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AN INVESTIGATION OF THE EFFECT OF UNIAXIAL STRESS
ON THE SPIN-RESONANCE OF Cr³⁺ IN Al₂O₃

by

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A THESIS SUBMITTED
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ABSTRACT

The spin-lattice interaction in Al₂O₃ containing 0.05% Cr³⁺ has been investigated by measuring the effect of uniaxial compressive stress on the electron-spin-resonance spectrum. Line shifts proportional to the applied stress have been observed at room temperature at a frequency of 10.1 Gc for all observable transitions, and for various directions of the stress, as a function of the angle between the applied magnetic field and the c-axis of the crystal. The strain in the crystal was measured directly by means of a strain gage cemented to it. The effects of strain are attributed to the addition of an effective spin-lattice Hamiltonian to the ordinary spin Hamiltonian of the form $H_{SL} = \sum_{i,j} D_{ij} S_i S_j$, where $D_{ij}$ is a symmetric, traceless tensor related to the strain in the crystal linearly by the expression $D_{ij} = \sum_{k,l} G_{ijkl} e_{kl}$, where $e_{kl}$ is the conventional strain and $G_{ijkl}$ is a symmetric, fourth-rank tensor called the magneto-elastic coupling tensor, or simply the G-tensor. Because of the trigonal symmetry of Al₂O₃, the G-tensor has but four independent components, $G_{33}$, $G_{11}$, $G_{44}$, and $G_{14}$. The following average values for these components were obtained in this experiment (in units of Gc/unit strain): $G_{33} = +166.$, $G_{11} = +129.$, $G_{44} = +41.3$, and $G_{14} = -14.5$ ($\pm 6.4$). The accuracy is $\pm 10\%$, except as noted.
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I. INTRODUCTION

Paramagnetic materials have been a subject of fundamental research in physics for more than a century. The Langevin theory\(^1\) was the first attempt to explain the phenomena of paramagnetism. This theory assumed a paramagnetic material to be made up of particles which have permanent magnetic dipole moments, and its predictions led to the well known Curie Law for the magnetic susceptibility. The theory was remarkably successful in explaining static properties without any knowledge of quantum effects. The dynamic properties of paramagnetic materials were originally of little interest since only bulk properties were observable in experiments.

More recently, the quantum theory has given rise to a new understanding of paramagnetism. Van Vleck, in his classic work,\(^2\) applied quantum mechanics to the equilibrium properties of paramagnetic substances. Later work which sought to determine the contribution of this system of magnetic dipoles, often referred to collectively as the spin system in electron paramagnetism, to the specific heat\(^3\) resulted in a new field of study, that of spin-lattice relaxation. This field has been the subject of much theoretical and experimental work in solid state physics, and a good review of these studies is given in a recent book by Pake.\(^4\)
The usual treatment of spin-lattice relaxation assumes the spin system to be in internal equilibrium at a well-defined "spin temperature". Under equilibrium conditions, this spin temperature is equal to the temperature of the lattice. If the equilibrium condition is disturbed, resulting in a spin temperature differing from that of the lattice, some type of interaction between the spin system and the lattice is necessary in order to restore equilibrium. This problem was considered originally by Waller\textsuperscript{5} and later by Heitler and Teller,\textsuperscript{6} Casimir and Du Pre,\textsuperscript{3} Kronig,\textsuperscript{7} and Van Vleck.\textsuperscript{8} According to these authors, there are two important kinds of relaxation processes in magnetically dilute solids. One of these is the direct or one-phonon process in which the spin system absorbs a quantum of energy from the vibrational degrees of freedom of the lattice or imparts a quantum of energy to the latter. This relaxation mechanism is analogous to simple absorption or emission in radiation theory. The second relaxation mechanism is that in which the spin system absorbs a quantum of one frequency and emits that of another. This is called the indirect or Raman process, for it is similar to inelastic scattering in optics.

The rate at which the spin system approaches equilibrium after having been disturbed by the absorption of energy is usually described by a differential equation.
energy levels simultaneously, and this precluded any
detailed comparison with the theory. Microwave tech-
niques, developed during World War II, have provided
the means for more detailed studies of paramagnetism
since they permit the observation of paramagnetic resonance.
Paramagnetic resonance experiments have been remarkably
successful in giving a description of the ground state
of the spin system and the effect of the crystalline
environment on the energy levels of paramagnetic ions in
solids. Likewise, microwave techniques have been used to
measure the spin-lattice relaxation times between single
pairs of energy levels for many paramagnetic solids.
Studies of this sort were essential for the development of
solid state masers. From the theoretical standpoint,
however, these experiments yielded little useful information
since the contribution of each type of interaction to spin-
lattice relaxation could not be determined.

A useful reformulation of Van Vleck's work has
been presented recently by Mattuck and Strandberg.\textsuperscript{11} Orbach\textsuperscript{12} has also contributed some equally useful theo-
retical work on spin-lattice relaxation. These authors
proposed experiments which, for the first time, could be
used to study the one-phonon process of spin-lattice
relaxation. Their work has stimulated several experimental
investigations, including the research described in this
thesis.
The recently developed techniques for the generation and detection of coherent lattice vibrations at microwave frequencies\textsuperscript{13,14} were, soon after their discovery, used by several workers to investigate spin-lattice interactions. Shiren and Tucker\textsuperscript{15} were the first to confirm the predictions of Mattuck and Strandberg using microwave ultrasonic methods. The acoustic-spin-resonance of Cr\textsuperscript{3+} in Al\textsubscript{2}O\textsubscript{3}, was subsequently reported by three groups working independently\textsuperscript{16,17,18}. Shiren\textsuperscript{19} has also performed similar investigations on several iron group ions in MgO.

The acoustic-spin-resonance experiments are performed by introducing lattice vibrations into the paramagnetic crystal at the same frequency as the Larmor frequency of the spins in an applied magnetic field. The vibrations of the crystal lattice produce a time dependent perturbation of the crystalline electric field. This, in turn, induces transitions between the spin states through the spin-orbit coupling. Thus, a measurement of the attenuation of the lattice vibrations as a function of the applied magnetic field yields information on the one-phonon spin-lattice interaction. These experiments are rather difficult to perform because the equipment required is complex and the samples to be studied must be prepared to rigid specifications. Since the lattice vibrations in such an experiment simply add a perturbation to the Hamiltonian
for the system, it would be wise to consider other methods for perturbing the system which would be easier to carry out.

Several perturbation methods have been reported in recent years for use in the investigation of paramagnetic solids. Bloembergen\textsuperscript{20} and his co-workers have used strong external electric fields as a perturbation in resonance experiments; however, their interest was not directed toward the problem of spin-lattice interactions. Artman and Murphy\textsuperscript{21} have used this technique in spin resonance experiments on Cr\textsuperscript{3+} in Al\textsubscript{2}O\textsubscript{3}, and a similar investigation was made by Kaiser, et al.\textsuperscript{22} on the optical emission lines. Walsh\textsuperscript{23} has used hydrostatic pressure as a perturbation in spin-resonance experiments on several iron group ions in MgO. The object of these experiments was to study crystalline potentials rather than spin-lattice interactions. The effect of uniaxial stress as a perturbation on the optical spectra of Cr\textsuperscript{3+} in MgO was reported by Schawlow, et al.\textsuperscript{24}

The fact that time-dependent strains are used in acoustic-spin-resonance experiments to study the coupling of the spin system to the lattice prompted the idea that static strains could be used as a perturbation to give complementary results. Even though Mattuck and Strandberg did not consider static strains in their theory, it appeared that their results would still apply in this case.
lines should occur for reasonable values of the applied stress.

(b) Good quality single crystals of ruby are available in any concentration of $\text{Cr}^{3+}$ desired.

(c) There is a large amount of theoretical and experimental information available on ruby in comparison with other paramagnetic materials.

(d) Single crystals of ruby are strong mechanically and should be able to withstand high compressive stresses.
II. THEOREY

A. Spin-Phonon Interactions

Mattuck and Strandberg\textsuperscript{11,28} have treated the theory of spin-phonon interactions in paramagnetic crystals. Their work is essentially a reformulation of Van Vleck's\textsuperscript{8} earlier theory with the results being somewhat easier to interpret. Although their theoretical work does not apply directly to the experimental work discussed in this thesis, the two are closely related, and we shall briefly consider the method which was used and the one-phonon interaction Hamiltonian obtained.

The theory is based on an often used model of a paramagnetic ion in a lattice of diamagnetic ions. Vibrations of the lattice modulate the crystalline electric field at the site of the paramagnetic ion which, in turn, perturbs the orbital motion of its electrons, and transitions between spin states are then induced by means of spin-orbit interaction. The following assumptions are made:

(a) All effects of spin-spin interaction except for energy-level broadening are neglected. Thus, only magnetically dilute crystals are considered.

(b) The effects of local lattice distortion produced by the presence of the paramagnetic ion are omitted.
they compute the matrix elements of $H_1$ between simultaneous eigenstates of $H_S$ and $H_L$. From this calculation, the interaction Hamiltonian for the direct or one-phonon process was found to be

$$H_{Direct} \approx \sum_{p,f} A^f p (a_p^+ a_p) \sum_{i,j} \left\{ 2 \beta \lambda B \mathcal{L}_{ij}^f S_i \right. $$

$$+ 2 \beta \lambda \mathcal{L}_{ij}^f (S_i B_j^* + S_j^* B_i) + \lambda \mathcal{L}_{ij}^f (S_i S_j^* + S_j S_i) \right\}, \tag{2-3}$$

where the first term contains the dependence on phonon creation and annihilation operators and the second contains the dependence on spin operators. The terms $\mathcal{L}_{ij}^f$ and $\mathcal{L}_{ij}$ are tensors which include the effects of the perturbation to the crystal potential and of the excited electronic states. This method for expression the influence of the excited states is similar to that which is commonly used for the spin Hamiltonian.

Mattuck goes on to examine the relative magnitudes of the terms in $H_{Direct}$. As a result of the "Van Vleck Cancellation" the two $\mathcal{L}$-tensors are the same order of magnitude. Then the linear terms in the spin operator vary according to $2 \beta \lambda B$, where $\beta \approx 10^{-20}$ erg/G. A typical value of $\lambda$ is $100 \text{ cm}^{-1}$ or $10^{-14}$ erg, and $B$ is about 3 kG for microwave experiments at X-band frequencies. Thus, $2 \beta \lambda B \approx 10^{-30}$ erg$^2$. The quadratic terms in the spin operator vary according to $\lambda^2 \approx 10^{-28}$ erg$^2$. Hence, for microwave resonance experiments, the effect of the
B. The Total Hamiltonian for Stress Experiments

The theoretical work of Mattuck and Strandberg which is discussed in the previous section is concerned only with spin-phonon interactions, and the effects of static strains as perturbations are therefore not considered. It is evident, however, that the same interactions govern the effect of time independent strains on the spin-resonance spectrum as govern the effect of time dependent strains on transitions between spin states. Moreover, Mattuck's theory can be modified to treat the case of static stress applied to a paramagnetic crystal. If the perturbation of the crystal field due to an applied stress is assumed to be linear in the strain, then $H_I$ for the direct process becomes

$$ (2-4) \quad H_I = \sum_{i,j} V_{ij} e_{ij}, $$

where $V_{ij}$ is a function of the electron coordinates and $e_{ij}$ is the strain. The perturbation calculation for this case yields the same result for $H_{Direct}$ given in eq. (2-3) except for the omission of the term which involves phonon operators.

Although the work of Mattuck and Strandberg is restricted to cases in which the medium crystal field approximation is valid, an inspection of the spin Hamiltonian indicates that the form of $H_{Direct}$ is of a
more general nature. The spin Hamiltonian may be defined as an effective Hamiltonian which is designed to explain the transitions between the ground state energy levels observed in spin-resonance experiments. If terms smaller than the spin-orbit interaction are neglected, the spin Hamiltonian may be written as

\[ H_S = \beta g_{ij} B_i S_j + D_{ij} S_i S_j \]

where \(B\) is the applied magnetic field, \(S\) is the spin operator, \(\beta\) is the Bohr magneton, and \(g_{ij}\) and \(D_{ij}\) are tensors whose components are usually determined experimentally. The spectroscopic splitting factor, \(g_{ij}\), contains the contributions of the admixed higher lying orbital states, and the contribution of a noncubic crystal field is contained in \(D_{ij}\). Both \(g_{ij}\) and \(D_{ij}\) are strongly dependent on the local symmetry and strength of the crystal field at the site of the paramagnetic ion. Thus, small distortions of the crystal field induced by the application of stress are reflected by changes in \(g_{ij}\) and \(D_{ij}\). Since these changes are small, they may be incorporated into a perturbation Hamiltonian which we shall call the spin-lattice Hamiltonian, \(H_{SL}\), which has the same form as eq. (2-5);

\[ H_{SL} = E_{ij} B_i S_j + F_{ij} S_i S_j \]
where $E_{ij}$ and $F_{ij}$ are again tensors which are related to the crystal field. Note that this Hamiltonian is the same as the portion of $H_{\text{direct}}$ which contains only spin operators.

Thus, the results of a spin-resonance experiment in which uniaxial stress is applied to the crystal under investigation should be explained by a total Hamiltonian which is the sum of the spin and spin-lattice Hamiltonians,

$$(2-7) \quad H = H_S + H_{SL}$$
C. The Absorption Spectrum of Cr$^{3+}$ in Al$_2$O$_3$

The optical and paramagnetic resonance spectrum of Cr$^{3+}$ in Al$_2$O$_3$, ruby, has been studied intensively, and detailed knowledge is available for both the excited states and the ground state of this system. The optical absorption and emission spectrum was investigated by Deutchbein$^{30}$ and later by Sugano and Tsujikawa$^{31}$. Knowledge of the ground state has been provided by paramagnetic resonance experiments.$^{32}$ A theoretical analysis of the absorption spectra was performed by Sugano and Tanabe$^{33}$ in 1958. Their analysis was based on the crystal-field theory in the strong cubic field scheme, treating the spin-orbit interaction and the low-symmetry crystal field as perturbations. Although this treatment explained many aspects of the observed spectrum fairly well, several discrepancies existed which could not be resolved. In 1961, Sugano and Peter$^{34}$ revised this work and included the effect of configuration mixing and covalency on the energy spectrum. This effort was quite successful in clearing up the problems encountered by the earlier work.

Trivalent chromium has a configuration of 3d$^3$, and the lowest multiplet of the free ion is a $^4F$ term. Thus, the ground state for the free ion has a sevenfold orbital degeneracy and a fourfold spin degeneracy. Fig.
(2-1) shows how this degeneracy is lifted for \( \text{Cr}^{3+} \) in \( \text{Al}_2\text{O}_3 \), using the data and group theoretical notation presented by Sugano and Peter.\textsuperscript{34} Since we are mainly interested in spin-resonance experiments, the complete splitting is shown only for the ground state, and the first few excited states are included simply to show their separation from the ground state. The crystal field at the site of the \( \text{Cr}^{3+} \) ion has a strong octahedral component due to the six nearest neighbor oxygen ions, sixfold cubic coordination, and a small trigonal component along the optic or c-axis due to a distortion of the octahedron (see section III-A for a discussion of this structure). Since the octahedral component of the crystal field is stronger than the electrostatic interaction term of the Hamiltonian, the strong field approximation is used to determine the splittings. According to Sugano, the ground state is an orbital singlet with a fourfold spin degeneracy. The trigonal component of the crystal field together with the spin-orbit interaction further splits the ground state into two Kramers doublets. According to Kramers Theorem, the remaining degeneracy may only be removed by the application of a magnetic field.

The behavior of the ground state energy levels in a magnetic field is described by the spin Hamiltonian. Since the \( \text{Cr}^{3+} \) ion is located in an axially symmetric crystal field in \( \text{Al}_2\text{O}_3 \), the spin Hamiltonian is given by
Fig. (2-1) Energy Levels for Cr$^{3+}$ in Al$_2$O$_3$ (not to scale)
\((2-8)\) \(H_S = g_\parallel B_z S_z + g_\perp (B_x S_x + B_y S_y) + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right], \)

where the effective spin, \(S\), is \(3/2\). The paramagnetic resonance experiments carried out on this material have determined that \(2D = -0.3824\) \(\text{cm}^{-1}\), \(g_\parallel = 1.984^{\pm}0.0006\), and \(g_\perp = 1.9867^{\pm}0.0006\).\(^{32}\) Fig. (2-1) shows the splitting of the spin states under a magnetic field which is normal to the \(c\)-axis. In the following work, we shall refer to transitions between two spin states by the numbers 1-2, etc., where the levels are numbered 1, 2, 3, and 4 from top to bottom. It should be noted that the zero field splitting of the ground state of \(0.38\) \(\text{cm}^{-1}\) corresponds to a frequency in X-band region whereas the first excited state is removed from the ground state by an energy of \(14,000\) \(\text{cm}^{-1}\) which corresponds to a frequency in the optical region.
predicted by eq. (2-6). Since the new value of \( g \) differs from the former one by about one percent, the magnitude of the added energy term which is linear in the spin operator is approximately \( g \beta B/100 \). On the other hand, the added energy term which is quadratic in the spin operator is \( D = g \beta B \) for typical values of the magnetic field. Thus, since the effect of an applied uniaxial stress will be the addition of a small axial perturbation, among others, to the crystal field, we may conclude that the dominant term in the spin-lattice Hamiltonian for ruby is quadratic in the spin.

In view of the argument given above, the spin-lattice Hamiltonian for \( \text{Cr}^{3+} \) in \( \text{Al}_2\text{O}_3 \) is assumed to be

\[
H_{SL} = D_{ij} S_i S_j
\]

\[
= \mathbf{S} \cdot \mathbf{B} \cdot \mathbf{S},
\]

where \( D_{ij} \) is a second rank tensor. We shall also assume that \( D_{ij} \) is linearly proportional to the strain, \( e_{kl} \),

\[
D_{ij} = G_{ijkl} e_{kl},
\]

where \( G_{ijkl} \) is a fourth rank tensor called the magnetoelastic coupling tensor or simply the G-tensor. The strain is related to the applied stress by Hooke's Law,

\[
e_{kl} = \sigma_{kl} \epsilon_{mn} T_{mn},
\]
energy. More sophisticated arguments might prove more satisfactory, but for the moment, we shall just assume that the G-tensor is symmetric and try to justify this assumption later on experimental grounds. With this assumption, the number of independent components of the G-tensor is reduced from 36 to 21. Further, the D-tensor, $D^{(1)}_{ij}$, may be assumed to be traceless since it may be written as the sum of a traceless tensor, $D^{(f)}_{ij}$, and a diagonal tensor such that

$$(2-15) \quad D^{(\omega)}_{ij} = D^{(f)}_{ij} + \frac{1}{3} \delta_{ij} \sum_k D^{(\omega)}_{kk}$$

Since the addition of a diagonal tensor to this term of the Hamiltonian merely changes the energy eigenvalues by a constant value, it will be dropped from further consideration. This same procedure is commonly used in the spin Hamiltonian, and the traceless condition limits the maximum number of independent components of the G-tensor to 16. Any further reduction in the number of independent components is brought about by the symmetry properties of the crystal field since the G-tensor, like the tensors associated with the spin Hamiltonian, must reflect the symmetry of the lattice.

For convenience in the following work, we shall rewrite eqs. (2-11) and (2-12) using the Voigt notation, which is commonly used in work dealing with the elastic
properties of crystals. The terms, $D_{ij}$, $T_{mn}$, and $e_{kl}$, which are written as symmetric, second-rank tensors in a three dimensional space become vectors in a six dimensional space, and the symmetric fourth-rank tensors become second-rank tensors. Thus,

\begin{equation}
\begin{align*}
D_{ij} &= G_{jk} e_{ki}, \quad j, k = 1, 2, \cdots, 6 \\
e_{ki} &= S_{ki} T_{ij}, \quad i, k = 1, 2, \cdots, 6
\end{align*}
\end{equation}
III. EVALUATION OF THE G-TENSOR FOR RUBY

In this section we shall present the details of how the theory derived in the previous section is applied to the case of Cr$^{3+}$ in Al$_2$O$_3$. First, we shall derive the form of the magneto-elastic coupling tensor, hereafter referred to as the G-tensor, for any paramagnetic ion in this lattice. Second, we shall diagonalize the total Hamiltonian, spin Hamiltonian plus spin-lattice Hamiltonian, for the case of an ion with an effective spin of 3/2 in an axial crystal field. The result will be in the form of a fourth order equation in the energy which may be solved for the energy eigenstates. This result applies to the case of Cr$^{3+}$ in Al$_2$O$_3$ among others. Third, we shall use this equation in energy to find how the magnetic field required for resonance at a fixed microwave frequency depends upon the applied stress. This step relates the experimental results to a linear combination of functions which may be calculated. The coefficients of the functions are related to the components of the G-tensor. Fourth, we shall derive the exact form of these coefficients for several directions of applied stress. This step yields a set of equations which may be solved simultaneously for the components of the G-tensor after a suitable fit to the experimental results is obtained with the various coefficients.
Fig. (3-1) A Portion of the $\text{Al}_2\text{O}_3$ Lattice
(from Geschwind and Remeika)
tensor be identical to the initial tensor eliminates many of the components. The general similarity transformation for a fourth rank tensor such as the G-tensor is

\[(3-1) \quad G_{ij}^k\ell = \epsilon_{pq} \delta_{ij}^q \delta_{ks} \delta_{lt} G_{pqrs} \]

where the \( \delta_{ij} \) are the components of the general rotation matrix, \( \Gamma \), in three dimensions. Since \( G \) is unchanged by the interchange of \( i \) with \( j \) and \( k \) with \( l \), eq. (3-1) may be rewritten, using the Voigt notation, as

\[(3-2) \quad G_{ij}^k = \Gamma_{k}^{\ell} G_{\ell k}, \quad k, \ell = 1, 2, \ldots, 6, \]

where \( \Gamma_{kl} \) is in general a 36x36 matrix the individual components of which are determined by the rotation desired. Here we are interested in the orthogonal transformations for the point group \( \Sigma \)m which has the representation:

\[
F = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix} \quad C_2 C_3 = \begin{pmatrix}
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1 \\
\end{pmatrix} \\
\sigma = \begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix} \quad C_2 C_3^2 = \begin{pmatrix}
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\
\frac{-\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1 \\
\end{pmatrix} \\
I = \begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix} \quad \sigma C_3 = \begin{pmatrix}
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\
\frac{-\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\]
\[
C_2 = \begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\quad \quad \quad \sigma C_3^2 = \begin{pmatrix}
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
\[
C_3 = \begin{pmatrix}
-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1
\end{pmatrix}
\quad \quad \quad I C_3 = \begin{pmatrix}
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
\[
C_8^2 = \begin{pmatrix}
-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1
\end{pmatrix}
\quad \quad \quad IC_3^2 = \begin{pmatrix}
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

The use of $C_3$ which is a 120° rotation about the z-axis and $\sigma$ which is a reflection through the yz plane leads to a G-tensor of the form

\[
(3-3) \ G = \begin{pmatrix}
G_{11} & G_{12} & G_{13} & G_{14} & 0 & 0 \\
G_{12} & G_{11} & G_{13} & -G_{14} & 0 & 0 \\
G_{13} & G_{13} & G_{11} & 0 & 0 & 0 \\
G_{41} & -G_{41} & 0 & G_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & G_{44} & G_{41} \\
0 & 0 & 0 & 0 & G_{14} & \frac{1}{2}(G_{11}-G_{12})
\end{pmatrix}
\]

When the conditions that $D$ be traceless and that $G$ be symmetric are employed, the final form of the G-tensor for the case of $\text{Cr}^{3+}$ in $\text{Al}_2\text{O}_3$ becomes
Thus, the number of independent components of the G-tensor which are to be determined experimentally is four, namely $G_{11}$, $G_{33}$, $G_{44}$, and $G_{14}$.

It should be emphasized that there is a G-tensor of the form of eq. (3-4) for each of the two groups of sites in ruby. In general, the application of a uniaxial stress to the crystal will distort the crystal field in one way at the first set of Cr$^{3+}$ sites and in another way at the second set Cr$^{3+}$ sites. Through inspection of Fig. (3-1) it may be seen that the application of a stress along the c-axis will affect the two groups of sites in the same way. This would also be true for a stress applied in the XY plane were it not for the fact that $\alpha \neq 0^\circ$. A stress applied in any other direction, however, produces very different effects on the two groups of sites. It is
rather difficult to estimate quantitatively the effect of the presence of two G-tensors on the experimental results. If there is much difference between the components of the two tensors, one might expect to see a broadening or even a splitting of the spin-resonance lines which is dependent upon the applied stress.
B. Diagonalization of the Total Hamiltonian

It was shown in section II that the results of a spin-resonance experiment in which uniaxial stress is applied as a perturbation may be explained by an effective Hamiltonian,

\[ H = H_S + H_{SL} \]

where \( H_S \) is the ordinary spin Hamiltonian and \( H_{SL} \) is a perturbation Hamiltonian called the spin-lattice Hamiltonian. We now wish to diagonalize this Hamiltonian and solve for the energy eigenvalues for the ground state of \( \text{Cr}^{3+} \) in \( \text{Al}_2\text{O}_3 \) which has a fictitious spin, \( S = 3/2 \).

Neglecting the small anisotropy in \( g \), the spin Hamiltonian given in eq. (2-7) is

\[ H_S = g\beta \overrightarrow{B} \cdot \overrightarrow{S} + D (S_x^2 - S_y^2) \]

where \( D = -5.733 \text{ Gc} \) and \( g\beta = 2.7789 \text{ Gc/kG} \). The proper spin-lattice Hamiltonian for this case was given in eq. (2-9) as

\[ H_{SL} = D_{ij} S_i S_j \]

Expanding eq. (3-7) we have

\[ H_{SL} = D_{11} S_x^2 + D_{22} S_y^2 + D_{33} S_z^2 \]

\[ + D_{23} (S_y S_z + S_z S_y) + D_{13} (S_x S_z + S_z S_x) \]

\[ + D_{12} (S_x S_y + S_y S_x) \].
Now if we redefine the terms, $D_{ij}$, using the Voigt notation and impose the traceless condition on $D$ we have

$$
\begin{align*}
D_{11} &= D_1 & D_{22} &= D_2 & D_{33} &= D_3 & D_{12} &= D_{13} = D_{23} = D_{33} \\
D_{13} &= D_5 & D_{23} &= D_4 & D_{1} + D_{2} &= -D_3
\end{align*}
$$

(3-9)

Thus, eq. (3-5) becomes

$$
H = g \beta B \cdot \vec{S} + D(S_z^2 - \frac{S}{4}) + D_1 S_x^2 + D_2 S_y^2
$$

$$
+ D_3 S_z^2 + D_4 (S_y S_z + S_z S_y) + D_5 (S_x S_z + S_z S_x)
$$

$$
+ D_6 (S_x S_y + S_y S_x)
$$

(3-10)

In order to find the energy eigenstates and eigenvalues of eq. (3-10), we use as a basis the eigenstates of $S_z$ which are defined by

$$
S_z |m_s\rangle = m_s |m_s\rangle
$$

(3-11)

where

$$
|m_s\rangle = |\frac{3}{2}\rangle, |\frac{1}{2}\rangle, |-\frac{1}{2}\rangle, |-\frac{3}{2}\rangle
$$

(3-12)

The spin functions are assumed to satisfy the orthogonality condition

$$
\langle m_s | m_s' \rangle = \delta_{m_s m_s'}
$$

(3-13)

The eigenfunctions of $H$ will be linear combinations of the four spin functions

$$
H |\kappa\rangle = E_\kappa |\kappa\rangle
$$

(3-14)
where

\[
(3-15) \quad |\ell_k\rangle = a_{k_1}^{\ell} |\frac{3}{2}\rangle + a_{k_2}^{\ell} |\frac{1}{2}\rangle + a_{k_3}^{\ell} |-\frac{1}{2}\rangle + a_{k_4}^{\ell} |-\frac{3}{2}\rangle .
\]

To solve for the four energy eigenstates, substitute eq. (3-15) in eq. (3-14), multiply by \(\langle 1|\) and sum over the states using the orthogonality condition. This operation gives a system of four homogeneous equations

\[
(3-16) \quad \sum_{j=1}^{4} (H_{i,j} - E_k \delta_{i,j}) a_{k,j}^i = 0, \quad i = 1, 2, 3, 4,
\]

where

\[
(3-17) \quad H_{i,j} = \langle m_{s_i} | H | m_{s_j} \rangle,
\]

and \(1, j = 1, 2, 3, 4\) corresponds to \(m_{s_1}, m_{s_2} = 3/2, 1/2, -1/2,\) and \(-3/2.\)

The substitution of eq. (3-10) for \(H\) in eq. (3-16) yields the following secular determinant after making use of the matrix elements of the spin operators:

\[
(3-18) \quad \begin{vmatrix}
\frac{3}{2} GB \cos \Theta + D + \alpha - E & \frac{\sqrt{3}}{2} GB \sin \Theta + \delta^* & \epsilon^* & 0 \\
\frac{\sqrt{3}}{2} GB \sin \Theta + \delta & \frac{1}{2} GB \cos \Theta - D - \alpha - E & GB \sin \Theta & \epsilon^* \\
\epsilon & GB \sin \Theta & -\frac{1}{2} GB \cos \Theta - D - \alpha - E & \frac{\sqrt{3}}{2} GB \sin \Theta - \delta^* \\
0 & \epsilon & \frac{\sqrt{3}}{2} GB \sin \Theta - \delta & -\frac{3}{2} GB \cos \Theta + D + \alpha - E
\end{vmatrix} = 0
\]
where

\[ G.B = g\beta B \]
\[ \alpha = \frac{3}{2} D_3 \]
\[ \epsilon = \sqrt{\frac{3}{2}} \left[ D_1 - D_2 + 2i D_6 \right] \]
\[ S = \sqrt{3} \left[ D_5 + i D_4 \right] \]
\[ \epsilon + \epsilon^* = \sqrt{3} (D_1 - D_2) \]
\[ S + S^* = 2\sqrt{3} D_5 \]
\[ E = \hat{\imath} B \sin \theta + \hat{\jmath} B \cos \theta \]
\[ S = \hat{\imath} S_x + \hat{\jmath} S_y + \hat{k} S_z \]

Note that the magnetic field is assumed to be in the xz plane, and \( \vec{B} \) intersects the z-axis with the angle \( \theta \). If the zero level for the energy is chosen midway between the \( \frac{1}{2} \) and \( \frac{3}{2} \) states, we have the additional condition on the solutions that

\[ (3-19) \quad E_1 + E_2 + E_3 + E_4 = 0 \]

Since the stress to be applied to the crystal is very small, one may assume that the terms \( D_3 \), \( D_5 \), and \( D_{12} \) are much smaller than the terms \( GB \) and \( D \). The expansion of eq. (3-18) yields, neglecting terms which involve \( \alpha, \epsilon \), and \( S \) to higher than first order,

\[ F(E) = E^4 - \alpha E^2 + \beta E + \gamma + D_3 F_{D_3} \]
\[ + D_5 F_{D_5} + D_{12} F_{D_{12}} = 0 \]
where

\[ D_{12} = D_1 - D_2 \]
\[ \alpha = \left( 5/2 \, G^2 B^2 + 2 D^2 \right) \]
\[ \beta = 2 \, G^2 B^2 D \left( 1 - 3 \cos^2 \theta \right) \]
\[ \gamma = D^4 + 9/16 \, G^4 B^4 + \frac{1}{2} \, G^2 B^2 D^2 \left( 1 - 6 \cos^2 \theta \right) \]
\[ F_{D_3} = 3/2 \left[ -4 D E^2 + 2 G^2 B^2 E \left( 1 - 3 \cos^2 \theta \right) \right. \]
\[ \left. + 4 D^3 + G^2 B^2 D \left( 1 - 6 \cos^2 \theta \right) \right] \]
\[ F_{D_{12}} = 3 \, G^2 B^2 \sin^2 \theta \left( D - E \right) \]
\[ D = -5.733 \, Gc \]
\[ G = 2.7789 \, Gc/kG \]
\[ F_{D_5} = -6 \, G^2 B^2 \sin \theta \cos \theta \left( 2 E + D \right) \]
C. Calculation of Strain Dependence

The experimental measurements upon the stressed samples are made with a spin-resonance spectrometer using a method which will be described presently. The results simply give a value of the shift in the magnetic field for the resonance condition for some change in the applied stress. The purpose of this section is to show how the measured quantity, dB/de, may be obtained from the secular equation of the diagonalized Hamiltonian given in eq. (3-20).

The secular equation is a fourth order equation in the energy and is a function of six variables in all.

\[ F = F(E, B, D_3, D_5, D_{12}, \Theta) \]

(3-21)

where each of the terms have been defined earlier.

The total derivative of this function is

\[ df = F_E \, dE + F_B \, dB + F_{D_3} \, dD_3 + F_{D_5} \, dD_5 \]

\[ + F_{D_{12}} \, dD_{12} + F_\Theta \, d\Theta = 0 \]

(3-22)

where \( F = \frac{\partial F}{\partial x} \). There are four values of the energy, E, which are solutions of eq. (3-21) for each value of \( \Theta, B, D_3, D_5, \) and \( D_{12} \). When the ith value of the energy is used in eq. (3-22), we shall write it as
Hence, in a spin-resonance experiment, one may hold $\theta$ and $E_0$ constant while applying stress to give the dependence of the magnetic field at resonance upon the strain, e. From eq. (3-27) we have

$$\frac{dB}{de} = \frac{d}{dD_{12}} \frac{dD_{12}}{de} + \frac{d}{dD_3} \frac{dD_3}{de} + \frac{d}{dD_5} \frac{dD_5}{de},$$

where $dB/de$ is measured, $dD_{12}/de$, $dD_3/de$, and $dD_5/de$ are calculated, and the coefficients $\partial B/\partial D_{12}$, etc. are defined by eq. (3-27) as

$$\frac{\partial B}{\partial D_m} = \frac{\left(\frac{\partial F_E}{\partial D_m} - \frac{\partial F_B}{\partial D_m}\right)}{\left(\frac{\partial F_E}{\partial F_B} - \frac{\partial F_B}{\partial F_b}\right)}$$

where $m = 12, 3, \text{and } 5$. The terms which appear in eq. (3-29) are derived from eq. (3-20), assuming that $D_3$, $D_5$, and $D_{12}$ are much smaller than $GB$ and $D$. The terms not previously defined in eq. (3-20) are

$$F_E = 4E^3 - E\left(5G^2B^2 + 4D^2\right) + 2G^2B^2D\left(1 - 3\cos^2\theta\right)$$

$$F_B = G^2B \left[-5E^2 + 4DE\left(1 - 3\cos^2\theta\right) + \frac{9}{4}G^2B^2\right] + D^2\left(1 - 6\cos^2\theta\right)$$

$$F_\theta = 6G^2B^2D\cos\theta \sin\theta \left(2E + D\right)$$

The terms $\partial B/\partial D_{12}$, $\partial B/\partial D_3$, and $\partial B/\partial D_5$ are functions of the energy required for a transition, $E_0$, the magnitude of the applied magnetic field, $B$, and the angle, $\theta$, between $B$ and the c-axis.
Fig. (3-2) defines a system of reference axes which shall be used to denote the orientation of the samples under investigation. In Fig. (3-2) we define:

\[ \begin{align*}
    \text{XYZ} & \quad \text{Crystallographic axes} \\
    \text{xyz} & \quad \text{Reference axes defined by } \vec{B} \text{ and the crystallographic } c\text{-axis} \\
    \vec{B} & \quad \text{Direction of applied magnetic field} \\
    \Theta & \quad \text{Angle between } \vec{T} \text{ and } \vec{z} \\
    \vec{T} & \quad \text{Direction of applied stress} \\
    \vec{e} & \quad \text{Direction of measured strain} \\
    \Theta & \quad \text{Angle between } \vec{T} \text{ and } \vec{z} \\
    \vec{e} & \quad \text{Angle between xz-plane and XZ-plane}
\end{align*} \]

Note that \( \vec{T}, \vec{e}, \) and \( \vec{B} \) are in the xz-plane because of the design of the experimental apparatus. One should also keep in mind that \( H_{SL} \) has been derived in the xyz system; whereas the G-tensor is referenced to the XYZ system. The elastic compliance constants, \( s_{kl} \), also refer to the XYZ system.

If we assume that the effect of strain upon the two types of sites in ruby may be represented by an average G-tensor of the form derived earlier, then \( D \) may be found by substitution in eq. (2-16).

\[ (3-32) \quad D_j = \sum_{k} C_{jk} e_k , \quad j, k = 1, 2, \ldots, 6 , \]
Fig. (3-2) Definition of coordinate systems for strain experiment with Cr$^{3+}$ in Al$_2$O$_3$

(a) Principal axes
(b) Projection of Al$^{3+}$ sites on a plane normal to the c axis
where \( e \) again represents the strain. The components of strain are given by

\[
(3-33) \quad e_{ki} = s_{ki} T_i, \quad i, k = 1, 2, \ldots, 6,
\]

where the \( s_{ki} \) are the elastic compliance constants, and the \( T_i \) are the components of stress. Equations (3-32) and (3-33) are written in Voigt notation. The elastic compliance matrix for the trigonal structure of \( \text{Al}_2\text{O}_3 \) is

\[
(3-34) \quad s_{ij} = \begin{pmatrix}
    s_{11} & s_{12} & s_{13} & s_{14} & 0 & 0 \\
    s_{12} & s_{11} & -s_{13} & -s_{14} & 0 & 0 \\
    s_{13} & s_{13} & s_{23} & 0 & 0 & 0 \\
    s_{14} & -s_{14} & 0 & s_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & s_{44} & s_{14} \\
    0 & 0 & 0 & 0 & s_{14} & 2(s_{11} - s_{12})
\end{pmatrix}.
\]

The elastic constants of \( \text{Al}_2\text{O}_3 \), or corundum, have been carefully measured by Wachtman, et al. The results for the six independent compliance constants are given in Table (3-1) in units of \( 10^{-13} \text{ cm}^2/\text{dyne} \).
Table (3-1). Elastic compliance constants for Al₂O₃ (J. B. Wachtman, et al.\textsuperscript{41})

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (10⁻¹³ cm²/dyne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s₁₁</td>
<td>+2.353±0.002</td>
</tr>
<tr>
<td>s₃₃</td>
<td>+2.170± .002</td>
</tr>
<tr>
<td>s₄₄</td>
<td>+6.940± .008</td>
</tr>
<tr>
<td>s₁₂</td>
<td>-0.716± .007</td>
</tr>
<tr>
<td>s₁₃</td>
<td>-0.364± .006</td>
</tr>
<tr>
<td>s₁₄</td>
<td>+0.489± .005</td>
</tr>
</tbody>
</table>

Substitution of G and e in eq. (3-32) yields the components of D.

\[
(3-35) \quad D_{ij} = \begin{pmatrix}
G_{11}e_1 + \left( \frac{1}{2} G_{33} - G_{11} \right) e_2 - \frac{1}{2} G_{33} e_3 + G_{14} e_4 \\
\left( \frac{1}{2} G_{33} - G_{11} \right) e_1 + G_{11} e_2 - \frac{1}{2} G_{33} e_3 - G_{14} e_4 \\
- \frac{1}{2} G_{33} e_1 - \frac{1}{2} G_{33} e_2 + G_{33} e_3 \\
G_{14} e_1 - G_{14} e_2 + G_{44} e_4 \\
G_{44} e_5 + G_{14} e_6 \\
G_{14} e_5 + (G_{11} - \frac{1}{4} G_{33}) e_6
\end{pmatrix}
\]
\[
(3-37) \quad \mathbf{T}_I = \begin{pmatrix}
0 \\
0 \\
0 \\
0
\end{pmatrix}^T.
\]

According to (3-33), the strain is

\[
(3-38) \quad \mathbf{e}_I = \begin{pmatrix}
\varepsilon_{13} \\
\varepsilon_{13} \\
\varepsilon_{33} \\
0 \\
0
\end{pmatrix}^T,
\]

where \( \varepsilon_{33} \) is measured directly in the experiment since it is along the direction of the applied stress. Substitution in eq. (3-36) yields

\[
(3-39) \quad \begin{cases}
D_{12} = 0 \\
D_3 = \frac{1}{2} G_{33} \varepsilon_{33} \left( 2 - \frac{(\varepsilon_{1} + \varepsilon_{2})}{\varepsilon_{3}} \right) = \varepsilon_{33} \left[ G_{33} \left( 1 - \frac{\varepsilon_{13}}{\varepsilon_{33}} \right) \right] \\
D_5 = 0
\end{cases}
\]

Note that the only component of the G-tensor which appears in this case is \( G_{33} \). Using eq. (3-39), eq. (3-31) for this case is

\[
(3-40) \quad \frac{d \mathbf{B}}{d\varepsilon_{3}} = G_{33} \alpha \frac{d \mathbf{B}}{dD_3},
\]
Using eq. (3-44), eq. (3-31) for this case becomes

\[ \frac{dB}{de_1} = \left[ G_{11} - \frac{1}{2} G_{33} \right] \alpha + G_{14} \beta \frac{\partial B}{\partial D_2} + G_{33} \gamma \frac{\partial B}{\partial D_3}, \]

where

\[ \alpha = 2 \left( 1 - \frac{S_{13}^2}{S_{11}} \right) = +2.608 \]

\[ \beta = \frac{2 S_{14}}{S_{11}} = +0.416 \]

\[ \gamma = \frac{1}{2} \left( \frac{2 S_{13} - S_{12}}{S_{11}} - 1 \right) = -0.502 \]

Since \( G_{33} \) is determined in Case I, a measurement which determines \( dB/de_1 \) gives an equation in \( G_{11} \) and \( G_{14} \).

**Case III:** \( (\Theta = 90^\circ, \overline{\Phi} = 45^\circ) \)

For this case the stress, \( T \), is applied in the XY-plane at \( \Theta = 90^\circ \) and \( \overline{\Phi} = 45^\circ \). Here the xyz system does not coincide with the XYZ system. Tensors which are written in the xyz system will be denoted by a prime to distinguish them from tensors in the XYZ system.

First find \( D' \) in the xyz system by performing a
similarity transformation upon \( D \) of the form

\[
(3-47) \quad D' = \Gamma D \Gamma^{-1},
\]

where

\[
(3-48) \quad \Gamma = \begin{pmatrix}
\cos \Phi & \sin \Phi & 0 \\
-\sin \Phi & \cos \Phi & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]

We shall use the convention that the angle, \( \Phi \), through which any rotation takes place is to be taken as positive when the rotation is counterclockwise as seen by an observer looking back toward the origin from the positive end of the axis of rotation. In this case \( \Phi = +45^\circ \). After rotation we find

\[
(3-49) \quad D' = \begin{pmatrix}
\frac{1}{2} D_1 + \frac{1}{2} D_2 + 2 \left( \frac{1}{2} \right) D_6 \\
\frac{1}{2} D_1 + \frac{1}{2} D_2 - 2 \left( \frac{1}{2} \right) D_6 \\
D_3 \\
\frac{1}{2} D_4 - \frac{1}{2} D_5 \\
\frac{1}{2} D_4 + \frac{1}{2} D_5 \\
-\frac{1}{2} D_1 + \frac{1}{2} D_2
\end{pmatrix}
\]

As before, there are only three terms of interest. With the use of eq. (3-35) these are

\[
\begin{cases}
D_{12}' = D_1' - D_2' = 2 D_6 \\
\quad = 2 \left[ G_{14} e_5 + (G_{11} + G_{33}) e_6 \right]
\end{cases}
\]
\begin{equation}
(3-50)
\begin{cases}
D'_3 = D_3 = \frac{1}{2} G_{33} (2e_3 - e_2 - e_1) \\
D'_5 = \frac{1}{\sqrt{2}} (D_4 + D_5) \\
= \frac{1}{\sqrt{2}} \left[ G_{44} (e_5 + e_4) + G_{44} (e_6 + e_1 - e_2) \right]
\end{cases}
\end{equation}

Now find the components of the strain, \(e\), in the XYZ system. The applied stress, \(T'\), in the xyz system is

\begin{equation}
(3-51) \quad \begin{pmatrix}
1 \\
0 \\
0 \\
0 \\
0 \\
\end{pmatrix} T' \quad ,
\end{equation}

and upon rotation into the XYZ system we have

\begin{equation}
(3-52) \quad \begin{pmatrix}
\frac{1}{2} \\
\frac{1}{2} \\
0 \\
0 \\
0 \\
\end{pmatrix} T' \quad ,
\end{equation}

Hence, the strain is

\begin{equation}
(3-53) \quad \begin{pmatrix}
\frac{1}{2} \left( s_{11} + s_{12} \right) \\
\frac{1}{2} \left( s_{11} + s_{12} \right) \\
2s_{13} \\
0 \\
2s_{14} \\
2(s_{11} - s_{12}) \\
\end{pmatrix} T' \quad .
\end{equation}
In this case we measure $e_1'$, so it will be convenient to extract it from eq. (3-53) at this point. For a rotation about the $z$-axis $s_{11}' = s_{11}$, and eq. (3-53) becomes

\[
\begin{bmatrix}
\frac{1}{2} (1 + \frac{s_{12}}{s_{11}}) \\
\frac{1}{2} (1 + \frac{s_{13}}{s_{11}}) \\
\frac{s_{13}}{s_{11}} \\
0 \\
\frac{s_{14}}{s_{11}} \\
(1 - \frac{s_{12}}{s_{11}})
\end{bmatrix}
\]

Now substitution of eq. (3-54) in eq. (3-50) yields

\[
\begin{align*}
D_{12}' &= e_1' \left[ G_{14} \frac{1}{2} \left( \frac{5s_{14}}{s_{11}} + (G_{11} - \frac{1}{4} G_{33}) \frac{1}{2} \left( 1 - \frac{s_{12}}{s_{11}} \right) \right) \right] \\
D_3' &= e_1' \left[ G_{33} \frac{1}{2} \left( \frac{2s_{13}}{s_{11}} - 1 - \frac{s_{12}}{s_{11}} \right) \right] \\
D_5' &= e_1' \left[ G_{44} \frac{1}{2} \left( \frac{s_{14}}{s_{11}} \right) + G_{14} \frac{1}{2} \left( 1 - \frac{s_{12}}{s_{11}} \right) \right]
\end{align*}
\]

Using eq. (3-55), eq. (3-31) for this case becomes

\[
\frac{dB}{de_1'} = \left[ G_{14} \times + (G_{11} - \frac{1}{4} G_{33}) \beta \right] \frac{\partial B}{\partial D_{12}} + G_{33} \gamma \frac{\partial B}{\partial D_3} + \left[ G_{44} \delta + G_{14} \varepsilon \right] \frac{\partial B}{\partial D_5},
\]

where

\[
\begin{align*}
\alpha &= 2 \frac{s_{14}}{s_{11}} = +0.416 \\
\beta &= 2 \left( 1 - \frac{s_{12}}{s_{11}} \right) = +2.608 \\
\gamma &= \frac{1}{2} \left( \frac{2s_{13} - s_{12}}{s_{11}} - 1 \right) = -0.502 \\
\delta &= \frac{1}{2} \left( \frac{s_{14}}{s_{11}} \right) = +0.147 \\
\varepsilon &= \frac{1}{2} \left( 1 - \frac{s_{12}}{s_{11}} \right) = +0.922
\end{align*}
\]
It should be noted that the coefficients for \( \partial B/\partial D_{12} \) and \( \partial B/\partial D_3 \) are the same in this case as those for Case II. A measurement of \( dB/d\ell ' \), here gives additional information since the coefficient of \( \partial B/\partial D_5 \) is not zero but involves both \( G_{44} \) and \( G_{14} \).

Case IV: \( (\Theta = 45^\circ, \Phi = 0^\circ) \)

For this case the stress, \( T \), is applied in the XZ-plane at \( \Theta = 45^\circ \) and \( \Phi = 0^\circ \). Again the \( xyz \) system coincides with the \( XYZ \) system; however, one must perform a rotation to find the components of the strain in the \( XYZ \) system. The applied stress, \( T' \), in the \( xyz \) system is

\[
(3-58) \quad \vec{T'} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} T',
\]

and upon rotation into the \( XYZ \) system we have

\[
(3-59) \quad \vec{T'} = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} T'.
\]

Hence, the strain is
Using eq. (3-62), eq. (3-31) for this case becomes

\[
\frac{dB}{d\epsilon_1} = \left[ \left( G_{11} - \frac{1}{4} G_{33} \right) \alpha + G_{14} \beta \right] \frac{dB}{D_{12}} + G_{33} \gamma \frac{dB}{D_3} + \left[ G_{44} \delta + G_{14} \beta \right] \frac{dB}{D_5},
\]

(3-63)

where

\[
\begin{align*}
\alpha &= \frac{4 \left( S_{11} - S_{12} \right)}{\left( S_{11} + S_{33} + S_{44} + 2S_{12} \right)} = +1.144 \\
\beta &= \frac{4S_{14}}{\left( S_{11} + S_{33} + S_{44} + 2S_{12} \right)} = +0.182 \\
\gamma &= \frac{\left( 2S_{33} - S_{11} - S_{12} \right)}{\left( S_{11} + S_{33} + S_{44} + 2S_{12} \right)} = +0.252 \\
\delta &= \frac{2S_{44}}{\left( S_{11} + S_{33} + S_{44} + 2S_{12} \right)} = +1.293
\end{align*}
\]

(3-64)

The results for the coefficients of \( \partial B/\partial D_{12} \) and \( \partial B/\partial D_3 \) are the same as those in Cases II and III; however, the coefficient of \( \partial B/\partial D_5 \) does yield a new equation in \( G_{44} \) and \( G_{14} \).

**Case V:** \( (\Theta = 90^\circ, \Phi = 30^\circ) \)

For this case the stress, \( T \), is applied in the XY-plane at \( \Theta = 90^\circ \) and \( \Phi = 30^\circ \). The derivation of the form of eq. (3-31) for this case follows that used in Case III. The final result is
\[
\frac{dB}{d\xi_1} = \left[ (G_{11} - \frac{1}{4} G_{23}) \alpha + G_{14} \beta \right] \frac{dB}{D_1 D_2} + G_{33} \gamma \frac{dB}{D_3} + \left[ G_{44} S + G_{14} \xi \right] \frac{dB}{D_5} ,
\]

where

\[
\begin{align*}
\alpha &= 2 \left( 1 - \frac{S_{12}}{S_{11}} \right) = +2.608 \\
\beta &= 2 \left( \frac{S_{14}}{S_{11}} \right) = +0.414 \\
\gamma &= \frac{1}{2} \left( \frac{2S_{13} - S_{12}}{S_{11}} - 1 \right) = -0.502 \\
S &= \left( \frac{S_{14}}{S_{11}} \right) = +0.208 \\
\epsilon &= \left( 1 - \frac{S_{12}}{S_{11}} \right) = +1.304
\end{align*}
\]

The result for the coefficient of $\partial B / \partial D_3$ is the same as in Cases II, III, and IV. The coefficients of $\partial B / \partial D_{12}$ and $\partial B / \partial D_5$ yield new equations in $G_{11}$, $G_{14}$, and $G_{44}$.

Equations (3-40), (3-45), (3-56), (3-63), and (3-65) comprise the set of equations which may be solved simultaneously to give the values of the four independent components of the $G$-tensor. The set of equations presented is highly redundant; however, this overdetermination of the elements of $G$ provides a good test of the assumptions made in the theoretical analysis.
IV. PREPARATION OF SAMPLES

A. Crystal Structure of $\alpha$Al$_2$O$_3$

Pure aluminum oxide, Al$_2$O$_3$, in the stable $\alpha$ phase is commonly referred to as sapphire or corundum. Its crystal structure has been examined in detail, and the results are presented in several references. The point group of Al$_2$O$_3$ is $\overline{3}m$. Fig. (4-1a) is a stereographic projection showing the symmetry elements, the rectangular system XYZ to which the elastic constants are referred, and the hexagonal coordinate system $x$yuz which is used for Miller Bravais indices. The three dimensional space group is a member of the trigonal system. It is represented by the symbol $D_{3d}$ in the Schönflies notation and by $R\overline{3}2/c$ in the international system. The important constants of the rhombohedral unit cell are: $c = 13.00320$ Å, $a = 4.76280$ Å, $\alpha = 55-17'$, and $\alpha_{rh} = 5.12$ Å. A portion of the unit cell is shown in Fig. (4-1b) which is adapted from a recent publication. The solid circles represent the aluminum sites while the open circles represent the oxygen sites. Each aluminum ion has six oxygen ions as its nearest neighbors which are situated approximately on the corners of an octahedron. The octahedron is severely distorted as the dimensions indicate, and its axis of threefold rotational symmetry is parallel to the z or c-axis.
Fig. (4-1) Crystal Structure of Al₂O₃

(a) Stereogram of the point group 3m
(b) A portion of the Al₂O₃ lattice
(from Geschwind and Reemika)\textsuperscript{44}
It may be seen from Fig. (4-1a) that the Z or c-axis is a three-fold rotation-inversion axis. The diad symbols indicate the three two-fold axes which are normal to the c-axis. The heavy lines indicate the three mirror-planes which contain the c-axis and bisect the angles between the two-fold axes. The XYZ system is not uniquely defined by Fig. (4-1a) alone in that any one of six directions might be chosen for +X. The opposite ends of a two-fold axis may be distinguished however as has been pointed out by Wachtman, et al. ⁴¹ We will follow their convention and assume the +X direction to coincide with the +a direction. This convention is demonstrated in Fig. (4-2) which shows stereograms of the poles of prominent planes in sapphire. Fig. (4-2a) shows the letter symbols of morphological crystallography which can be assigned by measuring the angles between the poles. Fig. (4-2b) shows the corresponding Miller-Bravais indices. The letter symbols have been chosen to agree with the ones used by Winchell ⁴⁵ in a distance table for corundum. This table is reproduced in Fig. (4-3). Fig. (4-3) together with Fig. (4-2a) provide all the information necessary to interpret back-reflection Laue photographs of corundum crystals for which the orientation is unknown.
Fig. (4-2) Stereograms of poles of prominent planes in sapphire (from Wachtman et al.)

Fig. (4-3) Distance table for sapphire (from Winchel)
B. Alignment Apparatus

In order to manufacture the various samples needed in the experiment it was necessary to assemble a set of apparatus which was capable of cutting large single crystals into rectangular rods. In addition the axis of each sample was required to be accurately aligned with a known direction in the crystal. The degree of precision required led to the choice of X-ray equipment for the alignment of the samples and of a diamond saw with a precision rotating table for the cutting.

Fig. (4-4a) shows a photograph of the X-ray apparatus. The X-ray unit consists of a General Electric XRD-5 power supply with a tungsten target CA-7 X-ray tube installed in a horizontal tube mount. Attached to the tube mount is a support for a back-reflection Laue X-ray camera. When the camera is in place, a pin-hole collimator is inserted into the tube mount through the hole in the camera. The camera mount is designed so that it may be rotated about a vertical axis which is perpendicular to the axis of the collimator, and the entire assembly may be translated along an axis which is perpendicular to both of these axes. This freedom of movement enables one to adjust the camera so that the collimator falls in the region of highest X-ray emission
(a) X-Ray Camera

(b) Diamond Saw

Fig. (4-4) Apparatus for Aligning and Cutting Samples
from the tube. The film holder slides into the mount from above; it is designed to accept 5"x7" Kodak Medical X-ray Film. A typical crystal is shown in the path of the X-ray beam.

In order to facilitate the cutting of a single crystal along a preferred direction, a special mounting device is used. This permits the crystal to be transferred from the alignment operation to the cutting operation without changing its relative orientation. The crystal is attached to a polished pyrex glass block which is then attached to an aluminum carrier block. Hysol type 2020 epoxy adhesive with hardener type C has been found to be a satisfactory cement. The carrier block is oriented by means of two closely fitting dowel-pins on a Felker type HVC-12B rotary table. This precision table allows the crystal to be rotated about a vertical axis and a horizontal axis independently. The crystal may also be translated along the direction of the X-ray beam so that the distance between the sample and the film may be set. When the table is accurately aligned with respect to the X-ray beam, it performs the function of a goniometer.

The apparatus used for cutting the crystals is shown in Fig. (4-4b). The saw is a Felker model 80-BQ which is especially designed for use with diamond abrasive cut-off wheels. The crystal, with its carrier
block, is attached to the table of the saw in a manner similar to that used on the X-ray table. The precision rotating tables are identical except for the addition of a second axis along which the saw table may be translated. A low-speed motor drive has been added to this axis of translation so the crystal may be fed into the saw blade at a uniform rate. Water mixed in a ratio of 40:1 with Cimcool S-2 is used for cooling and flushing the work. Six-inch-diameter metal bonded diamond slicing saws have proved to be suitable for cutting most crystals.

Each table was carefully aligned so that the graduations on each position indicator gave a valid reading of the orientation of the table. We shall not go into the details of how this was done. A good estimate of the possible error in setting a desired orientation of each table is $\pm 0^\circ - 4'$. The limiting factor in aligning and cutting a sample is the accuracy with which one can read the back reflection Laue photographs. This error is nearly an order of magnitude higher than the error in setting the tables.
C. Procedure for Preparation of Samples

The samples used in this experiment were cut from a standard boule of Al₂O₃ doped 0.05% by weight with Cr₂O₃ which gives a concentration of approximately 1.5 x 10¹⁹ Cr³⁺ ions/cm³. The crystal was manufactured by the Linde Company by the Verneuil flame fusion technique. The crystal was not of the low-strain variety; however, higher quality crystals are available. According to Olt, slow grown ruby crystals in a disc boule form have the lowest internal strain. A crystal of this type would have been a better choice for this experiment.

The X-ray exposures were made at a sample-to-film distance of three centimeters with a power supply setting of 50 kVp and 20 ma. Initial pictures were made with a 0.050 inch diameter pinhole collimator, and final-alignment pictures were made with a 0.010 in. diameter pinhole collimator using exposure times of twelve minutes and one hour respectively. After the development of the film a stereographic projection was made according to the procedure described by Cullity. Two holes drilled through the back of the camera at equal distances from the center of the hole for the collimator exposed the film in two small spots which were then used to locate the center of the X-ray picture. A Greninger chart and a twelve inch diameter Wulff net were used to plot a
sterographic projection of the picture. The accuracy of the aligning and cutting process is limited for the most part by the degree of precision to which one can read the X-ray picture. In this case an accuracy of plus or minus $0^\circ \pm 20'$ is reasonable.

Five samples were cut in the form of rectangular rods 0.575 in. long and 0.125 in. square in cross-section. The orientation of the axis of each rod may be specified with respect to the crystal XYZ axes by specifying the value of $\Phi$ and $\Phi$ in Fig. (3-2a). This data is given in Table (4-1). A number is assigned to each rod which will serve to identify it for future reference. A Norton $52$ type

Table (4-1). Orientations of the ruby samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\Theta$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0^\circ \pm 0^\circ -20'$</td>
<td>$0^\circ \pm 0^\circ -20'$</td>
</tr>
<tr>
<td>2</td>
<td>$90^\circ$</td>
<td>$0^\circ$</td>
</tr>
<tr>
<td>3</td>
<td>$90^\circ$</td>
<td>$45^\circ$</td>
</tr>
<tr>
<td>4</td>
<td>$45^\circ$</td>
<td>$0^\circ$</td>
</tr>
<tr>
<td>5</td>
<td>$90^\circ$</td>
<td>$30^\circ$</td>
</tr>
</tbody>
</table>
V. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Electron-Spin-Resonance Spectrometer

The electron-spin-resonance spectrometer used in this experiment is of conventional design. Fig. (5-1) shows a block diagram of the equipment which was used. The microwave power from the klystron is divided at a directional coupler, part of the power going to the frequency measurement apparatus and the rest being divided at a magic tee. Half the power is sent to the sample cavity and half to a microwave discriminator. A circulator isolates the input power to the cavity from the reflected power, half of which goes to the detection system while the other half goes to the discriminator. A specially designed power supply (see Appendix B) uses the output of the discriminator to stabilize the frequency of the klystron and lock it to the resonant frequency of the sample cavity. Provision is made for sweeping the large magnetic field so the resonance condition is established at some time during the sweep. A small low-frequency modulation field is superimposed upon the larger field. Thus, in passing through a resonance the reflected power from the cavity will be modulated with an amplitude proportional to the derivative of the resonance absorption. The detection system is narrow-banded about
Fig. (5-1) Block Diagram of EPR Spectrometer
the modulation frequency to improve the signal-to-noise ratio. A phase sensitive detector converts the signal to a d-c output which is proportional to the derivative of the absorption. This output may be sent to a d-c recorder in order to produce a visible record of the absorption versus magnetic field. A nuclear resonance gaussmeter is used to find the magnitude of the magnetic field to a high degree of accuracy.

During the course of this experiment a modification of the spectrometer described above was developed. It is shown in Fig. (5-2) in the form used when the klystron is stabilized to a reference cavity. This spectrometer is a superheterodyne type and has a greater sensitivity, under the conditions of unity coupling to the sample cavity or low input power to the crystal detector, than the simple crystal detection type. The new contribution here is in the method for the generation of the local oscillator signal. Most superheterodyne spectrometers described elsewhere utilize a second klystron for the local oscillator. Some type of control system is used to stabilize the local oscillator to a frequency which differs from the frequency of the signal to be received by an amount equal to the i-f frequency. The system in Fig. (5-2) does away with the local oscillator klystron by deriving the local oscillator signal from the main klystron. A small amount of power
Fig. (5-2) Superheterodyne EPR Spectrometer
is taken from the main klystron and is amplitude
modulated at a frequency which is the desired i-f
frequency. Two specialized microwave diodes are used
for this purpose; a phase shifter placed between them
allows the percent modulation to be set to a maximum
value. At this point the frequency spectrum of the
modulated wave has three components, the carrier and
upper and lower side-bands. A rectangular band-pass
cavity was constructed from a section of waveguide
for the purpose of removing the carrier and one side-
band from the spectrum. The resonant frequency of this
cavity is tuned to the frequency of the side-band to
be passed by means of a .10 in. diameter sapphire rod
which is inserted into a region of high electric field.
The side-band which is passed by the cavity performs the
function of a local oscillator for a magic tee balanced
mixer. One further advantage of this system is that
the local oscillator signal has a constant phase rela-
tionship to the signal to be detected. Thus, one may
perform phase-sensitive detection at the i-f frequency
which eliminates noise from frequency modulation of the
klystron. A spectrometer using this scheme should have
a further improved signal-to-noise ratio.
**Fig. (5-3a)**
TE$_{101}$ Rectangular Cavity

**Fig. (5-3b)**
Sample Orientation
to apply the stress in the system. The forward end of
the screw is spherical in shape to be made with a similar
spherical depression in the brass cylinder. The quartz
rod extends across the center of the cavity and rests
against a 0.125 x 0.125 x 0.075 in. thick quartz pad
which is bonded to the sample with epoxy cement. At
the other end of the quartz rod is a flat brass pad
which helps to prevent chipping of the quartz when stress
is applied.

This apparatus has been used to apply stresses
as high as 2.0 x 10^9 dynes/cm^2 to samples of ruby.
Since no failures resulted in any part of the system, it
is very likely that much higher stresses could be ob-
tained if necessary.

Measurements using the ESR signal from diphenyl-
picrylhydrazyl indicate that there is no change in the
resonant frequency of the cavity when stress is applied
to a sample.
C. **Experimental Method**

The procedure used for the determination of \( \frac{dB}{d\theta} \) was rather simple. As has been mentioned earlier, the samples were cut in such a manner that the c-axis could be placed in the plane of rotation of the applied magnetic field. Thus, one could determine \( \frac{dB}{d\theta} \) for all observable transitions at any angle \( \theta \) of the applied magnetic field. Although the orientation of the sample was known to a high degree of accuracy, the direction of the c-axis with respect to the markings on the base of the rotating magnet had to be determined experimentally. This was done by observing the resonance signal from the 2-3 high field transition in ruby and simultaneously rotating the magnet until the lowest magnetic field for the resonance condition was reached. Near \( \theta = 90^\circ \), Fig. (5-4) shows that for this transition \( \frac{dB}{d\theta} \) is approximately 15 gauss/degree which is more than adequate for setting the field perpendicular to the c-axis to within \( \pm 0^\circ - 20^\circ \).

With the resonant frequency of the cavity adjusted to 10.1 Gc\( \pm 0.05\% \), the strain dependence of four transitions was studied at room temperature. The 2-3 low and high field transitions could be observed for all values of \( \theta \); however, the highest magnetic field obtainable was 4.8 kG which prevented the observation of the 1-2 and 3-4 tran-
sitions over the entire range of $\Theta$. The 1-3 and 2-4 transitions are only observable over a small range of $\Theta$ at 10.1 Gc so no measurements were made on them.

A Baldwin-Lima-Hamilton type K strain indicator was used to measure the strain in the samples. This indicator reads directly in micro-inches per inch when used with the type FAP-12-12 S-6 strain gages. Measurements made with the type A-19 gages had to be corrected due to their low resistance and gage factor. The indicator is an a-c bridge which measures small changes in the resistance of the gages. For compensation against possible errors caused by temperature variations of resistance, two identical gages were used. In this case a spare sample equipped with a dummy strain gage was placed in good thermal contact with the outside of the cavity. This gage formed one arm of the bridge circuit while the gage attached to the sample formed another arm. The manufacturer specifies an accuracy for the indicator of $\pm 5 \mu''/''$; however, the instrument appeared to be resettable with less than this amount of error.

In order to determine $d\Omega/d\epsilon$ in each case, a small amount of stress was applied to the sample and the reading of the strain indicator was noted. The magnetic field was adjusted to the value for resonance by observing the derivative of the absorption. The zero of the derivative indicated the center of the line. The NMR gaussmeter was used to measure the magnetic field at
this point. Next the strain was increased by 50 μ"/", and the change in the magnetic field necessary to find the center of the resonance line was noted. Succeeding measurements were taken as the strain was further increased up to a maximum of about 400 μ"/". Finally the strain was reduced to its original value to provide a check of the initial measurement. If the shift in magnetic field is assumed to be a linear function of the change in the strain, then the slope of the best straight line fit to the data yields dB/de.
VI. RESULTS

A. Experimental Measurements

The results of the experimental work performed on the five samples of ruby will be presented in this section. Following sections will be devoted to a fit of the results to the theory and an analysis of the experimental errors. Individual samples will be referred to by number for simplicity, since the orientation of each sample has been listed earlier in Table (4-1).

The direct results of the resonance experiment are values of $\Delta B$ as a function of $\Delta e$. Since a nuclear-resonance gaussmeter was used to determine the shift of the resonant magnetic field, the units of $\Delta B$ are frequency, $f_{\text{NMR}}$. This frequency may be converted to Gauss by dividing by a conversion factor of 4,257.76 cycles/Gauss for proton ($^1\text{H}$) resonance. The calibration of the strain indicator was such that $\Delta e$ could be read directly in units of micro-inches/inch. Typical results for the measurements of $\Delta B$ vs. $\Delta e$ are shown in Fig. (6-1) for two cases.

It may be seen that the data represented by the circles may be fitted to a straight line with very little error, and this is representative of about ninety percent of all the measurements. Such a linear fit was the ex-
Fig. (6-1) Typical Experimental Results
the most part, the data represent only an average value for the shifts of the lines. We shall return to the question of the change in the shape of the lines under stress later.

As we have pointed out before, the information which is needed to determine the components of the G-tensor is the rate of change of the resonant magnetic field with respect to the strain. This is just the slope, dB/de, of the straight lines in Fig. (6-1). Hence, the intercept is of no consequence, and, rather than present the raw data, we shall use only the values of dB/de which give the best linear fit to the data.

The following twenty graphs, Figs. (6-2) through (6-21), show the results obtained for dB/de, in units of kG/unit strain, as a function of the angle, θ, between the applied magnetic field and the c-axis of the ruby crystal. The results for the 1-2, 2-3 high field, 2-3 low field, and 3-4 transitions are presented in order for each of the five samples. Data obtained with the type A-19 strain gages, gage #1, are represented by the squares, and data obtained with the type FAP-12-12-S6 strain gages, gage #2, are represented by the circles. Measurements on samples 1, 2, and 3 were made with both types of gage; however, measurements on rods 4 and 5 were made only with the latter, or more accurate, gage. The solid curve on each graph represents a least-squares
**Fig. (6-10)**

**Rod 3**

\( \Theta = 90^\circ, \Phi = 45^\circ \)

1-2 Transition
- Gage No. 1
- Gage No. 2
- Calculated Fit

**Fig. (6-11)**

**Rod 3**

\( \Theta = 90^\circ, \Phi = 45^\circ \)

2-3 High Field Transition
- Gage No. 1
- Gage No. 2
- Calculated Fit

**Fig. (6-12)**

**Rod 3**

\( \Theta = 90^\circ, \Phi = 45^\circ \)

2-3 Low Field Transition
- Gage No. 1
- Gage No. 2
- Calculated Fit

**Fig. (6-13)**

**Rod 3**

\( \Theta = 90^\circ, \Phi = 45^\circ \)

3-4 Transition
- Gage No. 2
- Calculated Fit
fit to the data according to the theory which will be discussed in a following section.

An interesting, and at first unexpected, result of these measurements was the observation of an occasional splitting of the resonance lines which was dependent on the applied stress. In most cases this splitting was very small and could be detected only by careful observation of the shape of the lines. Often this effect was present in lines which were either broadened or split into two or more components by local strains in the crystal. An applied stress was observed to broaden a single line or to change the relative shape of a multiple line. Fortunately, this effect was quite strong for the 1-2 transition of rod 4 over the entire range of $\theta$. Fig. (6-22) is a reproduction of the derivative curves obtained for the 1-2 transition of rod 4 at $\theta = 80^\circ$. Part (a) of this figure shows a single line with a width of 16 Gauss which was present under the condition of zero strain. Part (b) shows how this line was split into two components, each with a width of about 13 Gauss and an amplitude of about half that of the original line, under the condition of an indicated strain of 300 $\mu"/"$. The splitting is large enough in this case to allow the center of each component to be determined, and one line is found to be shifted down in field by 3 Gauss from the
Fig. (6-22) Strain Dependent Splitting
$\Theta = 45^\circ, \Phi = 0^\circ$, 1-2 Transition, $\theta = 80^\circ$
(a) $e = 0$  (b) $e = -300 \mu \text{in/in}$
Further, since there should be an equal number of \(\text{Cr}^{3+}\) ions in each set of sites, a single line should split into two lines, each with an amplitude equal to half the amplitude of the original line. According to the results shown in Fig. (6-22), this assumption has also been verified.
in which a dummy strain gage compensates against changes in the ambient temperature. The dummy gage used in this experiment was attached to a spare sample which was placed in thermal contact with the apparatus. Further, gage #2 was selected on the basis of its low temperature coefficient of 6 μ"/" apparent strain per °F change in temperature. Under these conditions, the errors due to drifts in the indication of strain were found to be negligible.

(d) In order to measure the strain along the axis of a sample, the strain gage must be attached so that its wire grid is parallel to this axis. Although the gages used were very small, it was possible to align them with the axis of a sample to within ±1°. This error simply reduces the gage factor of the strain gage by an amount proportional to the sine of this angle, about one percent in this case.

There are also several sources of error in the measurement of the magnetic field required for resonance:

(a) First, the magnetic field must be set to a value which corresponds to the center of the resonant absorption line. As described in section IV-C, this was done by observing the derivative of the absorption curve and adjusting the magnetic field until the output of the phase-sensitive detection system indicated that the zero point of the derivative had been reached. The
precision of this method for finding the center of a resonance line depends upon the slope of the derivative signal. The precision is highest, of course, for narrow lines with a strong absorption. Unfortunately, both the strength and the shape of the lines observed in this experiment were dependent upon the transition under observation and the direction of the applied magnetic field. In addition, the presence of strain dependent splitting of the lines influenced the precision of this measurement. So many variables are involved here that a detailed evaluation of the error in each measurement would be difficult; however, a rough estimate reveals that the center of a typical line could be found within ±0.2 Gauss, although errors of the order of a few gauss were undoubtedly present in some cases.

(b) Once the magnetic field had been adjusted to the desired value, it was measured by means of a nuclear-magnetic-resonance gaussmeter. Because the line-width of the proton resonance is very narrow, a small modulation field is superimposed on the field to be measured so the resonant absorption may be observed on an oscilloscope. In these measurements, the peak-to-peak amplitude of the modulation field was the order of a few Gauss. Thus, there was a possible error
in the adjustment of the frequency of the nuclear resonance oscillator to the proper value. The average error in this respect was found to be less than ±0.1 Gauss. Since the frequency could be measured to better than one part in $10^5$, no further errors were introduced into the measurement of the magnetic field.

An attempt has been made in Fig. (6-1) to show the magnitude of the errors discussed above by means of error bars. The error in the measurement of strain is assumed to be ±5 μ"/" or 4% whichever is greater. The error in the measurement of the magnetic field is assumed to be ±1 Gauss, where this represents the error for a broad or weak line rather than that of an average line. It is important to note that the dominant errors are constant in magnitude, and therefore, the measurements made at the maximum indicated strain will have the lowest percent error.

To determine the best value for dB/de for each set of measurements one should use the standard least-squares technique with the data weighted according to its relative precision. In addition, a variance for each value of dB/de should be calculated for use in weighting these data in a statistical fit to the theory. This is a rather long and complicated task even with a high-speed digital computer, and it is important to ask whether such an all-out effort is needed in this case.
Since most of the measurements were found to fit a straight line with relatively little deviation, it was decided that the values of dB/de could be obtained with sufficient precision by graphical methods.

Let us now consider some of the sources of error which will influence the fit of these data to the theory:

(a) The values obtained for dB/de should have a precision of ±3% in the cases in which the error in ΔB is not large. Otherwise, the results are most reliable when the magnitude of dB/de is large.

(b) There are also sources of error in the value of the angle, θ, between the magnetic field and the c-axis. These arise from inaccuracy in the X-ray alignment (±0.3°), misalignment of the apparatus which places the c-axis out of the plane of rotation of the magnetic field (±1° max.), and error in the determination of a reference point for θ on the base of the magnet (±0.3°). Hence, this error is ±1° or less.

(c) Finally, errors in the angles θ and Φ which specify the direction of the applied stress may be as large as ±0.5°.
Table (6-1). Results for least-squares fit to data

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>A(1)</th>
<th>A(2)</th>
<th>A(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Gc/u. st.)</td>
<td>(Gc/u. st.)</td>
<td>(Gc/u. st.)</td>
</tr>
<tr>
<td>1</td>
<td>29.517</td>
<td>234.477</td>
<td>-3.907</td>
</tr>
<tr>
<td>2</td>
<td>246.782</td>
<td>-84.728</td>
<td>-7.027</td>
</tr>
<tr>
<td>3</td>
<td>190.686</td>
<td>-68.217</td>
<td>-11.452</td>
</tr>
<tr>
<td>4</td>
<td>98.296</td>
<td>40.760</td>
<td>50.831</td>
</tr>
<tr>
<td>5</td>
<td>194.775</td>
<td>-67.108</td>
<td>-10.302</td>
</tr>
</tbody>
</table>

These constants were used to calculate dB/de vs Θ for each rod and each transition, and the results are shown by the solid curves in Figs. (6-2) through (6-21). Although the variances of the constants were not calculated, an inspection of the curves shows that the fit to the data is quite good.

The equations derived in part III may now be used to solve for the components of the G-tensor. Unfortunately, there are only four independent equations to be solved simultaneously for the four unknowns, and this limits the reliability of the calculation in that the components of the G-tensor are not over-determined. The results obtained for the four independent components
of the G-tensor for Cr$^{3+}$ in ruby are given, along with their standard deviation, in Table (6-2) in units of Gc/unit strain.

Table (6-2). Components of the G-tensor for ruby

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Gc/u. st.)</td>
<td>Gc/u. st.</td>
</tr>
<tr>
<td>$G_{33}$</td>
<td>+166.</td>
<td>24.</td>
</tr>
<tr>
<td>$G_{11}$</td>
<td>+129.</td>
<td>15.</td>
</tr>
<tr>
<td>$G_{44}$</td>
<td>+41.3</td>
<td>6.3</td>
</tr>
<tr>
<td>$G_{14}$</td>
<td>-14.5</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Since the number of measurements which are involved in the calculation of $G_{33}$ and $G_{11}$ is quite large, the true error in the values of these components is less than ten percent. The value of $G_{44}$ is somewhat less precise, and the error for the component $G_{14}$ is at least thirty percent.

We have mentioned several times that there are actually two groups of non-equivalent sites for the Cr$^{3+}$ ion in Al$_2$O$_3$, and therefore, the results presented above are an average of the components of two G-tensors of the form given in eq. (3-4). According to section III-A, one
set of sites may be transformed into the other by a reflection through the XY plane and a rotation about the Z-axis of 8.6°. Thus, the components of one G-tensor may be expressed in terms of the other by performing these operations upon it.

Let us assume for the moment that the rotation about the Z-axis is small enough to be considered a second order effect and consider the changes in the G-tensor upon reflection through the XY plane. Performing this operation, one finds that the only difference between the two tensors is the sign of $G_{14}$. Since the experiment determines only an average value of $G_{14}$, a result of zero would be expected for this component. The value of $G_{14}$ given in Table (6-2) is not zero within the experimental error, but it is indeed quite small in comparison with the other components. Further, since two lines were resolved in the measurements made on the 1-2 transition in rod 4, these data should yield information on the two types of sites separately. The method of least-squares was applied to the data represented by the triangles in Fig. (6-14), and the results are given in Table (6-3) in units of Gc/unit strain.
VII. CONCLUSIONS

The results of this experimental work verify that the effects of uniaxial stress on the spin-resonance spectrum of \( \text{Cr}^{3+} \) in \( \text{Al}_2\text{O}_3 \) may be attributed to an additional term in the spin Hamiltonian of the form \( D_{ij}S_iS_j \) where \( D_{ij} \) is a tensor related to the strain by a magneto-elastic coupling tensor \( G_{ij} \). The average values for the components of the \( G \)-tensor for ruby have been determined in this experiment, but unfortunately, the actual value of the component \( G_{14} \) is still somewhat in doubt. Also, because of an insufficient number of independent measurements, the assumption that the \( G \)-tensor is symmetric has not been verified experimentally.

Tucker\(^{57}\) has also measured the components of the \( G \)-tensor for ruby, and his results obtained by acoustic-spin-resonance techniques are compared with the results of this experiment in Table (7-1) in units of Gc/unit strain.
Table (7-1). Comparison of results for the G-Tensor for ruby by acoustic-spin-resonance and uniaxial stress techniques

<table>
<thead>
<tr>
<th>Acoustic-spin-resonance (E. B. Tucker\textsuperscript{57})</th>
<th>Uniaxial stress (present work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Gc/u. st.)</td>
<td>(Gc/u. st.)</td>
</tr>
<tr>
<td>$G_{33} = 172.$</td>
<td>$G_{33} = +166.$</td>
</tr>
<tr>
<td>$G_{11} = 125.$</td>
<td>$G_{11} = +129.$</td>
</tr>
<tr>
<td>$G_{44} = 52.3$</td>
<td>$G_{44} = +41.3$</td>
</tr>
<tr>
<td>$G_{14} = 52.3$</td>
<td>$G_{14} = -14.5$</td>
</tr>
</tbody>
</table>

The result for $G_{33}$ given here differs somewhat from the value reported earlier by Tucker\textsuperscript{16} and from the value obtained by Dobrov et al.\textsuperscript{17} It should be noted that the acoustic experiments give only the magnitudes of the components of the G-tensor; whereas the stress experiments yield the signs as well as the magnitudes. Thus, the acoustic measurements should give a more reliable value of $G_{14}$ in this case because the attenuation of acoustic waves is insensitive to the difference in the sign of $G_{14}$ for the two sets of Cr\textsuperscript{3+} sites in ruby. The agreement between the two sets of results for the remaining components is
surprisingly good.

We have mentioned earlier that the energy level structure for the ground state of Cr$^{3+}$ in Al$_2$O$_3$ is similar to that for Cr$^{3+}$ in MgO, and therefore, one might expect a comparable strength for the spin-lattice interaction for these two systems. The components of the G-tensor for Cr$^{3+}$ in MgO have been measured recently by both acoustic-spin-resonance and uniaxial stress techniques.\textsuperscript{19,26} The value of $G_{44}$ in a cubic crystal, such as MgO, may be compared with the value of $G_{33}$ in a trigonal crystal, such as Al$_2$O$_3$, and this is presented in Table (7-2) in units of cm$^{-1}$/unit strain.

\begin{table}[h]
\centering
\caption{Comparison of similar components of the G-tensor for Cr$^{3+}$ in MgO and Al$_2$O$_3$
\begin{tabular}{lll}
\hline
&MgO:Cr$^{3+}$ & MgO:Cr$^{3+}$ & Al$_2$O$_3$:Cr$^{3+}$ \\
Acoustic-spin-resonance & Uniaxial stress & Uniaxial stress \\
(N. S. Shiren\textsuperscript{19}) & (Watkins and Feher\textsuperscript{26}) & (present work) \\
(cm$^{-1}$/u. st.) & (cm$^{-1}$/u. st.) & (cm$^{-1}$/u. st.) \\
\hline
$G_{44} = 6.5$ & $G_{44} = +4.2$ & $G_{33} = +5.6$ \\
\hline
\end{tabular}
\end{table}
the spin-lattice relaxation time in this material.\textsuperscript{58,59}
This discrepancy has been attributed to the presence of exchange interactions, and this explanation has been borne out by the work of Gill\textsuperscript{60} on the relaxation of exchange-coupled ion pairs. Nisida\textsuperscript{61} has recently reported measurements of the concentration and temperature dependence of $T_1$ for ruby at low temperatures, and his results may prove to agree with more exact computations of the one-phonon relaxation time using the $G$-tensor.

In another recent paper, Blume and Orbach\textsuperscript{62} have attempted to calculate the relaxation times for Mn$^{2+}$ in a cubic environment in the low temperature region, where the direct process is expected to be dominant. Their estimates of the interaction coefficients, based on a point-charge model, were found to agree with the magnitudes, but not the signs, of the components of the $G$-tensor reported by Watkins and Feher\textsuperscript{26} for Mn$^{2+}$ in MgO. It appears that calculations of this sort would be useful in the case of Cr$^{3+}$ in Al$_2$O$_3$.

It is interesting to compare the results of the uniaxial stress experiments on the spin-resonance spectrum of ruby reported here to those of Schawlow\textsuperscript{63} on the optical spectrum. Schawlow found that the zero field splitting of the first excited state, which gives rise to
the so-called R lines, decreases when stress is applied along the c-axis. In contrast, our measurements show that the zero field splitting of the ground state increases under the same conditions. The fact that these results are opposite in sign has been of considerable interest to other workers in this field.

Another interesting result of the experiments reported here is the splitting of the electron-spin-resonance lines by an applied stress. As we have shown, this splitting can be attributed to the presence of non-equivalent sites for the Cr$^{3+}$ ions in Al$_2$O$_3$. Both splittings of the optical lines$^{22}$ and splittings of the spin-resonance lines$^{21,65}$ of ruby have been observed by the application of an external electric field; however, these are first order effects, since the electric field has a definite sign as well as a definite direction. The removal of this type of degeneracy by the application of uniaxial stress has not been reported before, and this subject is worthy of further investigation.
VIII. APPENDICES

A. Computer Calculations

This section describes a computer program which was written in order to fit the data obtained in this experiment to the theory. According to eq. (3-28), we wish to fit the results for dB/de to an equation of the form

\[
(A-1) \quad \frac{dB}{de} = A(1) \frac{\partial B}{\partial D_1} + A(2) \frac{\partial B}{\partial D_2} + A(3) \frac{\partial B}{\partial D_3}
\]

where \(A(1), A(2),\) and \(A(3)\) are the constants to be determined and \(\partial B/\partial D_1, \partial B/\partial D_2,\) and \(\partial B/\partial D_3\) are functions of the microwave frequency, the applied magnetic field, and the angle, \(\theta,\) between the field and the c-axis of the ruby crystal. Since the constants in eq. (A-1) are linear combinations of the components of the G-tensor they will be different for each direction of the applied stress. Thus, the problem is to find the best values of \(A(1), A(2),\) and \(A(3)\) for each rod.

The method of least-squares for a non-polynomial case is described by Hamming.\(^{56}\) Using the normal equations given by Hamming, we find that the solution of our problem amounts to solving the following system of three equations in the three unknowns \(A(1), A(2),\) and \(A(3):\)
MAIN PROGRAM

C LEAST SQUARES FIT OF STRESSED RUBY DATA

DIMENSION SUM(3),I,J,A(3),B(3),F(3),AUX(10),N(10),B(10)

READ INPUT TAPE 5,4,NROD,I,J,TH,B0,DBDE,WT,NCTRL

CALL STRESS(1,TUHM,DD,DBD12,DBD3,DBD5)

SUM(1,1)=SUM(1,1)+(DBD12*DDBD3)*WT
SUM(1,3)=SUM(1,3)+(DBD12*DDBD5)*WT
SUM(1,4)=SUM(1,4)+(DBD12*DBDE)*WT
SUM(2,1)=SUM(2,1)+(DBD3*DDBD12)*WT
SUM(2,2)=SUM(2,2)+(DBD3*DBDE)*WT
SUM(2,3)=SUM(2,3)+(DBD5*DDBD12)*WT
SUM(3,1)=SUM(3,1)+(DDDB5*DBD12)*WT
SUM(3,2)=SUM(3,2)+(DDDB5*DBDE)*WT
SUM(3,3)=SUM(3,3)+(DDDB5*DBD12)*WT

SUM(1,1)=SUM(1,1)+(DBD12*DDBD3)*WT
SUM(1,3)=SUM(1,3)+(DBD12*DDBD5)*WT
SUM(1,4)=SUM(1,4)+(DBD12*DBDE)*WT
SUM(2,1)=SUM(2,1)+(DBD3*DDBD12)*WT
SUM(2,2)=SUM(2,2)+(DBD3*DBDE)*WT
SUM(2,3)=SUM(2,3)+(DBD5*DDBD12)*WT
SUM(3,1)=SUM(3,1)+(DDDB5*DBD12)*WT
SUM(3,2)=SUM(3,2)+(DDDB5*DBDE)*WT
SUM(3,3)=SUM(3,3)+(DDDB5*DBD12)*WT

SUM(1,1)=SUM(1,1)+SUM(2,2)+SUM(3,3)-SUM(1,2)*SUM(1,3)*SUM(1,2)*SUM(2,1)*SUM(2,2)

IF(DELTA) 102,300,102

A(1)=A(1)/DELTA
A(2)=SUM(1,1)*(SUM(2,4)+SUM(3,3)-SUM(2,3)*SUM(3,4))+SUM(1,4)*
1SUM(3,1)*SUM(2,3)-SUM(2,1)*SUM(3,3)+SUM(1,3)*SUM(2,1)*SUM(3,4)-
2SUM(3,1)*SUM(2,2)

A(3)=A(3)/DELTA
WRITE OUTPUT TAPE 6,3,NROD;A(I),I=1,3
CARDS COLUMNS

LABEL

MAGNETIC FIELD SHIFTS IN STRESSED RUBY SUBROUTINE DONOHO RICE
SUBROUTINE STRESS (I,J,TH,B0,DBDD12,DBDD3,DBDD5)
DIMENSION E(4)
FNMF(E)= G2*B*(1.5.*E**2+4.*D*E+C3+2.25*G2*B2+D2*D*C6)
FNRF(E)=3.*G2*B2*E*C3-0.5*D*E**2+0.6*D*D2+1.5*G2*B2*D*C6
FNSF(E)=(-6.*G2*B2*CF*SF*(2.*E+D))
FNTF(E)=3.*G2*B2*SF**2*(D-E)
ET=10.100
D=1-5.733)
D2=D*D
G=2.7189
G2=G*G
TH=TH/57.29578
CF=COSF(TH)
SF=SINF(TH)
C3=1.-3.*CF*CF
C6=1.-6.*CF*CF
B=B0
K=0
3 K=K+1
IF(K<25)4,300,300
4 B2=B*B
AL=2.5+G2*B2+2.*D2
BE=2.*G2*B2*D*C3
DEL=D-1.5*G*B
CALLEDENERGY(AL,BE,GA,DEL,E)
FT=E(I)-E(J)-ET
FTP=FNNF(E(J))/FNMF(E(J))-FNNF(E(I))/FNMF(E(I))
B=B-FT/FTP
IF(ABSF(FT/FTP)<0.0001)5,5,3
5 B2=B*B
DEN=FNNF(E(J))*FNNF(E(I))-FNNF(E(I))*FNNF(E(J))
TOP=FNNF(E(I))*FNRF(E(J))-FNNF(E(J))*FNRF(E(I))
TOPS=FNNF(E(I))*FNSF(E(J))-FNNF(E(J))*FNSF(E(I))
TOPT=FNNF(E(I))*FNTF(E(J))-FNNF(E(J))*FNTF(E(I))
DBDD3=TOPT/DEN
DBDD5=TOPS/DEN
DBDD12=TOPT/DEN
300 RETURN
END
B. Stabilized Klystron Power Supply

Fig. (B-1) shows the circuit diagram of a klystron power supply which was designed for use with a paramagnetic-resonance spectrometer. The design incorporates a simple system for stabilizing the frequency of a klystron to the resonant frequency of a microwave cavity. The major innovation in the use of an unconventional power supply for the reflector potential which permits a d-c correction voltage to be inserted at a point of low potential. This correction voltage is derived from a microwave discriminator such as those shown in Figs. (5-1) and (5-2). Measurements indicate that a klystron may attain a short-term frequency stability of one part in $10^8$ using this system, and the long-term frequency stability is determined by the stability of the microwave cavity used as a reference.

The following is a description of the operation of this circuit:

1. The circuit consists of four power supplies, two high gain D. C. amplifiers and two modulation waveform generators.

2. V-1 through V-4 comprise a regulated, 300 Vdc, 100 mA power supply. This powers the modulation section, the D. C. amplifiers, and the reflector supply.
3. V-5 through V-10 comprise a regulated, 250 to 500 Vdc, 60 mA power supply. This is the BEAM SUPPLY.

4. V-11 through V-14 comprise a regulated -300 Vdc, 40 mA power supply. This is the negative supply for the two d-c amplifiers.

5. The REFLECTOR SUPPLY is made up of V-15, V-16, and d-c amplifier A-2. One half of V-15 is a 20 kc free-running blocking oscillator while the other half is an amplifier whose grid to cathode bias is controlled by A-2. V-16 provides a fixed bias on the amplifier so that A-2 may supply the required 100 volt variation in its output voltage and remain within the ratings specified by the manufacturer. The supply is regulated by a low-voltage secondary winding in the output transformer whose rectified output is exactly concealed by the setting of the REFLECTOR VOLTAGE helipot which forms a voltage divider network. Thus, any variations in the output of the REFLECTOR SUPPLY are fed back to control the gain of the amplifier portion of V-15. In addition, the setting of the helipot determines the reflector voltage since it is calibrated by a pot in the voltage divider network. This supply operates between -50 to -900 Vdc at no output current.

6. V-17 is a free-running multivibrator which may be controlled in frequency over a small range around 1,000 cps. One half of V-18 is a clipper for this square wave
ACKNOWLEDGEMENTS

I would like to express my appreciation to the faculty and staff of the physics department of Rice University for their assistance during the course of my graduate study. I am particularly indebted to Dr. Paul L. Donoho, who proposed and directed this research, for he has been a constant source of aid, encouragement, and inspiration. Credit must go to him for most of the original ideas presented in this thesis.

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I would also like to thank the Ohio Oil Company for granting me a fellowship during the 1961-62 school year, and Mrs. Mary Comerford for typing this thesis.

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