}B_x \right] S_z \right\} \\
+ e \left[ -8\sqrt{1/18} \frac{B_{15}}{B_5} S_x - 8/3 B_{22} S_y + (8/3 B_{31} + 1/3B_{33}) S_z \right]. \]

8.2 \text{ U}^3+: \text{CaF}_2

A. Eigenvalues and Eigenfunctions of \( H_s \)

The spin Hamiltonian is (q.v. Section 2.3)

(8.2-1) \[ H_s = g_{||} \phi B_z S_z + g_{\perp} \phi (B_x S_x + B_y S_y) \]

\[ = g_B \frac{\phi}{2} \begin{pmatrix}
  g_{||} \cos \theta & g_{\perp} \sin \theta e^{-i\phi} \\
  g_{\perp} \sin \theta e^{i\phi} & -g_{||} \cos \theta
\end{pmatrix} \]

where \( B_x = B \sin \theta \cos \phi \), \( B_y = B \sin \theta \sin \phi \), and \( B_z = B \cos \theta \).

The quantities \( \theta \) and \( \phi \) are the standard angles in a spherical polar coordinate system. The Hamiltonian is valid only for an ion whose axis of symmetry is the \( z \)-axis. Diagonalization of (8.2-1) yields the energy eigenvalues,

(8.2-2) \[ E_{\pm} = 1/2 \phi B \sqrt{g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta} \]

\[ \equiv \pm 1/2 \phi B g(\theta). \]
The eigenfunctions corresponding to $E_+$ and $E_-$ are respectively,

\begin{equation}
\psi_+ = \begin{pmatrix}
(2g)^{-1/2}(g+g_{||}\cos \theta)^{1/2} e^{-i\phi} \\
(2g)^{-1/2}(g+g_{||}\cos \theta)^{-1/2} g_\perp \sin \theta
\end{pmatrix},
\end{equation}

\begin{equation}
\psi_- = \begin{pmatrix}
(2g)^{-1/2}(g+g_{||}\cos \theta)^{-1/2} g_\perp \sin \theta \\
-(2g)^{1/2}(g+g_{||}\cos \theta)^{1/2} e^{i\phi}
\end{pmatrix}.
\end{equation}

These eigenvalues and eigenfunctions are valid for each type of magnetic ion if the symmetry axis of each ion is taken to be the z-axis.

B. The Spin-Lattice Hamiltonian

It is necessary to find the particular form of the spin-lattice Hamiltonian for each type of magnetic ion corresponding to longitudinal elastic waves propagated along the axis of a $\text{CaF}_2$ rod. The rod is in the form of a rectangular cylinder with each face perpendicular to a cubic axis of the crystal. The waves will thus be propagated along the symmetry axis of one type of magnetic ion, and perpendicular to the symmetry axes of the other two types. The geometry of the experiment is illustrated in Figure 7a. The $xyz$ coordinate system is selected as the laboratory system and the $\text{CaF}_2$ crystalline coordinate system. The magnetic field, $\vec{B}$, is rotated about $y$ in the $x$-$z$ plane, and $\theta$ is measured with respect to $z$.

For purposes of using the spin and spin-lattice
Hamiltonians, a coordinate system $x'y'z'$ must be chosen for each type of magnetic ion. The types of ion will be referred to as "x", "y", and "z", where "x" refers to the ions with their symmetry axis along the x-axis of the xyz coordinate system, etc. The ion coordinate system, $x'y'z'$, is identical with the xyz system for the "z" ions. The arrangement for the "x" ions is shown in Figure 7b, and that for the "y" ions is shown in Figure 7c.

For a longitudinal (001) wave, the displacement vector is

\begin{equation}
\tilde{u} = \hat{x} u_0 \cos (k_0 z - \omega t),
\end{equation}

and the corresponding strain tensor is

\begin{equation}
(u_{ij}) = e \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\end{equation}

where $e = -u_0 k_0 \sin (k_0 z - \omega t)$.

(a) "z" Ions

Eq. (2-56) becomes, in Voigt notation

\begin{equation}
\begin{cases}
F_1 = E_{13} e \\
F = E_{13} e \\
213 \\
F_3 = E_{33} e \\
F_1 = 0, i > 3.
\end{cases}
\end{equation}
Therefore, since $B_y = 0$, from eq. (2-55),

\[(8.2-8) \quad H_{SL}^{(z)} = 2eB \left[ E_{13} \sin \Theta S_x + E_{33} \cos \Theta S_z \right].\]

(b) "x" Ions

In the $x'y'z'$ coordinate system for "x" ions (Figure 7b), the strain tensor is

\[(8.2-9) \quad (u'_{ij}) = -e \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

\[(8.2-10) \quad \begin{cases} F_1 = -E_{11} e \\ F_2 = -E_{12} e \\ F_3 = -E_{13} e \\ F_i = 0, \ i > 3. \end{cases} \]

Therefore, since $B_{y'} = 0$,

\[(8.2-11) \quad H_{SL}^{(x)} = -2eB \left[ E_{11} \sin \Theta' S_x' + E_{13} \cos \Theta' S_z' \right].\]

(c) "y" Ions

In the $x'y'z'$ coordinate system for "y" ions (Figure 7c), the strain tensor is

\[(8.2-12) \quad (u'_{ij}) = e \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

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\[ F_1 = E_{11} e \]
\[ F_2 = E_{12} e \]
\[ F_3 = E_{13} e \]
\[ F_1 = 0, \ i > 3. \]

Therefore, since \( B_z' = 0 \),

\[ H_{SL}^{(y)} = 2eB \left[ E_{11} \cos \phi' S_{x'} + E_{12} \sin \phi' S_{z'} \right]. \]

8.3 \( \text{Cr}^{3+}:\text{Al}_2\text{O}_3 \)

The coordinate systems for the ruby sample are illustrated in Figure 16. The \( xyz \) coordinate system is the laboratory system. The magnetic field rotates about \( y \) in the \( z-x \) plane making an angle \( \Theta \) with the \( z \)-axis. The crystalline coordinate system is designated by \( x'y'z' \). The \( z \) and \( z' \) axes coincide, and the \( x' \) axis makes an angle \( \gamma \) with respect to the \( x \)-axis.

The eigenvalues and eigenfunctions of the spin Hamiltonian have been obtained numerically. This calculation yields four energy levels which vary in a complex manner with the magnitude and direction of the external magnetic field. For convenience, the energy levels (for a given angle, \( \Theta \)) are labeled 1 through 4 in order of decreasing energy. Since the quantity of interest is the magnitude of the magnetic field for electron paramagnetic resonance as a function of angle (for fixed frequency), it is plotted in Figure 17 for the transitions.
of interest.

The spin-lattice Hamiltonians for both longitudinal and transverse waves along the z-axis are required. The longitudinal waves will be considered first.

A. Longitudinal Waves

For a longitudinal wave propagated along the z-axis, the elastic strain (in Voigt notation) is

\[(8.3-1) \begin{cases} e_3 = e \\ e_i = 0, \ i \neq 3. \end{cases}\]

Therefore, combining eqs. (2-61) and (2-67),

\[(8.3-2) \begin{cases} D_1 = -1/2 \ G_{33} \ e \\ D_2 = -1/2 \ G_{33} \ e \\ D_3 = 0 \ \ e \\ D_i = 0, \ i > 3. \end{cases}\]

With the use of eq. (2-59), one obtains

\[(8.3-3) \ H_{SL} = \frac{3}{2} \ G_{33} \ \left[ S_z^2 - \frac{5}{4} \right].\]

This Hamiltonian is valid for both types of ion, and it is valid in both the xyz and x'y'z' coordinate systems since \( z = z' \).

B. Transverse Waves

For transverse waves propagated along \( \varepsilon'(z) \), the dis-
placement vector is

\( (8.3-4) \quad \mathbf{u}' = u_0 (\mathbf{\hat{z}}' \cos \phi + \mathbf{\hat{j}}' \sin \phi) \cos (kz' - \omega t), \)

where \( \phi \) is the angle between the direction of polarization of the wave and the \( x' \)-axis (See Figure 16b.). The strain components are

\( (8.3-5) \quad \begin{cases} 
  e'_4 &= e \sin \phi \\
  e'_5 &= e \cos \phi \\
  e'_1 &= 0, \ i \neq 4,5, \\
\end{cases} \)

where \( e = -u_0 k \sin (kz' - \omega t) \). Therefore,

\( (8.3-6) \quad \begin{align*}
  D'_1 &= e (G_{14} \sin \phi + G_{25} \cos \phi) \\
  D'_2 &= e (-G_{14} \sin \phi + G_{25} \cos \phi) \\
  D'_3 &= 0 \\
  D'_4 &= e G_{44} \sin \phi \\
  D'_5 &= e G_{44} \cos \phi \\
  D'_6 &= e (G_{25} \sin \phi + G_{14} \cos \phi). 
\end{align*} \)

Now, the numerical calculations for matrix elements involving \( S_x \) and \( S_y \) have been made only for the \( xyz \) coordinate system. In order to use those results, one must find the value of the \( D \) tensor in the \( xyz \) system. This can be done by applying a similarity translation to \( D'_{ij} \) with the rotation matrix,
(8.3-7) \[ \mathbf{\bar{R}} = \begin{pmatrix} \cos \gamma & \sin \gamma & 0 \\ -\sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

that is,

(8.3-8) \[ \mathbf{\bar{D}} = \mathbf{\bar{R}} \cdot \mathbf{\bar{D}'} \cdot \mathbf{\bar{R}}^{-1} \]

The result is

(8.3-9) \[ \mathbf{\bar{D}} = \begin{pmatrix} (G_{14} \sin \psi \mp G_{25} \cos \psi) & (G_{14} \cos \psi \mp G_{25} \sin \psi) & G_{44} \cos(\phi - \gamma) e \\ (G_{14} \cos \psi \pm G_{25} \sin \psi) & (-G_{14} \sin \psi \pm G_{25} \cos \psi) & G_{44} \sin(\phi - \gamma) \\ G_{44} \cos(\phi - \gamma) & G_{44} \sin(\phi - \gamma) & 0 \end{pmatrix} \]

where \( \psi \equiv (\phi + 2 \gamma) \). The corresponding spin-lattice Hamiltonians in the xyz system are

(8.3-10) \[ H_{\text{SL}} = e \left[ (G_{14} \sin \psi \mp G_{25} \cos \psi) (S_x^2 - S_y^2) \\ + (G_{14} \cos \psi \pm G_{25} \sin \psi) (S_x S_y + S_y S_x) \\ + G_{44} \cos(\phi - \gamma) (S_z S_x + S_x S_z) + G_{14} \sin(\phi - \gamma) (S_y S_z + S_z S_y) \right] \]
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X. BIBLIOGRAPHY


10. Mattuck and Strandberg, op. cit.


20. Mattuck and Strandberg, op. cit.


22. R. S. Title, et al., op. cit.


24. R. S. Title, et al., op. cit.

25. Amnon Yariv, op. cit.


27. Baker and Bleaney, op. cit.

28. Amnon Yariv, op. cit.


30. B. R. Judd, op. cit.


32. C. Kittel, op. cit, Chapter 4


34. Ibid., p. 55


37. W. Low, op. cit., p. 34

38. Elliot and Stevens, op. cit.

-100-
39. Amnon Yariv, op. cit.
41. R. B. Hemphill, op. cit.
42. W. G. Cady, op. cit., p. 55
43. R. B. Hemphill, op. cit., p. 25
45. Ibid.
46. R. N. Claytor, Ph.D. Thesis, Rice University, Houston, Texas (May, 1961)
47. Ibid.
49. Landau and Lifshitz, op. cit., p. 36. f.
51. Wachtman, et al., op. cit.
52. The Valpey Crystal Corporation, Holliston, Mass.
53. R. N. Claytor, et al., op. cit.
54. W. G. Cady, op. cit., p. 444
55. Ibid., p. 444
57. Ibid., p. 101
59. R. A. Heising, op. cit., p. 105
60. Ibid., p. 70
61. The Armstrong Products Co., Warsaw, Indiana.


63. The Adolf Meller Co., Providence 4, Rhode Island

64. R. B. Hemphill, op. cit.

65. The Harshaw Chemical Co., 1945 East 97th St., Cleveland 6, Ohio

66. The Linde Co., Division of Union Carbide, Crystal Products Division, 1375 Peachtree St., N. E., Atlanta, Georgia

67. R. S. Title, et al., op. cit.

68. Huffman and Norwood, op. cit.

69. P. L. Donoho, Physics Dept., Rice University, Houston 1, Texas (private communication)

70. E. B. Tucker, op. cit.

71. R. B. Hemphill, op. cit., p. 89

72. Mattuck and Strandberg, op. cit., p. 1213

73. Bleaney, Llewellyn, and Jones, op. cit.

74. S. A. Al'tshuler, et al., op. cit., p. 886


76. P. L. Donoho, op. cit.