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ANALYSIS OF ELECTRON SPIN RESONANCE SPECTRA 
OF THE GADOLINIUM ION IN SODA SILICA GLASSES

by

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I. INTRODUCTION

The technique known as electron spin resonance (ESR) has been used to study many different types of materials. The primary requirement is that the substance to be investigated must contain unpaired electron spins. Under suitable conditions, information can be obtained about local electric (crystal) fields caused by the surroundings of a magnetic ion and about magnetic interactions between magnetic ions. ESR can therefore be used as a very sensitive probe to study the electric and magnetic fields in a material at the atomic level.

For the present investigation, a simple glass doped with about 0.07 atomic per cent gadolinium has been selected for study. The rare earths comprise the periodic table series between atomic numbers 57 and 71 and are built up by the addition of from one to 14 electrons to the 4f shell. All the ions of this group except the end members lanthanum and lutetium are paramagnetic and any of these could be introduced into the glass as a magnetic impurity to be studied by ESR. However, \text{Eu}^{2+} and \text{Gd}^{3+} have a zero orbital angular momentum contribution to the ion total angular momentum, because their 4f shells contain 7 unpaired electrons and by Hund’s rules, \( S = 7/2 \) and \( L = 0 \). This fact makes these ions very attractive for ESR studies because their 4f electrons are relatively isolated. They cannot interact with their surroundings via the usual spin-orbit interaction and consequently, the resonance
lines resulting from these ions are relatively narrow and in-
tense enough to be seen even at room temperature. The rest of
the rare earth ions have such wide lines that it is necessary
to reduce the temperature to at least 4°K to observe them.

There are many working definitions of a glass but for our
purposes the one given by Mackenzie (1) will suffice. A glass
is any isotropic material, organic or inorganic, in which
three-dimensional atomic periodicity is absent and the viscos-
ity of which is greater than $10^{14}$ poise. By three-dimensional
atomic periodicity is implied a long range order of greater
than about 20 angstrom units. It is this lack of periodicity
which really distinguishes a glass from the crystalline mate-
rials generally considered in solid-state studies. Glasses
are usually obtained from a liquid by rapid cooling and this
freezes in the disorder of the liquid, the type and amount of
disorder depending on the conditions of cooling.

There are very many glass systems. The elements oxygen,
sulphur, selenium and tellurium will form glasses by them-
selves and at least one of these must be a constituent of any
inorganic glass. Winter (2) and Imaoka (3) have done exten-
sive studies on the glass forming ranges of binary and trinary
glasses. The most important glasses are the phosphate, silic-
cate and borate glasses. These are formed by combining $P_2O_5$, $SiO_2$, or $B_2O_3$ with alkali or alkaline-earth oxides, and oxygen
is the dominant element in all these glasses. Even a simple
binary glass such as the soda-silica system considered here
has a complicated phase diagram (4) and care must be taken to
insure that the samples do not even partially devitrify.

The theory of the structure of glasses is either heaven
or a no man's land for the theoretician, depending on one's
taste. On the one hand, substantially different theories
abound for even the same system, and almost any sort of theory
seems to have some truth to it. On the other hand, no gener­
ally applicable theory has been developed for even a single
system and each glass must be considered as a separate world.

In 1932, Zachariasen (5) proposed what is now known as
the random network theory in which the oxides B\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2},
GeO\textsubscript{2}, P\textsubscript{2}O\textsubscript{5} and As\textsubscript{2}O\textsubscript{5} were designated as "glass formers" or
"network formers" and the alkali and alkaline-earth oxides
were called "network modifiers." In silica glasses, for ex­
ample, a continuous network of SiO\textsubscript{4} tetrahedra made up by the
sharing of tetrahedra corners would be modified by the addi­
tion of alkali metal ions, which would have to fit into the
spaces left by the tetrahedra. Crystalline silicates contain
these SiO\textsubscript{4} units arranged in a symmetrical, periodic fashion,
whereas in the glass no such periodicity exists. X-ray dif­
fraction studies by Warren (6-9) were consistent with this
model. Warren (10) criticized the crystallite theory of
Randall et al. (11) which proposed that glasses were really
formed from aggregates of very small crystals of the same type
formed in chemical compounds of the glass constituents. This
theory was based on x-ray studies of vitreous SiO\textsubscript{2} in which
Randall found peaks which corresponded to peaks in the mineral cristobalite. He calculated the crystallite size to be of the order $10^{-6}$ to $10^{-7}$ cm in SiO$_2$. This is of the same order of magnitude as the unit cell of cristobalite and it was on this basis that Warren criticized the "crystallite" theory, since crystallinity implies a regular repetition in a volume certainly larger than a unit cell.

The random network theory of Zachariasen as supported by Warren's x-ray data was widely accepted and applied to nearly all glass systems subsequently studied (12), even though the theory was based on studies of a very limited class of glasses and a restricted range of glass-forming in these systems. Weyl and Marboe (12) claim that had the x-ray work started with a TeO$_2$ glass or a TiO$_2$ - Ta$_2$O$_5$ glass which contained TeO$_6$, TiO$_6$ or TaO$_6$ octahedra as the structural units the theory of the structure of glasses would have taken a much different course, since tetrahedra of the SiO$_4$ type would not have been thought necessary for all glass structures.

Urnes (13) has described several criticisms of Warren's work, especially by Valenkov and Porai-Koshits (14) who proposed what they also called a crystallite theory of glass. Urnes considers this an unfortunate choice for a name and calls it, instead, the modern crystallite theory to distinguish it from that of Randall. This new crystallite theory essentially says that in glasses the ions will occur in groups of various size and that the order within the groups will be
high compared to the average order in the glass, so that these groups can be considered to be small distorted crystals separated by zones of less order. This idea does not require a continuous glass structure but rather implies heterogeneity on a microscopic scale, with no sharp boundary between the glassy and the crystalline states.

Thus there has grown up and still exists a considerable controversy in the literature concerning the basic nature of glass. Even the structure of pure vitreous silica is not yet completely determined (15, 16), and this substance is uncomplicated as glasses go. The facts seem to point to the conclusion, however, that while many industrial advances in glass technology have been made (17) from purely empirical cut-and-try methods, the present picture of glass structure at the atomic level is only now slowly beginning to emerge. This is because more powerful physical methods are being used to study glass systems.

In the past, most glass studies have been concerned with bulk properties (17) such as viscosity, density, specific heat, thermal conductivity and expansion, hardness, strength, optical transmission, and electrical conductivity and dielectric properties. The newer physical methods which can be used to probe the basic structures of glasses are x-ray (12, 13) and neutron (13, 18, 19) diffraction, infrared (12, 20) and optical (21) spectroscopy, electron microscopy (22, 23), Mössbauer effect (24, 25), nuclear (26) and electron
paramagnetic resonance. No one of these methods tells the whole story or even a large part of it. Whereas, for example, x-ray analysis will usually completely determine the structure of a single crystal, only very broad, hard to interpret, spectra result when this method is used on glasses. The most fruitful approach, then, is to study a glass system with as many different techniques as can be applied, and attempt to infer glass structure from results of many workers.

Many ESR studies have been done on radiation damage in glasses (27), but relatively little has been done by way of substituting magnetic impurity ions in a glass and studying their resonances. In fact, about a dozen papers (28 - 41) constitute the entire literature on the subject.

The first ESR study of transition metal ions in glasses was done by Sands (28), who studied some 34 soda-lime-silica base glasses. Almost all of his samples had resonances which he could not explain at $g = 6.0$ and $g = 4.2$. This $g$ is a number which is useful for describing energy level splittings and will be defined precisely later. Then Castner, Newell, Holton and Slichter (29) assumed crystal field effects to be dominant in their study of iron in a soda-lime-silica glass and used the orthorhombic spin Hamiltonian

$$ H_0 = E(S_x^2 - S_y^2) $$

(1)

to obtain an isotropic $g$ value of 4.28. Thus, they explained Sand's resonances as being due to Fe$^{3+}$ as an impurity. Tucker
(32) used Fe$^{2+}$, Fe$^{3+}$ and Mn$^{2+}$ in soda-silica glasses and pro-
pose that the Mn$^{2+}$ resonances came from the Mn$^{2+}$ ion being
situated in two different types of sites. Garif'yanov et al.
(31, 33, 34) studied Cr$^{3+}$, Cr$^{5+}$, Mn$^{2+}$ and Gd$^{3+}$ in various
glasses but the papers are not at all clear as to just what
the composition of the samples was, or what the results were.
Chepeleva, Lazukin and Dembovskii (37) put gadolinium in a
Tl$_2$SeAs$_2$Se$_3$ chalcogenide glass and found prominent spectral
features at $g$=2, 2.7 and 5.9 but offered no theoretical ex-
planation other than that each resonance was caused by a
strong crystal field in three different sites.

Wickman, Klein and Shirley (42) extended the ideas of
Castner et al. (29) and used the strong crystal field Hamil-
tonian

$$\mathcal{H}_0 = D(S_z^2 - \frac{1}{3} S(S+1)) + E (S_x^2 - S_y^2)$$

(2)
to calculate all the possible $g$ values for $S = 5/2$ and applied
their theory to polycrystalline ferrichrome A. They also
pointed out several very useful properties of Equation 2.
More recently, investigations have been done on Cr$^{3+}$ ions in
phosphate glasses (36, 39), and Mn$^{2+}$ in borate glasses (40,
41). Griscom, Bray and Griscom (41) studied Mn$^{2+}$ in both
glasses and crystalline compounds of the lithium borate system
and concluded that the manganese sites in the glasses were
probably randomly distorted versions of the site in the
Li$_2$O·4B$_2$O$_3$ compound. They relied on the analysis of Wickman
et al. (42) but did not restrict the crystal field strength relative to the Zeeman energy of the ion. This allowed them to compute all possible g values for the principal directions of Equation 2, and they presented their computations in a form that is extremely useful for fitting data.

The purpose of the present study is to investigate the ESR spectra of the Gd$^{3+}$ ion in the soda-silica glass system. This is accomplished at several frequencies and temperatures and over a wide range of composition in the soda-silica system and the soda-silica-yttria system. The spectra are interpreted with the aid of a spin Hamiltonian analysis which both modifies and extends to $S = 7/2$ some aspects of the work of Wickman, Klein and Shirley (42), and of Griscom, Bray and Griscom (41). The analytical results are presented in a form which allows them to be used in interpreting other $S = 7/2$ spectra, including nuclear magnetic resonance studies with a quadrupole interaction.
II. THEORY

A. The Resonance Phenomenon

The basic requirement for an electron spin resonance experiment is that the sample to be studied must contain unpaired electron spins. Many substances such as organic free radicals, impurity doped semiconductors, radiation damaged solids and diamagnetic solids containing small amounts of transition series ions contain unpaired electrons. In particular, most of the theory of paramagnetic resonance in solids was developed from studies of iron and rare earth group ions which were substituted for 0.01% to 1.0% (43, 44) of the metal ions in diamagnetic salts. This low concentration of paramagnetic ions allowed them to be treated as non-interacting (with each other) and hence they became probes with which to study the local electric fields produced by the non-magnetic surroundings.

The energy of a magnetic moment \( \mu \) in a magnetic field \( \mathbb{H} \) is

\[
e = -\mu \cdot \mathbb{H}.
\]  

We also have that (45) the magnetic moment of an ion is proportional to its total angular momentum so that \( \mu \propto h \mathbb{J} \) or

\[
\mu = -g\mathbb{J} = \gamma h \mathbb{J} = g \left( \frac{e \hbar}{2mc} \right) \mathbb{J}
\]  

(4)
where $\beta$ is the Bohr magneton. Thus the Zeeman Hamiltonian for a free ion can be written as

$$\mathbf{H}_z = g\beta H_z \mathbf{J} \cdot \mathbf{J}$$  \hspace{1cm} (5)$$

If, for example, we let $H = H_z \mathbf{J}$ and use the angular momentum wave functions $|J, m\rangle$, then

$$\mathbf{H}_z |J, m\rangle = g\beta H_z J_z |J, m\rangle$$

$$= g\beta H_z m |J, m\rangle$$  \hspace{1cm} (6)$$

and

$$\varepsilon_m = \langle J, m | \mathbf{H}_z | J, m \rangle = g\beta H_z m$$  \hspace{1cm} (7)$$

are the electronic Zeeman energy levels for the free ion. Now suppose for simplicity that $J = 1/2$. We then have two energy levels $\varepsilon_{1/2}$ with the energy separation

$$\Delta \varepsilon = \varepsilon_{1/2} - \varepsilon_{-1/2} = g\beta H_z$$  \hspace{1cm} (8)$$

The ion can be caused to undergo a transition from the state $\varepsilon_{-1/2}$ to the state $\varepsilon_{1/2}$ by exposing it to electromagnetic radiation of frequency $\nu$. Then we have

$$\hbar \nu = \Delta \varepsilon = g\beta H_z$$  \hspace{1cm} (9)$$

This is the basic resonance relation and shows that the field and frequency are proportional. It is customary to define

$$\hbar \nu = g_{\text{eff}} \beta H_z$$  \hspace{1cm} (10)$$
where $g_{\text{eff}}$ is the effective $g$ value and can be used to describe any resonance, whether or not the magnetic ion is a free ion or is incorporated into a solid. In the free ion case $g_{\text{eff}} = g_L$, the Landé $g$, but in a solid, $g_{\text{eff}}$ has no simple origin because of the complex interactions between the paramagnetic ion and its surroundings.

Electron spin resonance is useful for studying the lowest energy levels of an ion, and it turns out that the splittings of these levels correspond to frequencies in the microwave region ($10^9$ to $10^{11}$ Hz) so that on the frequency scale the region is above nuclear magnetic resonance and below infrared spectroscopy. In principle, the experiment could be performed by either varying the frequency of the radiation while holding the field at a fixed value, or by holding the frequency fixed while sweeping the field. The latter method is almost always used because microwave oscillators usually can be swept over only about 10% of their average frequency, and their power output varies with frequency.

The resonance signal contains components in-phase and out-of-phase with the incident radiation so that a complex susceptibility can usefully be defined such that $\chi = \chi' - i\chi''$. The dispersion component $\chi'$ is in-phase and the absorption component $\chi''$ is out-of-phase. The experimental apparatus can be adjusted to detect either component.

By introducing phenomenologically the exponential decay time constants $T_1$ and $T_2$ for the magnetization parallel and
perpendicular to the applied field, Bloch (46) was able to
derive expressions for the magnetization as a function of fre­
quency. Pake (45, p. 29) relates these expressions to $\chi'$ and $\chi''$ and the results are:

$$
\chi' = \frac{1}{2} \chi_0 \omega_0 T_2 \frac{T_2(\omega_0 - \omega)}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} 
$$

$$
\chi'' = \frac{1}{2} \chi_0 \omega_0 T_2 \frac{1}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} 
$$

where $\chi_0$ is the static Curie susceptibility. Usually the term
in $H_1^2$ in the denominator is taken to be small compared to the
other terms and if we define $a = \frac{1}{2} \chi_0 \omega_0 T_2$ and $x = T_2(\omega_0 - \omega)$ then

$$
\chi' = \frac{ax}{1 + x^2} 
$$

and

$$
\chi'' = \frac{a}{1 + x^2} 
$$

The absorption $\chi''$ thus corresponds to a Lorentzian line shape
and is a good approximation for many resonances. It also pro­
vides a basis for qualitative discussion of resonances in
general. The first derivative of $\chi''$ is what is usually gotten
from the experiment and this is illustrated along with $\chi'$ and
$\chi''$ in Figure 1.
Figure 1. The dispersion (top), absorption (center) and absorption derivative (bottom). The absorption corresponds to a Lorentzian line shape and the absorption derivative is what is usually obtained from the experiment.
\[ a = \frac{1}{2} x_0 \omega_0 T_2 \]

\[ x = T_2 (\omega_0 - \omega) \]

\[ x' = \frac{a x}{1 + x^2} \]

\[ x'' = \frac{a}{1 + x^2} \]

\[ \frac{d x''}{d x} = -\frac{2a x}{(1 + x^2)^2} \]
B. Spin Hamiltonians

The energy of a paramagnetic ion in a solid is a complicated function of the coordinates and spins of the unpaired electrons in the ion and of the coordinates and charges of the surrounding ions which produce the crystal field. In this section, the derivation of the so-called spin Hamiltonian will be sketched, and some of the physical arguments for applying it to S-state ions will be outlined.

The development of the spin Hamiltonian idea for paramagnetic ions is due mainly to Abragam and Pryce (47, 48). Neglecting interactions with the nuclear moment, the Hamiltonian for an ion in a solid is given by

\[ H = H_F + V + H_{LS} + H_{SS} + H_H \]  \hspace{1cm} (15)

where

\[ H_F = \sum_i \left( \frac{p_i^2}{2m} - \frac{ez}{r_i} \right) + \sum_{j<k} \frac{e^2}{r_{jk}} \]  \hspace{1cm} (16)

is the energy of the free ion due to the configuration of the electrons and gives levels split by about \( 10^5 \text{cm}^{-1} \).

\[ V = \sum_{\mathbf{n}} V(x_n, y_n, z_n) \]  \hspace{1cm} (17)

is due to the crystal field and is of the order \( 10^4 \text{cm}^{-1} \) in the iron series and \( 10^5 \text{cm}^{-1} \) in the rare earth series.

\[ H_{LS} = \lambda \mathbf{L} \cdot \mathbf{S} \]  \hspace{1cm} (18)
is the spin-orbit Hamiltonian and is of the order $10^2$ to $10^3 \text{cm}^{-1}$.

$$
\kappa_{\text{SS}} \propto \left[ (\mathbf{L} \cdot \mathbf{S})^2 + \frac{1}{3} (\mathbf{L} \cdot \mathbf{S}) - \frac{1}{3} \mathbf{L}(\mathbf{L}+1)\mathbf{S}(\mathbf{S}+1) \right]
$$

(19)

and represents the spin-spin interaction within the ion and
is of the order $1 \text{ cm}^{-1}$.

$$
\kappa_{\text{HF}} = \sum \frac{\hbar}{2mc} \left( \mathbf{l}_i \cdot \mathbf{S}_i \right) \cdot \mathbf{H} = \beta (\mathbf{L}+2\mathbf{S}) \cdot \mathbf{H}
$$

(20)

is the interaction energy due to the external magnetic field
and is of the order $1 \text{ cm}^{-1}$. The most general Hamiltonian
would also include a hyperfine term to describe the inter­
action between the unpaired electrons and the nuclear magnetic
moment.

Next, the eigenvalue problem for $\kappa_{\text{HF}} + V$ is considered as
solved, Pryce (47), with the eigenvalues $E_0$, $\cdots$, $E_n$, $\cdots$ and
the eigenstates $|\psi_0>$, $\cdots$, $|\psi_n>$, $\cdots$. This constitutes the un­
perturbed Hamiltonian which determines the basis functions,
and contains no spin operators. The perturbation is now taken
as

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

(21)

and the new eigenvalue equation to be solved is

$$
\kappa'|\psi> = E|\psi>
$$

(22)

where

$$
\kappa = \kappa^0 + \kappa'
$$

(23)
and

$$|> = |o> + \sum_{n \neq 0} |n>$$ \hspace{1cm} (24)

Pryce (47) then obtains a new Hamiltonian $\mathcal{H}_s$ which operates only on the lowest orbital level $|o>$ of the unperturbed case, and which is given by

$$\mathcal{H}_s = E_o + P_o K^i P_o - \sum_{n \neq 0} \frac{P_o K^i P_n K^i P_o}{(E_n - E_o)} \hspace{1cm} (25)$$

In this equation $P_i$ is the projection operator for the state $|i>$. Thus, for $K^i$ as given by Equation 21

$$\mathcal{H}_s = E_o + 2\beta S \cdot S - \sum_{n \neq 0} \frac{<o|L_i|n><n|L_i|o>}{(E_n - E_o)} (\lambda S_j + \beta H_j) (\lambda S_i + \beta H_i) \hspace{1cm} (26)$$

Define

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{<o|L_i|n><n|L_j|o>}{(E_n - E_o)} \hspace{1cm} (27)$$

and rearrange Equation 26 to get

$$\mathcal{H}_s = E_o + 2\beta (\delta_{ij} - \Lambda_{ij}) S_i H_j - \lambda^2 \Lambda_{ij} S_i S_j - \beta^2 \Lambda_{ij} H_i H_j \hspace{1cm} (28)$$

The last term, which is spin independent, and $E_o$, which is constant, may be omitted, since they give rise to a constant shift of all the energy levels. This yields the desired spin Hamiltonian. Let

$$g_{ij} = 2(\delta_{ij} - \Lambda_{ij}) \hspace{1cm} (29)$$
be the g tensor, and

\[ D_{ij} = -\lambda^2 \Lambda_{ij} \]  

(30)

to get

\[ k_s = 2H_i g_i S_j + S_i D_{ij} S_j. \]  

(31)

The spin-spin interaction \(k_{ss}\) was not specifically included in the derivation, but its inclusion merely gives rise to terms which can be lumped into \(g_{ij}\) and \(D_{ij}\). This spin Hamiltonian operates entirely within the manifold spanned by \(|o>\) and the eigenvalues are appropriate to the energy variations from the lowest level of the paramagnetic ion. The effects of higher levels have been lumped into the tensors \(g_{ij}\) and \(D_{ij}\). It is customary to write

\[ k_s = \beta H \cdot g \cdot S + D(S_z^2 - \frac{1}{3}S(S+1)) + E(S_x^2 - S_y^2) \]  

(32)

which assumes the principal axis system of \(\Lambda_{ij}\). Any anisotropy of the moment (failure to line up with \(H\)) is described by the g tensor. Axial crystal fields due to trigonal or tetragonal symmetry are represented by the D term and the lower symmetry orthorhombic crystal fields are given by the E term.

This spin Hamiltonian is the most general one of second degree in the spin variables, and although the original derivation had in mind the iron group ions, the same Hamiltonian, together with higher order terms and a somewhat different
physical basis in detail, has been given for other ions as well (43, 49), and so will be adopted as the starting point for discussion of gadolinium ion resonances. There has been much discussion in the literature concerning S-state ions. Specifically, these ions are:

- Mn$^{2+}$ and Fe$^{3+}$ with the 3d$^5$ configuration and the term $^6S_{5/2}$;
- Gd$^{3+}$ and Eu$^{2+}$ with the 4f$^7$ configuration and the term $^8S_{7/2}$;
- Cm$^{3+}$ in the 5f$^7$ configuration and the term $^8S_{7/2}$.

In early resonance work it was noticed that the Mn$^{2+}$ ion gave spectra which showed energy level splittings even though there is no orbital angular momentum and one should have $\Lambda_{ij} = 0$. Other S-state ions showed similar splittings and the question arose: how are the levels split by a crystal field or spin-orbit mechanism? Abragam and Pryce (48) proposed that the combined action of the crystal field term and the spin-spin interaction could give rise to a second order term proportional to $S_z^2 - \frac{1}{3}S(S+1)$ by considering the crystal field to produce a small ellipsoidal distortion of the normally spherically symmetric electronic charge density. The energy of the electronic spins would then depend on their orientation with respect to the symmetry axis. Van Vleck and Penney (50) proposed that the combined effect of the crystal field and the spin-orbit interaction within the ion could give rise to a fifth-order process. Elliott and Stevens (51) attributed the effect to a breakdown of Russell-Saunders coupling within the
f^7 configuration, while Pryce (52) thought that a spin-spin interaction between \( ^8S_{7/2} \) and another eight level state in a higher configuration might work. H. Wanatabe (53) outdid everyone and considered combinations of crystal field, spin-orbit and spin-spin mechanisms and came up with 12 fourth or higher order processes by which the \( ^6S_{5/2} \) ground state could be split. Lacroix (54) and Hutchison, et al. (55) also proposed ways to split the levels in an S-state ion. Wickman (56) studied several ions but could shed little or no light on the problem.

Despite the lack of a firm physical basis for doing so, the Hamiltonian given by Equation 32 has been used with notable success to fit resonance spectra (29, 41, 43), although for single crystal work with the gadolinium ion terms of the fourth and sixth power in spin variables have had to be added. For the rest of this dissertation, the discussion will be focused on the form of the spin Hamiltonian

\[
\mathcal{H}_S = g_0 \mathbf{H} \cdot \mathbf{S} + D(S_z^2 - \frac{1}{3}S(S+1)) + E(S_x^2 - S_y^2) \quad (33)
\]

where the g tensor of the (S-state) ion has been taken to be isotropic and equal to \( g_0(2,00) \), as in the free ion.

The crystal field part of this Hamiltonian is mathematically the same as the quadrupole Hamiltonian of nuclear magnetic resonance given by Slichter (57), with

\[
D = \frac{e^2 Q q}{12I(2I-1)} \quad (34)
\]
where \( I \) is the nuclear spin, \( Q \) is the quadrupole moment of the nucleus, \( q \) is the field gradient, and \( \eta \) is the asymmetry parameter.

\( \eta \) and \( q \) are related to the derivatives of the electric potential at the nucleus by

\[
\eta = \frac{\partial^2 V}{\partial z^2} - \frac{\partial^2 V}{\partial x^2}
\]

C. The Strong Crystal Field Case

Equation 33 can usefully be treated by perturbation theory in two extreme cases: (1) the strong Zeeman case where \( g_0^2 H \gg D, E \) and (2) the strong crystalline electric field case (CEF) where \( D, E \gg g_0^2 H \). The latter case will now be considered.

Consider the quadratic expression in the spin variables

\[
\mathcal{K}_0 = AS_x^2 + BS_y^2 + CS_z^2
\]

with \( A + B + C = 0 \). A coordinate system may be chosen \((42)\) such that \(|C| \geq |A|, |B| \) and \( A \geq B \). Now the Hamiltonian

\[
\mathcal{K}_0 = D(S_z^2 - \frac{1}{3}S(S+1)) + E(S_x^2 - S_y^2)
\]
is of this form and we have $E = \frac{A-B}{2}$ and $D = \frac{B}{2}$. Then

$$|\lambda| = \left|\frac{E}{D}\right| = \frac{|A-B|}{3|C|} \leq 1/3$$

(38)

and also, $E>0$ since $A>B$. Thus the sign of $\lambda$ is the same as the sign of $D$. By putting $\kappa_0$ in units of $D$, we need to consider only the one parameter operator

$$\kappa_0 = S_z^2 - \frac{1}{3}S(S+1) + \lambda(S_x^2 - S_y^2)$$

(39)

with $0<\lambda<1/3$ to cover all the physically distinct possibilities. Changing the sign of $\lambda$ only inverts the order of the resulting energy levels.

Castner et al. (29) showed that the energy levels occur in pairs and for the case of gadolinium with $S = 7/2$ we have four doubly degenerate energy levels. The application of the Zeeman term as a perturbation removes the degeneracies. Transitions can then be observed between these split levels. Figure 2 illustrates this situation.

It is convenient to choose as the basis set for the unperturbed problem the angular momentum wave functions $|S, m\rangle$, which have the properties

$$S_z |S, m\rangle = m |S, m\rangle$$

(40)

and

$$S^2 |S, m\rangle = S(S+1) |S, m\rangle$$

(41)

The raising and lowering operators $S_+ = S_x + iS_y$ and $S_- = S_x - iS_y$
Figure 2. The energy level diagram for Equation 33 under the assumption that the Zeeman term << crystal field term. The gadolinium ion has $S = \frac{7}{2}$ and so the free ion has an eightfold spin degeneracy. The strong crystal field splits the free ion level into 4 doubly degenerate levels and then the Zeeman field, treated as a perturbation, removes the remaining degeneracy.
FREE ION

$\epsilon_1, \psi_1^\pm$

$\epsilon_2, \psi_2^\pm$

$\epsilon_3, \psi_3^\pm$

$\epsilon_4, \psi_4^\pm$

+ STRONG CRYSTAL FIELD

$\nu = g\beta H$

+ ZEEMAN FIELD
have the useful properties

\[
S_+ |S,m> = \sqrt{S(S+1)-m(m+1)} |S,m+1>
\]

and

\[
S_- |S,m> = \sqrt{S(S+1)-m(m-1)} |S,m-1>.
\]

Now equation (39) can be rewritten as

\[
x_0 = S_x^2 - \frac{1}{3}S(S+1) + \frac{\lambda}{2}(S_+^2 + S_-^2)
\]

to make the matrix elements easy to calculate. The resulting 8 x 8 matrix can be factored into two 4 x 4 matrices with identical elements, one matrix having the basis set |7/2>, |3/2>, |-1/2>, |-5/2> and the other having the basis set |-7/2>, |-3/2>, |1/2>, |5/2>. (The wave functions will be written as |m> now since the S in |S,m> is always 7/2). The first matrix is

\[
\begin{array}{cccc}
|7/2> & |3/2> & |-1/2> & |-5/2> \\
|7/2> & 7 & \lambda \sqrt{21} & 0 & 0 \\
|3/2> & \lambda \sqrt{21} & -3 & 2\lambda \sqrt{15} & 0 \\
|-1/2> & 0 & 2\lambda \sqrt{15} & -5 & 3\lambda \sqrt{5} \\
|-5/2> & 0 & 0 & 3\lambda \sqrt{5} & 1 \\
\end{array}
\]

When the matrices are diagonalized the resulting energy eigenvalues and normalized eigenvectors are

\[
e_i, v_i = a_i |\pm 7/2> + b_i |\pm 3/2> + c_i |\mp 1/2> + d_i |\mp 5/2>.
\]

\[(i = 1, 2, 3, 4)\]
Each set of doubly degenerate levels can be split now by applying the Zeeman perturbation

\[ \mathcal{K}_z = \mathcal{K}_{z\perp} + \mathcal{K}_{z\parallel} \]

\[ = g_o \beta (H_x S_x + H_y S_y) + g_o \beta S_z H_z. \quad (46) \]

The parallel and perpendicular parts can most easily be treated separately. For the parallel case, the secular equation is

\[
\begin{pmatrix}
\psi^+ \\
\psi^-
\end{pmatrix} = \begin{pmatrix}
\varepsilon_1 + \delta - \varepsilon & 0 \\
0 & \varepsilon_1 - \delta - \varepsilon
\end{pmatrix}
\begin{pmatrix}
\psi^+ \\
\psi^-
\end{pmatrix} = 0
\tag{47}
\]

where

\[ \delta = \langle \psi^+_1 | g_o \beta H_z S_z | \psi^+_1 \rangle \]

\[ = \frac{1}{2} g_o \beta H_z [7a_1^2 + 3b_1^2 - c_1^2 - 5d_1^2] . \quad (48) \]

Then

\[ \Delta \varepsilon = (\varepsilon_1 + \delta) - (\varepsilon_1 - \delta) = 2\delta = \frac{1}{g_z} g_o \beta H_z \]

and so the effective g value for the perturbation applied parallel to the axis of quantization is

\[ g_z^1 = g_o [7a_1^2 + 3b_1^2 - c_1^2 - 5d_1^2] . \quad (50) \]

Now write
\[ \kappa_{z\perp} = g_o \beta (H_x S_x + H_y S_y) \]
\[ = \frac{1}{2} g_o \beta \left[ S_+ (H_x - i H_y) + S_- (H_x + i H_y) \right] \]
\[ = \frac{1}{2} g_o \beta \left[ S_+ + S_- \right] . \]  

Then for the perpendicular case the secular equation is

\[
\begin{array}{c|cc}
\psi_1^+ & \psi_1^- \\
\psi_1^+ & \epsilon_1 - \epsilon & (AH_- + BH_+) \\
\psi_1^- & (BH_- + AH_+) & \epsilon_1 - \epsilon \\
\end{array}
\]
\[ = 0 \]  

(52)

where

\[ <\psi_1^+ | \kappa_{z\perp} | \psi_1^-> = AH_- + BH_+ \]
\[ = g_o \beta \left[ H_- (\sqrt{7a_1 d_1} + \sqrt{15b_1 c_1}) + H_+ (\sqrt{12b_1 d_1} + 2c_1^2) \right] . \]  

(53)

The new energy levels are

\[ \epsilon = \epsilon_1 \pm \sqrt{AB (H_{-}^2 + H_{+}^2) + (A^2 + B^2) H_{+} H_{-}} \]
\[ = \epsilon_1 \pm \sqrt{H_{x}^2 (A+B)^2 + H_{y}^2 (A-B)^2} \]  

(54)

so

\[ \Delta \epsilon_x = g_x^i \beta H_x = 2H_x |A+B| \]  

(55)

\[ \Delta \epsilon_y = g_y^i \beta H_y = 2H_y |A-B| \]  

(56)

and

\[ g_x^i = 2g_o |a_1 d_1\sqrt{7} + b_1 c_1\sqrt{15} + 2\sqrt{3} b_1 d_1 + 2c_1^2| \]  

(57)
\[ g_y = 2g_0 |a_i d_i \sqrt{7} + b_i c_i \sqrt{15} - 2 \sqrt{3} b_i d_i - 2c_i |. \] (58)

Equations 50, 57 and 58 are functions of \( \lambda \) through the \( a_i, b_i, c_i \) and \( d_i \) and allow the calculation of all possible \( g \) values in the \( x, y, \) and \( z \) directions for all four energy levels and for all physically distinct values of \( \lambda \). The results of this calculation, for \( 0 \leq \lambda \leq 1/3 \), are given in Chapter IV.

D. The Exact Calculation

As pointed out by Griscom et al. (41), the study of glasses by electron spin resonance presents special problems. When a single crystal of the substance to be studied is available, the orientation of the crystal with respect to the external magnetic field may easily be varied, and the angular variation of Equation 33 may easily be mapped out, and fit to the formulas given by Low (49, p. 57). When the sample is polycrystalline the surroundings of each paramagnetic ion have a particular configuration and symmetry, but these surroundings (crystallites) are randomly oriented throughout the sample, so that the features of the resonance spectra are less well defined and do not depend on the sample orientation. The study of ESR powder patterns is fairly well developed and is surveyed by Swalen and Gladney (58). In a glass the paramagnetic ions and their surroundings are randomly oriented, as in a powder or polycrystalline substance, and in addition the ion
surroundings vary. That is, in a polycrystalline sample, the magnetic ions of a given type each see the same crystal field, but in a glass the ions of a given type see a distribution of crystal fields. Thus, in a glass, resonance features must be sought that are stationary with respect to crystal field strength as well as angle.

Consider the Hamiltonian given by Equation 32. This operator defines three principal axes, and as it stands, the z axis is the axis of quantization. Consider a sphere of unit radius, with its polar axis assigned to be the z axis. Let the angle 0 measure directions away from this polar axis. In a sample of N paramagnetic ions, the number dN of ions with their preferred (z) axes pointing in a direction somewhere in 0 to 0+d0 on the unit sphere can be found as follows. The dN ions all have their z axes lying within an annular ring on the sphere and the area of the ring is (2πSin0)d0 = circumference x width. Then we have

\[
\frac{\text{Area of ring}}{\text{Area of sphere}} = \frac{dN}{N} = \frac{2\pi \text{Sin} \theta d\theta}{4\pi}.
\]

(59)

So the distribution sought is

\[
dN = \frac{1}{2} N \text{Sin} \theta d\theta
\]

(60)

and this is largest when 0 = π/2. For a magnetic field along the polar axis, the greatest number of ions have their z axes lying in the plane perpendicular to the field and the
resonance spectrum should show a peak at this value of $\theta$. But this can also be done for the $y$ and the $x$ directions and so by taking the external field $H$ first in the $z$ direction, then in the $x$ and $y$ directions, major features of the spectra will be predicted, provided any exist. This does not produce all the major features since when $E \neq 0$ there can be peaks in the spectrum at angles other than $\pi/2$, as shown by Narita et al. (59), but features predicted in the $x$, $y$ and $z$ directions should be present in the spectra. For $H = H_z^k$ we have

$$k_z = \left[ g_0^2 E_z S_z - \frac{1}{3} D S (S+1) + D S_z^2 \right] + \frac{1}{2} E (S_z^2 + S_z^2).$$

Now put $x \rightarrow z$ (rotate about $y$) in Equation 61 to get, after simplification and rearrangement,

$$k_x = \left[ g_0^2 E_z S_z - \frac{1}{3} D S (S+1) + E S_z^2 + \frac{1}{4} (D-E)(S_z S_z + S_z S_z) \right]$$

$$+ \frac{1}{4} (D+E)(S_z^2 + S_z^2).$$

Also, put $y \rightarrow z$ (rotate about $x$) in Equation 61 to get

$$k_y = \left[ g_0^2 E_z S_z - \frac{1}{3} D S (S+1) - E S_z^2 + \frac{1}{4} (D+E)(S_z S_z + S_z S_z) \right]$$

$$- \frac{1}{4} (D-E)(S_z^2 + S_z^2).$$

The advantage in performing these transformations is that now all three directions can be treated exactly using only real matrix elements. The terms in brackets give diagonal elements only and the remaining term gives only second off-diagonal elements. The general form of the matrices is thus
\[
\begin{array}{c|cccccccc}
|7/2> & |5/2> & |3/2> & |1/2> & |-1/2> & |-3/2> & |-5/2> & |-7/2> \\
|7/2> & \frac{7}{2}d & R\sqrt{21} & & & & & \\
|5/2> & \frac{5}{2}d & 3R\sqrt{5} & & & & & \\
|3/2> & R\sqrt{21} & \frac{3}{2}d & 2R\sqrt{15} & & & & \\
|1/2> & 3R\sqrt{5} & \frac{1}{2}d & 2R\sqrt{15} & & & & \\
|-1/2> & 2R\sqrt{15} & \frac{1}{2}d & 3R\sqrt{5} & & & & \\
|-3/2> & 2R\sqrt{15} & \frac{3}{2}d & R\sqrt{21} & & & & \\
|-5/2> & 3R\sqrt{5} & \frac{5}{2}d & & & & & \\
|-7/2> & R\sqrt{21} & \frac{7}{2}d & & & & & \\
\end{array}
\]

where

\[md = g_0 S M + \frac{1}{2}D \left( \frac{21}{4} - m^2 \right) + \frac{1}{2}E \left( 3m^2 - \frac{63}{4} \right) \]  

\[R = \frac{1}{2}(D+E) \]  

\[md = g_0 S M + \frac{1}{2}D \left( \frac{21}{4} - m^2 \right) - \frac{1}{2}E \left( 3m^2 - \frac{63}{4} \right) \]  

\[R = -\frac{1}{2}(D-E) \]  

\[md = g_0 S M - D \left( \frac{21}{4} - m^2 \right) \]  

\[R = E \]  

(64)  

(65)  

(66)

The solutions of these three matrices yield eigenvalues which are functions of the external field \(H\) and the crystal field parameters \(D\) and \(E\). Again, as in part C of this chapter, only the parameter \(\lambda = E/D\) need be considered and only in the range
$0 \leq \lambda \leq 1/3$, together with relative values of $H$ and $D$ or $E$. It is convenient to put the equations in dimensions of $\lambda H$ since then calculations can be done for a fixed value of $\lambda$ while the ratio $D/\lambda H$ is varied from 0 (pure Zeeman case) to about 10 (strong crystal field case). The strong crystal field case is thus included in this calculation, but not in nearly as convenient a form as in part C. In fact, this calculation does the problem exactly for the x, y and z directions as well as for the two perturbation theory extremes and every crystal field value in between. The calculations can then be displayed on graphs of $\frac{E_0 \lambda H}{\hbar \nu} = \frac{E_0}{g}$ versus $\frac{D/\lambda H}{\hbar \nu} = \frac{D}{\hbar \nu}$ for a fixed value of $\lambda$, and the values of $\lambda$ and $D$ necessary to fit the experimental data can then be determined.

E. Transition Probabilities

The relative intensities of two transitions depend on their respective transition probabilities. The transitions are caused by absorption of microwave power and this can be treated by adding to the Hamiltonian given by Equation 61 the perturbation

$$\mathcal{K}_1 = \mu \mathcal{H}_1(t) = \mathcal{K}_{12}^* \text{Cos} \omega t$$

$$= g_0 \delta (S_x I + S_y I + S_z K) \text{Cos} \omega t (\cos \beta_1 + \sin \beta_1). \quad (67)$$

The field

$$\mathcal{H}_1 = \hbar (\cos \beta_1 + \sin \beta_1) \text{Cos} \omega t = \hbar \text{Cos} \omega t \quad (68)$$

lies in the plane perpendicular to the Zeeman field $\mathcal{H} = H_k$. 
If the free ion spin had an anisotropic $g$ tensor associated with it then the correct form for $\mu$ would contain $g_x$, $g_y$ and $g_z$ (60) rather than the isotropic $g_0$ appropriate to an $S$-state ion. In any case, it would not be correct to use the $g$ values determined from Equations 61, 62, and 63, since these are only effective $g$ values and are merely another way to describe the energy level splittings.

Pake (45, p. 33) gives the formula

$$w_{mm'} = |\langle m'|\chi_l|m\rangle|^2 g(v)$$  \hspace{1cm} (69)

where $w_{mm'}$ is the probability per unit time that a paramagnet initially in the state $|m\rangle$ will be found in the state $|m'\rangle$ and $g(v)$ is the resonance line shape distribution with the property that

$$\int_{-\infty}^{\infty} g(v) dv = 1.$$ \hspace{1cm} (70)

The function $g(v)$ is often assumed to be a delta, Lorentzian or Gaussian function, but in what follows, it is not necessary to discuss $g(v)$. Instead, it is convenient to consider only

$$p_{mm'} = |\langle m'|\chi_l|m\rangle|^2$$ \hspace{1cm} (71)

in relative intensity comparisons. For any case except for $D = E = 0$, the crystal field terms of Equations 61, 62, and 63 cause mixing of the basis states $|m\rangle$. That is, the eight states spanned by $[|m\rangle]$ go over into eight linear combinations of the $|m\rangle$ states.
Let

\[ |a> = \sum_m a_m |m> \]

\[ |b> = \sum_m b_m |m> \]  \hspace{1cm} (72) \]

Then

\[ P_{ab} = |<a|K_1^ cornerstone |b>|^2 \]

\[ = \left( \frac{\hbar g_0 \beta}{2} \right)^2 \cos a <a|S_+ S_- |b> - i \sin a <a|S_+ - S_- |b> \]

\[ = \left( \frac{\hbar g_0 \beta h}{2} \right)^2 \left[ \cos^2 a <a|S_+ S_- |b> + \sin^2 a <a|S_+ - S_- |b> \right] \] .  \hspace{1cm} (73) \]

Now the axis of quantization is z and is in the same direction as the external \( \mathbb{H} \) field so that this is a reference direction, but even though the experimental arrangement is such that \( \mathbb{H}_\| \) is always perpendicular to \( \mathbb{H} \), the fact that all orientations of ions occur in the glass requires that \( \mathbb{H} \) be treated as confined to a plane rather than a single line perpendicular to \( \mathbb{H} \). The angle \( \alpha \) describes the orientation of \( \mathbb{H} \) in the x - y plane of the Hamiltonian principal axis system. Since all orientations are assumed to be equally likely, an average should be taken over \( \alpha \) and since the average value of \( \sin^2 \alpha \) and \( \cos^2 \alpha \) is 1/2 we get

\[ P = \left( \frac{\hbar g_0 \beta}{2} \right)^2 \left[ \frac{1}{2} <a|S_+ S_- |b>^2 + \frac{1}{2} <a|S_+ - S_- |b>^2 \right] \]

\[ = \left( \frac{\hbar g_0 \beta h}{2} \right)^2 \left[ <a|S_+ |b>^2 + <a|S_- |b>^2 \right] \] .  \hspace{1cm} (74) \]
Extensive computer calculations were made using this theory and the results are presented in Chapter IV.

Griscom et al. (41) have made this sort of calculation for $S = 5/2$ using a program written by Gladney (61). This particular program calculates the resonance positions in the manner in which they are experimentally determined, i.e., the frequency is held fixed and the resonance fields are calculated. However, to do this, an approximation technique involving Newton's method must be used together with iteration. This method is more useful for single crystal work. The program is lengthy and only works for $S \leq 5/2$.

The calculation method adopted in the present work is much shorter and simpler and involves no approximation techniques since the natural results of the matrix diagonalizations, namely the transition frequencies, are used directly and are converted by means of a simple division to give the same results as obtained by Griscom et al. (41).
III. EXPERIMENTAL DETAILS

A. Sample Preparation

The soda-silica system was chosen for study for several reasons. This system has only two components, forms glasses over a wide range of composition variation, and samples are relatively easy to make. Gd$_2$O$_3$ and Y$_2$O$_3$ were added in small amounts and can be considered to cause slight deviations from the basic soda-silica system. Two series of glasses were made, with the approximate molecular compositions

500SiO$_2$:xNa$_2$O:1Gd$_2$O$_3$ and 6SiO$_2$:5Na$_2$O:xGd$_2$O$_3$.

These series are shown in Figure 3, the ternary phase diagram for the soda-silica-gadolinium oxide system. The first series maintains a constant molar ratio between the silica and gadolinium oxide and the second series keeps a constant molar ratio between the soda and silica.

All the starting materials were obtained in powder form. Chromatographic grade silica gel powder from Baker was calcined at 1100°C for 10 hours to provide a source of pure silica. A spectrographic analysis showed less than 10 ppm iron in this silica, and any other impurities were present in even smaller concentrations. Na$_2$O was put in as Baker reagent grade Na$_2$CO$_3$. The Gd$_2$O$_3$ and Y$_2$O$_3$ were obtained at the Ames Laboratory, AEC, Ames, Iowa. Spectrographic analysis of the Gd$_2$O$_3$ revealed 900 ppm of europium, and smaller concentrations of several other impurities. Since the samples contained at
Figure 3. The sample compositions plotted on a ternary phase diagram. The grid lines are spaced 10 weight per cent apart. The glassy region boundary is given by the irregular and dashed line. A point at the SiO$_2$ apex is composed entirely of SiO$_2$. On the SiO$_2$--Na$_2$O baseline, a point at the first grid point away from the SiO$_2$ apex represents the composition 90% SiO$_2$--10% Na$_2$O. The relative distances of a point from the three apices represent the weight percentage contributions of the three constituents. Consider the sample point closest to the center of the diagram on the 6SiO$_2$:5Na$_2$O:xGd$_2$O$_3$ molar composition line. Construct a line through this point parallel to the SiO$_2$--Na$_2$O side of the diagram. This intersects the other two sides of the diagram at the divisions 20% from the SiO$_2$ and Na$_2$O apices and represents 20% Gd$_2$O$_3$. Similarly, lines constructed through this point parallel to the other two sides give 43% SiO$_2$ and 37% Na$_2$O. According to Table 1, this point then represents sample F7F.
most 0.20 mole per cent Gd₂O₃, the impurities were not bother-
some. The sample components were weighed to the nearest 0.1
mg and then mixed in a porcelain mortar, in 15 gram batches.

The samples containing 82% silica were placed in 40 ml
platinum dishes to avoid contamination and heated in an oxii-
dizing atmosphere in a silicon-carbide resistance furnace.
They were sintered at 825°C for 8 hours to allow CO₂ gas to
go off. Higher initial temperatures would cause bubbling and
loss of part of the glass sample due to the trapped CO₂. The
temperature was then raised to around 1400°C and held for 8
hours, after which the samples were air quenched to prevent
devitrification. Samples with high soda content are water
soluble to some extent, and so these were stored under CCl₄ to
prevent leaching. Due to the loss of CO₂ these samples suf-
fered weight losses of 0.3% to 1.50% and so the exact composi-
tion is not known. This weight loss would only be a problem
for relative intensity studies and the intensity work that was
done does not appear to have suffered (62).

The samples containing more than 82% silica were placed,
after mixing, in impervious alumina crucibles and heated in an
induction furnace which had been fitted with an alumina liner
to maintain an oxidizing atmosphere. The temperature was
raised to above 1750°C and held for one hour. The high tem-
perature was necessary to insure proper melting and mixing of

1Weight per cent unless otherwise specified.
the components. No intermediate heating stage was necessary for these samples because the soda content was too low to cause bubbling problems. A spectrographic analysis determined that no impurities were added by the alumina crucibles.

Again, the samples were rapidly quenched in air to prevent devitrification, and x-ray powder patterns established that all samples but one were glassy. The sample Y25Y, containing only 0.5% soda, solidified in two phases and one phase turned out to be crystalline while the other was glassy.

The samples were ground wet on silicon carbide paper and shaped into plates 11mm x 6mm x 1mm. Water soluble glasses were ground under absolute alcohol to prevent leaching.

Table 1 presents the composition of all the samples studied. The first preliminary samples studied contained 15% Gd₂O₃ and the resonance lines were several thousand gauss wide, very strong, and centered at g~2.0. As the amount of Gd₂O₃ was decreased, the character and intensity of the resonance lines began to change and 1% Gd₂O₃ was decided upon as an adequate amount to avoid dipolar broadening. Some samples with as little as 0.1% Gd₂O₃ were studied but the resonance character did not change noticeably and this small amount of Gd₂O₃ was very difficult to disperse in the other components when mixing the samples.

The F--F series composition requires some explanation. It was desired to study the effect of increasing the gadolinium ion concentration without causing the resonance line to
<table>
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<th>Na$_2$O</th>
<th>Gd$_2$O$_3$</th>
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<th>Na$_2$O</th>
<th>Gd$_2$O$_3$</th>
<th>Y$_2$O$_3$</th>
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*Y₂O₃ was substituted for Gd₂O₃ on a molecule to molecule basis for Gd₂O₃ concentrations greater than 1 weight %.*
broaden, so $Y_2O_3$ was substituted for $Gd_2O_3$ above 1% on a molar basis. Thus, for example, F7F would have the composition, by weight, 43% $SiO_2$, 37% $Na_2O$ and 20% $Gd_2O_3$. The conversion to molar per cent gives 52.36% $SiO_2$, 43.60% $Na_2O$ and 4.03% $Gd_2O_3$. But only 1% (by weight) is actually $Gd_2O_3$. This is 0.20 mole per cent. The remaining 3.83 mole per cent is $Y_2O_3$, which was substituted on a molecule for molecule basis for $Gd_2O_3$. Note that this does not mean that F7F contains 1% $Gd_2O_3$ and 19% $Y_2O_3$ by weight. As shown in Table 1, the gadolinium ion appears in concentrations of about 0.07 to 0.08 atomic per cent, so that this paramagnetic impurity is really quite dilute.

B. Double Bolometer Spectrometers

The most extensive set of resonance spectra were taken with an X-band (9.8 Ghz) double bolometer spectrometer using audio frequency field modulation. A K-band (24.0 Ghz) spectrometer was constructed using a design almost identical to that of the X-band and so only the X-band instrument will be described in detail.

The basic spectrometer is that of Feher (63), which utilizes optimum microwave bucking to keep the sensitivity constant regardless of the microwave power level. Figure 4 shows the microwave components. The microwave power source is a Laboratory for Electronics Model 814 Ultra-Stable Microwave Oscillator. This oscillator is tunable from 8.6 to 10.0 Ghz and is internally stabilized by means of a discriminator.
Block diagram of a double bolometer spectrometer. The microwave power is divided and half goes to the reference arm and half goes to the signal arm. The signal power is further split by the magic T, and half goes to the sample cavity while the other half is used for a sample power measurement. The slide screw tuner is adjusted so that far from resonance no power goes out the fourth arm of the magic T. During resonance, the sample absorbs power and unbalances the magic T so that a signal passes out the fourth arm of the T, mixes with the reference power in the balanced mixer, and is detected by the bolometers.
cavity arrangement. Directly outside this oscillator, some power is tapped off to allow the frequency to be measured, and then the power is split, half going to the signal arm and half to the reference (or microwave bucking) arm. The reference arm is used to provide rf bias power on the bolometers and contains a phase shifter and attenuator which are used to pick out the $\chi'$ or $\chi''$ component of the signal, as desired. The power in the signal arm is adjusted with attenuators and then goes to the magic T, the heart of any electron spin resonance spectrometer. The power splits, half going to the sample cavity and half to the terminated arm which contains a bolometer for measuring the power incident on the sample. The sample cavity iris and the slide screw tuner are adjusted so that these two arms of the T are balanced and no power gets out of the fourth arm of the T. This action is similar to balancing a Wheatstone bridge for a null voltage reading.

As the magnetic field is changed, and the resonance condition is reached, the sample absorbs microwave power and unbalances the T. This causes a signal to go out the fourth arm of the T and enter the balanced mixer, where some of the klystron noise is cancelled. The power change causes the resistance of the bolometers to change and the resulting voltage change is passed through the bolometer biasing circuit to the preamplifier, as shown in Figure 5. The amplified signal then passes to the lock-in amplifier and is then displayed on a strip chart recorder. The electronic equipment associated
Figure 5. The bolometer biasing circuit. The 6 v battery provides a d-c bias for the bolometers which changes their resistance from 140 to 200 ohms to balance the two bridge circuits. The power meter is used to adjust the reference arm power so that about 8 mw of rf power fall on the bolometers at all times, and the combination of d-c plus rf power biases the bolometers into their most sensitive range. The transformer allows the signal to pass from the bolometers to the preamplifier.
PREAMPLIFIER DIFFERENTIAL INPUT

S.I.E G16115
TRANSFORMER
9.5K

9.5K

28

25μf

25μf

25-0-25μa

100

200

200

200

BOLOMETER

2500

BOLOMETER

(NARDA 610)

POWER METER

6 VOLT

+
with the spectrometer is exhibited in Figure 6. The lock-in amplifier receives a 35 Hz reference signal from the audio oscillator, and part of this same signal is amplified and used to drive the magnetic field modulation coils. Thus the resonance is modulated at 35 Hz and also detected at 35 Hz. This lock-in detection greatly reduces the noise in the signal and also causes the first derivative of the absorption, rather than the resonance absorption, to be displayed. This too is an advantage, since the derivative is much more sensitive to details in the resonance than is the absorption. The scan unit controls the magnetic field sweep rate and range and also produces marker signals for the strip chart.

C. The Crystal Spectrometer

Figure 7 shows a very simple C-band (5.5 GHz) crystal spectrometer which was constructed in order to complete the frequency variation study for these samples. The microwave power is generated by a Raytheon 6115A Klystron operated unstabilized from a PRD Type 812 Universal Klystron Power Supply. The PRD filament supply was 6.3 V a-c, and was replaced by a 6 volt battery. This greatly reduced klystron noise at 60 Hz. The power level is adjusted with attenuators and sent to the magic T. Here it divides, half going to the sample and half to a terminated arm containing a slide screw tuner. The tuner is adjusted to give a null (no power out the fourth arm) and then is detuned slightly to bias the detector crystal in
Figure 6. Block diagram of the associated spectrometer electronics. The signal from the bolometers passes from the preamplifier to the lock-in amplifier, which has a reference channel driven at the same frequency as the field modulation. The detected signal is then displayed on a strip chart. The chart is marked by signals from the scan unit which controls the magnetic field scan rate and range.
CHART MARKER
SCAN UNIT I—
SIGNAL OUT
35 hz
REFERENCE
FROM KLYSTRON MODE DETECTOR CRYSTAL
SAWTOOTH WAVE FOR KLYSTRON MODULATION MODULATION TO KLYSTRON
BOLOMETER BIAS
TEKTRONIX TYPE 122 LOW-LEVEL PREAMPLIFIER
EMC MODEL RJB LOCK-IN AMPLIFIER
VARIAN G-10 GRAPHIC RECORDER
CHART MARKER SCAN UNIT
35 hz
REFERENCE
SELECTOR PANEL
35 hz
HP MODEL 20IC AUDIO OSCILLATOR
SCOPE
VARIAN G-10 GRAPHIC RECORDER
EMC MODEL RJB LOCK-IN AMPLIFIER
VARIAN G-10 GRAPHIC RECORDER
TEKTRONIX TYPE 122 LOW-LEVEL PREAMPLIFIER
BOLOMETER BIAS
SCOTT 250-AR POWER AMPLIFIER
FROM KLYSTRON MODE DETECTOR CRYSTAL
SAWTOOTH WAVE FOR KLYSTRON MODULATION MODULATION TO KLYSTRON
HARVEY-WELLS 12" MAGNET
35 hz FIELD MODULATION
HARVEY-WELLS HS-1050 MAGNET POWER SUPPLY
HP MODEL 20IC AUDIO OSCILLATOR
SELECTOR PANEL
35 hz
HP MODEL 20IC AUDIO OSCILLATOR
Figure 7. The C-band (5.5 GHz) crystal spectrometer. The microwave power level is adjusted by the attenuators and is then split by the magic T. Half the power goes to the sample cavity and the other half is absorbed in the termination. The slide screw tuner is adjusted so that far from resonance only enough power to bias the crystal detector goes out the fourth arm of the magic T. When the sample absorbs power during resonance, the T becomes unbalanced and a signal passes out the fourth arm of the T and is detected with a 1N23G diode. The detected signal is then passed directly to the lock-in amplifier.
the fourth arm. The tuner is also used to adjust for \( \chi' \) or \( \chi'' \) in the detected signal. The crystal detector output is then put directly to the lock-in detector, and from there the associated electronics are just as for the bolometer case.

D. Use of a Multi-Channel Analyzer

For resonance work, a multi-channel analyzer can be used to advantage for two purposes:

(i) To digitize data so that it can be analyzed on a digital computer.

(ii) To increase the signal to noise ratio by the technique of continuous averaging (64), sometimes by several orders of magnitude.

For both of these purposes a RIDL Model 34-27 Scientific Analyzer System with a Model 24-2 400-Word Memory was used. This instrument has been modified by Torgerson (65) for use in electron spin and nuclear magnetic resonance. A block diagram of the spectrometer and analyzer system is given in Figure 8. The main difference from the systems previously described is that the analyzer system now controls the magnetic field scan rate and range and steps the field in 400 increments, each synchronized with the open time for a channel. At the end of each scan, the memory can immediately go from channel 399 back to channel 0, and a time delay must be introduced to stop the memory and allow the magnetic field to return to its starting value.
Figure 8. Block diagram of a spectrometer when an analyzer is used in the method of continuous averaging. The magnet scan range and rate are now controlled by the analyzer.
E. Field and Frequency Measurements

The magnetic field strength was measured at either the chart marker values or else every 50 channels, depending on which system was used. A Rawson-Lush Type 820M8 Rotating Coil Gaussmeter was used. This instrument was periodically calibrated in a 10,000 gauss field which was measured by using a nuclear magnetic resonance probe. This Gaussmeter gives the field to within 0.1% or 2 gauss, whichever is larger. The frequency was measured with a PRD Type 585B Wavemeter, and this meter was calibrated with a Hewlett Packard Model 540B Transfer Oscillator in conjunction with a frequency counter. The frequency values can be read from the wavemeter to an accuracy of ± 1 MHz. K-band frequencies were measured with a Microwave Associates Model 588 wavemeter, and the calibration chart accompanying the meter was used since the Transfer Oscillator can't be used above 12.4 Ghz. C-band frequencies were determined by using DPPH as a marker for g = 2.00 and calculating the frequency from the measured field value.

F. Data Taking Procedure

Most of the data were taken at liquid nitrogen temperatures (77°K) in order to increase the signal and to stabilize the sample cavity against frequency variations due to temperature changes. This was easily accomplished at X- and K-band frequencies by surrounding the sample cavity waveguide arm with a stainless steel can which was filled with helium gas.
for heat transfer purposes. This whole arrangement was then placed in a glass Dewar containing several liters of liquid nitrogen. After the sample temperature had stabilized, the spectrometer was tuned to the absorption mode, with about 1 mw of microwave power incident on the sample. Higher powers caused some saturation. Typical settings were a 3.0 second time constant and a 7,000 gauss scan in 15 minutes. When the analyzer was used, the scan rate was 2 seconds/channel for the same scan range. Shifts in the g values were not bothersome, as verified with a DPPH marker on some of the runs, and were accounted for by scanning the field in both directions and then averaging the g values.

As mentioned previously, the analyzer system was used for two purposes. The Y25YX and Z25Z samples have very weak resonances, and so 30 or more traces were averaged at X-band frequencies to build up the signal. The C-band spectrometer was totally unstabilized and the usual factor of four in sensitivity due to the Boltzmann factor could not be gained by using liquid nitrogen since the waveguide barely fit into the magnet gap and there was no room left for a Dewar. Therefore, the C-band data were taken at room temperature, and 19 traces were averaged.

For the purpose of making intensity comparisons two extended runs were made to take data on all the samples under conditions as nearly identical for each sample as could be attained. For these runs, one trace was taken for each
sample, and this was read out on paper tape, onto an X-Y plotter, and also onto the usual strip chart.
IV. RESULTS AND DISCUSSION

A. Features of the Data

The strength of the crystal field experienced by the gadolinium ion in the soda-silica glass system is evidently of the same order of magnitude as the external magnetic fields used in ESR work. This is demonstrated by Figure 9, in which the ESR spectra obtained at seven frequencies are presented. For the high frequency range, 38 to 24 Ghz, there is only a single asymmetric line about 100 gauss wide at \( g \approx 2.0 \). The high field side is broadest and falls off slowly for several thousand gauss, while the low field side falls rather sharply to the baseline.

At the intermediate frequencies of 16.3 and 13.4 Ghz, the main line broadens to 150 and 180 gauss respectively and a low field shoulder starts to emerge down to about \( g = 3 \). Now there is also a small resonance with \( g \approx 6 \). The \( g = 2 \) to \( g = 6 \) amplitude ratio is 58 at 16.3 Ghz and decreases to 16 at 13.4 Ghz.

The spectra becomes much more complex when the frequency is lowered into the X-band region, 8.5 to 10.0 Ghz. There is appreciable absorption over a 7000 gauss field range and very prominent peaks occur at \( g = 2.0, 2.9 \) and 5.9, with a hint of another peak around \( g = 3.5 \). These peaks are linked by featureless regions of high absorption. The low frequency trace taken at 5.4 Ghz shows very weak resonances at \( g \approx 2.8 \) and 6.0,
Figure 9. The ESR absorption derivative of gadolinium in glass as a function of frequency. The frequency decreases from top to bottom and the structure of the spectra changes drastically because the crystal field effects become significant at lower frequencies.
superimposed on a featureless background.

This drastic variation with the microwave frequency is one outstanding feature of the data. The other is the almost complete insensitivity to sample composition. As tabulated in Table 1, all samples had 1% (by weight) of Gd$_2$O$_3$ but otherwise contained from 0% to 50% Na$_2$O, or else had a Na$_2$O content of about 40% and a Y$_2$O$_3$ content varying from 0% to 20%. Except for two samples, all gave essentially the X-band spectra shown in Figure 9.

The sample Y25IX is of the same composition as Y25Y and contains only 0.5% Na$_2$O. However, this sample devitrified and the resulting spectra are given in Figure 10. The most prominent aspect is a resonance around $g = 7$ which is only 38 gauss wide as measured peak-to-peak on the absorption derivative. There is also a very broad absorption around $g = 2$.

The other special case is Z25Z, which contains no soda and, but for the small amount of Gd$_2$O$_3$, is vitreous silica. Figure 11 presents this case, and shows a distinct resonance at $g = 5.0$ and a very broad, indistinct absorption elsewhere.

By far, most of the data were taken at X-band frequencies, and both because it contains other interesting features and because it is crucial to the analysis of the whole problem, the results of the various X-band measurements will be covered in more detail now. Figure 12 shows a typical derivative trace, together with the absorption. The integration evidently loses much of the detail of the resonance. Several
Figure 10. The absorption derivative for the crystalline sample Y25YX. Trace (a) is a wide field scan and trace (b) is an average of 31 traces over the region around $g = 7$. 
SAMPLE Y25Y X
98.5% SiO₂
0.5% Na₂O
1.0% Gd₂O₃
- 9.779 Ghz

(a)
\[ \frac{dX''}{dH} \]

MAGNETIC FIELD H (Oe)

(b)
\[ \frac{dX''}{dH} \]

MAGNETIC FIELD H (Oe)
Figure 11. The absorption derivative for the soda-free sample Z25Z. Trace (a) is a wide field scan and trace (b) is an average of 43 traces over the region around $g = 5$. The small bumps are noise spikes which were not entirely averaged out.
SAMPLE Z25Z
99% SiO₂
1% Gd₂O₃
ν = 9.5 GHz

(b)

\( \frac{dx''}{dH} \)

MAGNETIC FIELD H(Oe)

1700 1600 1500 1400 1300 1200 1100 1000

MAGNETIC FIELD H(Oe)
Figure 12. The absorption and absorption derivative of a typical sample. The integration process evidently loses much of the detail of the resonance
SAMPLE N25N
76% SiO₂
25% No₂O
1% Ge₂O₃
\( \nu = 9810 \text{ MHz} \)
series of comparison runs were made in an attempt to correlate the absorption intensity and distribution with the glass composition, but the extremely long absorption tail on the high field side and the zero field absorption due to crystal field effects made the choice of baseline very uncertain, so that no really valid intensity comparisons could be made.

Slight variations with composition occur in the F--F series, where the \( g \approx 2 \) area loses intensity and the \( g \approx 2.8 \) and 6 areas gain intensity as the \( Y_2O_3 \) content increases. In the \(-25-\) series the area around \( g < 2 \) grows, \( g > 2 \) decreases and \( g \approx 2.8 \) grows as the \( SiO_2 \) content increases above 82%. Primarily this shows up as a decrease in the resonance peak on the low field side of \( g = 2 \), as illustrated in Figure 13. This peak reappears again at the very high \( SiO_2 \) end of the series. Figure 13 also compares two X-band traces from sample W25W, which contains 97.5% \( SiO_2 \). The scan rate is 7000 gauss in 15 minutes and there is a pronounced transfer of intensity around \( g = 2 \), depending on whether the field is scanned up or down in strength. This indicates some sort of a slow relaxation mechanism for the \( Gd^{3+} \) ions. Sample Y25Y containing 98.5% \( SiO_2 \) also shows this effect to a lesser degree, and lower \( SiO_2 \) content samples have been observed to show this tendency; but when the scan time is doubled, the up and down scan traces can be superimposed with almost no detectable variation. It was also observed that the area around \( g = 2.0 \) to 2.9 exhibited saturation effects and that the \( g = 2.8 \) peak
Figure 13. Relaxation effects in sample W25W. The spectrum depends on the scan direction for this sample. The low-field side of the \( g = 2 \) region does not have the peak that is characteristic of most of the other samples.
SAMPLE W25W
97.5% SiO₂
1.5% Na₂O
1.0% Gd₂O₃
INCREASING FIELD SCAN
DECREASING FIELD SCAN

5649 Oe

893 Oe

$g \sim 2$

$g \sim 6$
could be removed by increasing the microwave power incident on the sample to 10 mw or more. Consequently, all measurements were taken with 1 mw or less sample power. These relaxation effects are only mentioned for completeness and will not be discussed further.

The X-band data is temperature independent from room temperature down to 77°K, except for the usual fourfold increase in intensity due to the Boltzmann factor. However, when the temperature is reduced to 4.2°K, the derivative amplitude ratio of the g = 2 to g = 6 peaks is 1.8 compared to 3.0 at 77°K. This is shown in Figure 14. Figure 15 depicts the region around g = 6 for a typical sample. This is an average of 39 traces and a noticeable bump occurs around g = 7, indicating that there may be a very small crystalline phase present in the glass.

B. Results of the Exact Calculation

Equations 61, 62 and 63 were used to calculate the energy levels for the Hamiltonian given by Equation 33 for the cases where the external magnetic field is in the x or y or z direction. The ratio $D/\phi H$ was varied from 0 to 4.0 and the calculation was then done for $\lambda = E/D$ in the interval $0 \leq \lambda \leq 1/3$ in increments of 0.05. The computations were done on an IBM 360/50 system and the associated plotting facility was used to generate energy level graphs, such as the one for $\lambda = 0.30$ given by Figure 16. The graphs for other values of $\lambda$ are
Figure 14. The temperature dependence of sample K25K. At 4.2°K, the $g = 6$ peak-to-peak amplitude is about 65% larger relative to the $g = 2$ peak than at 77°K.
Figure 15. The $g = 6$ region for sample Q25Q. The $g$ values for this feature were taken to be those at the point halfway vertically between the derivative peaks, since no reliable baseline could be established. There is a small bump at $g = 7$, indicating the possible presence of a small crystalline phase in the glass.
SAMPLE Q25Q
82% SiO₂
17% Na₂O
1% Gd₂O₃
f = 9812 Mhz
AVERAGE OF 39 TRACES

314 Oe

g=5.7

g=6.0

466 Oe

g=6.4

6=7.0
Figure 16. The energy levels for Equation 33, for $E/D = 0.30$. The three diagrams are for the external H field taken to be along the x, y and z directions. The left side of each diagram corresponds to the strong Zeeman case, with eight equally spaced energy levels. The right side of each diagram corresponds to the strong crystal field case, with four pairs of energy levels. The energies are in units of nH so that the effective g value for a transition is given directly by the difference of the two levels involved. The levels are considered to be labeled 1 to 8 from highest energy to lowest energy, starting at the left hand side of each diagram. This labeling is carried through for all values of crystal field strength. Thus, for example, level 3y drops below level 4y in the region around $D/nH \approx 0.75$ and then crosses level 4y again at $D/nH \approx 1.13$ and remains above level 4y as $D/nH$ increases.
given in the Appendix, as is the computer program used. The levels are considered to be numbered 1 to 8 from highest to lowest energy. These graphs are sufficiently interesting that several general features will be pointed out, since they contain all the physically distinct cases for all crystal field strengths using the most general spin Hamiltonian of second degree in the spin operators. These features are:

(i) The $x$ levels never cross.

(ii) For $\lambda = 0$, the $x$ and $y$ cases are the same and for $\lambda = 1/3$, the $y$ and $z$ cases are the same except for an inversion of the order of the levels. This can also be shown directly from Equation 39.

(iii) Levels 1 and 2 for $x$ and $y$ always go off rapidly together to high energy values as $D/\beta H$ increases, and the lowest $y$ level always shoots off by itself to very negative energy values with increasing $D/\beta H$.

(iv) The $z$ case for $\lambda = 0$ gives energy levels which are always straight lines, since then the Hamiltonian is simply

$$\mathcal{H} = g_o \beta H Z S_Z + D(S_Z^2 - 1/3S(S+1))$$  \hspace{1cm} (75)

with

$$E_m = g_o m + \frac{D}{\beta H} (m^2 - \frac{21}{4})$$  \hspace{1cm} (76)

and for fixed $m$ ($m = \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2$) the levels are linear functions of $D/\beta H$.

(v) As $\lambda$ increases from 0 the levels begin to pair off (around $\lambda = 0.05$ for lower levels) and there is less crossing
of levels. By the time \( \lambda = 1/3 \) the pairing of adjacent levels is complete for \( D/\beta H > 3.0 \), and then results the strong crystal field case considered by Castner et al. (29) for \( S = 5/2 \).

The computer program automatically orders the eigenvalues from highest to lowest and it is sometimes difficult to decide whether levels are crossing or not, even when very many values of \( D/\beta H \) are used to make the computational mesh finer. The simple way to solve this problem is to look at the eigenvectors, or more usefully, at the transition probabilities as calculated from Equation 74. The eight eigenvectors, of course, represent the states available to the system and are made up of appropriate linear combinations of the basis set \([|m>]\). These states should change continuously as the \( D/\beta H \) value is changed slowly, so that the character of the states before and after crossing should not be very different, and the transition probability should also change regularly unless the two levels in question happen to be adjacent states, in which case the probability goes through a minimum at the crossover point.

For transitions involving a single microwave quantum \( hv \), it is thus found that two states that are adjacent for the strong Zeeman case (\( D/\beta H = 0 \)) can be tracked via the transition probability between the two states, and as \( D/\beta H \) becomes larger than about 3.0, these same two states go off parallel and are thus the ones between which a transition can take place when the Zeeman field is applied as a perturbation to the strong CEF case. In the process, the character of the states has
changed from being

$$\psi = |m>$$

(77)

at the pure Zeeman limit to being

$$\psi = a|m> + b|m+2> + c|m+4> + d|m+6>$$

(78)

at the strong CEF limit.

For the $x$, $y$ and $z$ cases considered here, transitions involving $|\Delta m| = \pm 2$ are always forbidden because the nature of the Hamiltonians is such that every eigenvector has either the form

$$\psi_a = a_1|7/2> + a_2|3/2> + a_3|-1/2> + a_4|-5/2>$$

(79)

or the form

$$\psi_b = b_1|5/2> + b_2|1/2> + b_3|-3/2> + b_4|-7/2>$$

(80)

and these forms occur alternately as the energy levels are traversed in order. Since the probability expression, Equation 74, contains the raising and lowering operators, states $|\Delta m| = \pm 2$ apart cannot be coupled since they are made up of the same $4$ basis vectors. Hence only odd quantum transitions are possible. This all goes back to the fact that when the external $H$ field is taken to be in the $x$, $y$ or $z$ direction, the $8x8$ matrix of the Hamiltonian can be factored into two $4x4$ matrices, each one having its vectors made up by a different $4$ vector subset of the $8$ basis vectors.
The energy levels given in Figure 16 are in units of $\beta H$ so that the difference between levels gives the effective $g$ value for the transition directly. Since we have, by definition

$$hv = g\beta H,$$

the results of the calculation can be summarized on a single graph derived from the energy levels. This is done by effectively normalizing the crystal field and Zeeman field by dividing $D/\beta H$ and $g_0$ by the effective $g$. This gives

$$D/g\beta H = D/hv$$

for the abscissa and $g_0/g$ for the ordinate. This essentially plots the magnetic field at which a transition occurs on the vertical axis increasing from 0 versus crystal field strength on the horizontal axis. This allows the data from all microwave frequencies to be placed on a single graph as shown in Figure 17. An additional scale which gives $g$ directly has been added to Figure 17. The point of the whole calculation is to find the best fit for the data on this graph and thus determine the crystal field parameters $D$ and $E$. This method produces a one-parameter family of graphs with $\lambda$ as the parameter, so the problem is first to find the best value of $\lambda$ and then to find the value for $D$ on this graph which best fits the data. Figure 18 presents a typical X-band spectrum with the prominent spectral features labeled. The X-band case was used
Figure 17. A graph of the effective g values for transitions between the energy levels of Figure 16. Main features of the data given in Figure 9 are shown by solid circles, and minor features are shown by empty circles. The vertical dashed line at $D/h\nu = 0.21$ locates, on the heavy solid lines, the principal features of a typical X-band spectrum such as that given in Figure 18. As the microwave frequency increases, the transitions collapse toward $g_0/g = 1.0$. Spectral features can be expected for glasses at points where the g value for a transition is nearly stationary with respect to variations in the crystal field strength.
Figure 18. A typical X-band spectrum. The prominent features are located on the dashed vertical line in Figure 17.
SAMPLE E25E
49% SiO2
50% Na2O
1% Gd2O3
ν = 9.8 GHz

BROAD, FEATURELESS
HIGH-FIELD TAIL

g~2

BROADENED
LOW-FIELD SIDE

g~3.5

g~5.9

7000 6000 5000 4000 3000 2000 1000 0
MAGNETIC FIELD H(Oe)
to determine the best values for \( \lambda \) and \( D \) and then the points for other frequencies were plotted to give a sort of self-consistency check to the theory. By studying graphs such as Figure 17 for the various values of \( \lambda \), the best values were found to be

\[
\lambda = 0.30 \\
\frac{D}{\hbar \nu} = 0.21.
\] (83)

Table 2 presents the parameters \( D \) and \( E \) in frequency units (Ghz) together with an error range.

**Table 2. Crystal field parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Best Value (Ghz)</th>
<th>Range (Ghz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D )</td>
<td>2.06</td>
<td>1.86 - 2.16</td>
</tr>
<tr>
<td>( E )</td>
<td>0.62</td>
<td>0.50 - 0.72</td>
</tr>
</tbody>
</table>

Based on these values for \( D \) and \( \lambda \), Table 3 gives the various features of the data from all frequencies that are plotted on Figure 17 and labeled by frequency along vertical lines.

The following discussion refers to Figure 17. For the 9.81 Ghz data the fit is excellent. The \( g = 2 \) resonance is caused by 2-3 \( y \), 4-5 \( y \) and 4-5 \( z \) transitions. The feature at \( g = 2.8 \) is caused by 5-6 \( y \) and 3-4 \( z \) transitions and the fact that the data point does not fall right on these transitions
Table 3. Spectral features as a function of frequency

<table>
<thead>
<tr>
<th>Frequency (Ghz)</th>
<th>D/\hbar</th>
<th>Effective g of features</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.4</td>
<td>0.054</td>
<td>1.98</td>
</tr>
<tr>
<td>23.12</td>
<td>0.089</td>
<td>2.01</td>
</tr>
<tr>
<td>16.30</td>
<td>0.126</td>
<td>1.98, 5.94</td>
</tr>
<tr>
<td>13.40</td>
<td>0.154</td>
<td>1.97, 5.88</td>
</tr>
<tr>
<td>9.81</td>
<td>0.210</td>
<td>2.0, 2.82, 5.89</td>
</tr>
<tr>
<td>8.60</td>
<td>0.240</td>
<td>1.98, 2.80, 5.90</td>
</tr>
<tr>
<td>5.35</td>
<td>0.385</td>
<td>2.82, 6.06</td>
</tr>
</tbody>
</table>

is not surprising since there is no way to determine the true g value for this feature because the spectra are so broad. Note also that the lines which map out the transitions as a function of crystal field strength are relatively stationary with respect to changes in D/\hbar. This is an additional criterion that must be met in the case of a glass in order to get resolved spectral features, since there probably exists a distribution of crystal field strengths due to the nature of glass. The g = 5.89 resonance apparently comes from the 6-7 y transition and a 2-3 z transition could cause the low field side broadening of this peak, and also might account for the g = 7 resonance observed in the crystalline sample. It is possible that all the samples have a very small crystalline phase, but since the x-ray patterns showed all but Y25YX to be glassy it
is more likely that the $g = 7$ would come from a place like the 6-7 $y$ transition for $D = 0.25$, since this transition is stationary with respect to $D/\Delta H$ at this point and no other lines cross over in this area to give broadening. The transitions 2-3 $y$, 3-4 $y$, 5-6 $z$, 1-2 $x$ and 7-8 $x$ account for the long featureless tail on the high field side of $g = 2$ since they are all distinctly non-stationary with respect to $D/\Delta H$. The 3-6 $y$ and 3-6 $z$ transitions come across $D/\Delta H = 0.21$ with a significant transition probability and certainly account for the broad bump in the data usually observed in the vicinity of $g = 3.6$.

Table 4 presents the relative transition probabilities for the transitions which take part in the X-band data features, and are listed in order of increasing magnetic field strength. They are all of the same order of magnitude.

As the microwave frequency is increased $D/\Delta \nu$ decreases and so the explanation for the higher frequencies must be sought to the left of $D/\Delta \nu = 0.21$ on the graph. In general, all the $|\Delta m| = \pm 1$ transitions collapse toward $g = 2.0$, the free ion value. The low field side collapses more quickly than does the high field side and this accounts for the asymmetry observed in all the higher frequency work. This causes the low field $- g>2$ side to be the sharpest. The true $g$ values for the observed data are hard to pin down to better than a few per cent because of this asymmetry, so that the $g<2$ points plotted for the higher frequencies are well within
Table 4. Transition probabilities for the X-band features

<table>
<thead>
<tr>
<th>Transition</th>
<th>Effective g value</th>
<th>Relative probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-3 z</td>
<td>6.87</td>
<td>11.3</td>
</tr>
<tr>
<td>6-7 y</td>
<td>5.95</td>
<td>11.5</td>
</tr>
<tr>
<td>5-8 z</td>
<td>5.07</td>
<td>4.7</td>
</tr>
<tr>
<td>3-6 y</td>
<td>3.78</td>
<td>8.8</td>
</tr>
<tr>
<td>3-6 z</td>
<td>3.60</td>
<td>9.9</td>
</tr>
<tr>
<td>3-4 z</td>
<td>2.96</td>
<td>12.4</td>
</tr>
<tr>
<td>5-6 y</td>
<td>2.92</td>
<td>13.4</td>
</tr>
<tr>
<td>2-3 y</td>
<td>2.84</td>
<td>3.2</td>
</tr>
<tr>
<td>5-6 x</td>
<td>2.62</td>
<td>13.3</td>
</tr>
<tr>
<td>3-4 x</td>
<td>2.51</td>
<td>13.2</td>
</tr>
<tr>
<td>5-8 z</td>
<td>2.06</td>
<td>5.2</td>
</tr>
<tr>
<td>4-5 y</td>
<td>1.99</td>
<td>14.8</td>
</tr>
<tr>
<td>4-5 z</td>
<td>1.97</td>
<td>15.0</td>
</tr>
<tr>
<td>7-8 x</td>
<td>1.80</td>
<td>8.5</td>
</tr>
<tr>
<td>1-2 x</td>
<td>1.63</td>
<td>8.5</td>
</tr>
<tr>
<td>3-4 y</td>
<td>1.47</td>
<td>13.6</td>
</tr>
<tr>
<td>5-6 z</td>
<td>1.43</td>
<td>13.9</td>
</tr>
<tr>
<td>2-3 y</td>
<td>1.19</td>
<td>11.3</td>
</tr>
</tbody>
</table>
the reasonable range. The low X-band (8.60 GHz) data fall on the transition curves very well at $g \approx 2$ and 2.8. The distinct loss of intensity on the low field side of $g = 2$ can be attributed to the fact that the $5-8$ transition no longer is stationary with respect to $D/\beta H$ in this region, and thus contributes only a smear over a wide range of $g$ values. This transition line is nearly vertical at $D/\beta H = 0.24$, and so even very small variations in crystal field strength cause this transition to give wildly different effective $g$ values.

Thus, this relatively simple calculation with a spin Hamiltonian has accounted for the major spectral features of the Gd$^{3+}$ ion in surroundings where the effect of the crystal field cannot be treated as a perturbation except at very high microwave frequencies. Not everything is satisfactory, however. The C-band (5.35 GHz) data and the $g - 6$ resonances at all other frequencies than 9.81 GHz do not fit the present picture. The C-band data could possibly be passed off as unreliable inasmuch as it was taken at room temperature with a spectrometer that had an unstabilized klystron. However, the C-band trace on Figure 9 represents an average of 19 traces and even though the resonances are very weak, they cannot be disregarded. The $g - 6$ resonances at 13.4 and 16.3 GHz are weak but the one at 8.60 GHz is not. The facts are that this resonance occurs at very nearly $g = 5.90$ wherever it is observed and its intensity decreases as the frequency is raised. One possibility is that there are regions in the glass where
there are a wide range of distortions which give rise to
enough sites with varying D to allow D/βH = 0.21 and hence get
the g = 5.9 resonance from the 6-7 γ transition and at the
same time manage to smear out the other features. Another
possibility is the case where λ = 0 and the H field is taken
in the z direction. Then the 3-6 z transition gives g = 6.00
for all values of D/βh/2. Unfortunately, the transition prob­
ability for this case is zero since there is no mixing of the
basis states upon addition of the crystal field and the states
involved are purely |3/2> and |-3/2>. A third possibility is
the |Δm| = ±3 transitions 3-6 γ and 3-6 z in the region
0<D/βh/2<0.07, but this is scarcely reasonable, since these
transition probabilities are down by at least a factor of 160
compared to the 4-5 γ or 4-5 z transitions which cause the
large absorption at g≈2. This leaves the first proposition,
namely that there is a distribution of sites for which
D/βh/2 = 0.21 sufficient to cause the g = 5.90 transition.
There appear to be no other reasonable possibilities within
the framework of the present theory, because other transitions
that are relatively stationary with respect to variations in
D/βH and have g≈6 simply don't occur, whatever the value of
λ. If the much more difficult calculations for general
orientations of H were performed, it is possible that a tran­
sition giving g = 5.90 would occur and be stationary with
respect to wide variations in D/βH.
C. Strong Crystal Field Results

The results of the strong crystal field calculation are presented in Figure 19. The energy level scheme is as given in Figure 2 and the 4 sets of curves in Figure 19 give all the possible g values in the x, y and z directions for the 4 doubly degenerate energy levels and for the range $0 < \lambda < 1/3$, which again covers all physically distinct cases. The only features of interest for the glassy case are those which are relatively stationary for variations in the parameter $\lambda$.

These are:

(i) $g = 10.0, 6.0$ and $2.0$ for $\lambda = 0$ for levels 2, 3 and 4 respectively.

(ii) $g_X = 5.5$ for $\lambda = 0.175$ for level 3.

(iii) $g_X = g_Y = g_Z = 5.0$ for $\lambda = 0.120$ for level 3.

The case of interest here is the isotropic $g = 5.0$. This could satisfactorily explain the $g = 5.0$ resonance obtained for sample Z252 which contains no soda, and but for the small amount of Gd$_2$O$_3$, is vitreous silica. The drastic change in the spectra with the introduction of even 0.5% Na$_2$O makes it reasonable to suppose that the Gd$^{3+}$ ion in vitreous silica has very different surroundings than it has in the soda containing glasses, and so the theory developed for the soda-silica glasses would not necessarily apply. It really does, however, since the strong CEF case is just a special calculation contained in the general case, but when done using perturbation theory, it comes out in a more useful form.
Figure 19. The g values for the strong crystal field case. When the Zeeman perturbation given by Equation 46 is applied to the energy level scheme of Figure 2, the twofold degeneracy of each of the four crystal field levels is removed. All the possible g values for the Zeeman field applied in the x, y or z directions are obtained by restricting lambda in Equation 39 to the range 0<\lambda<1/3. Energy level 3 has an isotropic g = 5.0.
I I I I I I r
^ ENEROY LEVEL 1
12.0 j-
9.0 —
» 6.0 —
^ ENERGY LEVEL 2
12.0-
9.0r
> 6.0
0.30
ENERGY LEVEL 3
12.0
9.0
» 6.0
0.30
ENERGY LEVEL 4
12.0
9.0
» 6.0
^ LAMBDA
D. The Soda-Silica System

The soda-silica glass system has been the object of very many investigations, the most important of which are summarized by Stanworth (66) and Morey (67). These older studies involved the measurement of bulk properties, such as the coefficient of thermal expansion and the heat capacity and many pictures of the glass structure were proposed, most of which involved rings and chains of SiO$_4$ tetrahedra such as are found in the pure crystalline silicates. Stanworth (66, p. 36) and Mackenzie (1, p. 7) outline some of these possibilities.

A survey of these bulk measurements for the soda-silica system reveals no anomalous behavior as in the soda-boric oxide system (66, p. 25). In that system, as the soda content increased from 0% to about 16% the expansion coefficient of the glass decreases. When more soda is added, the expansion coefficient begins to increase. Although most of the bulk studies reported were confined to less than about 90% SiO$_2$, properties such as the coefficient of linear expansion (67, p. 277) and index of refraction (67, p. 36) change rather regularly with composition. One outstanding aspect of the system is that the addition of soda to the pure silicate lowers the melting temperature considerably. The addition of 25% Na$_2$O drops this temperature from over 1700°C to around 800°C. This is attributed to breaking of Si-O-Si bonds by the Na$^+$ ions so that some of the tetrahedra corners no longer link two silicon atoms and the bonding in the glass is weakened.
That there are no observed bulk anomalies agrees with the spectral composition independence.

As previously noted, the basic building block of the silicates is a tetrahedron composed of 4 oxygen ions on the corners and a silicon ion at the center. The basic silicate structures are built up from these basic tetrahedra in five ways (68) depending on whether the tetrahedra share 0, 1, 2, 3 or 4 corners. The size of the gadolinium ion precludes its substitution for silicon in these tetrahedra. The ionic radius of O^2- is 1.32 Å (68, p. 171) and that of Gd^{3+} can be inferred to be 0.92 Å to 0.95 Å (69, p. 4). According to simple geometrical concepts of packing atoms, the coordination number of Gd^{3+} by the oxygens must be 6 or 8 (68). This merely means that the Gd^{3+} ion must seek a position in the space left by the structural silica tetrahedra. The fact that the sample that contained only silica and gadolinium oxide exhibited only a weak resonance at g = 5.0 and a very broad smear of absorption intensity elsewhere is taken to mean that the ion in these surroundings experiences very strong crystal field effects, with such a range of distortions that only an energy level situation that can give rise to an isotropic g value could give a resolvable resonance. On the other hand, the addition of even 0.5% Na_2O changes the spectra dramatically and it is evident that, although the pattern is still very broad, the Na^+ ions must be responsible for a more definite crystal field strength and symmetry at the Gd^{3+} sites.
Examination of Table 1 shows that even 0.5% Na₂O gives the samples four times as many sodium atoms as gadolinium atoms, which means that there are always enough Na⁺ ions to provide the more uniform CEF apparently experienced by the Gd³⁺ ions in the soda-silica glasses. If, as is usually assumed (70), the yttrium ions enter the same sort of sites as the gadolinium ions, then the fact that the resonances changed almost imperceptibly as the Y³⁺+Gd³⁺ ion total was raised from 1/4 to 5 times the Na⁺ ion total indicates that probably only one Na⁺ ion is necessary in whatever complex sort of structure is responsible for the Gd³⁺ CEF. One possibility is that the sodium ions are surrounded by 6 to 8 oxygen ions and that these structures occur together in groups filling silicon poor regions of the glass structure. The Gd³⁺ and Y³⁺ ions would then fit themselves into the spaces created between these more complex sodium structures. There is good evidence that alkali-silica glasses are heterogeneous on a microscopic scale. Electron microscopy work has shown (22, 23) that there are regions in Li₂O·SiO₂ glasses that are lithium rich. These regions can be several hundred Angstrom units in diameter and show up very much like tapioca in pudding: the tapioca corresponds to the lithium rich region and the surrounding goo is the silicate network structure. These glasses have also been leached with acids (71) and the leaching solution was found to contain alkali-metal cations and scarcely any SiO₂. The pore sizes differ and were studied by subsequent adsorption of
H$_2$O, CH$_3$OH and C$_2$H$_5$OH molecules.

It is interesting to note that Chepeleva et al. (37) observed spectra of the Gd$^{3+}$ ion with features nearly identical to those obtained here for soda-silica glasses. In that case, however, the host glass could scarcely have been more different. They used a Tl$_2$SeAs$_2$Se$_3$ glass and this contains no oxygen at all. Thus it would appear that perhaps the Gd$^{3+}$ ion seeks out sites that provide it with a reasonably uniform CEF, regardless of the origin. This also points out the fact that while the present study has determined what CEF parameters are probably responsible for the observed spectra, little more can be said about the Gd$^{3+}$ ion surroundings in detail, because the use of the spin Hamiltonian analysis lumps all our ignorance of the problem into two parameters. The D parameter describes axial distortions of the ion surroundings and the E term presumably takes care of every other sort of distortion. Castner et al. (29) deduced that the Fe$^{3+}$ ion in soda-silica glass must occur substitutionally in a silicon site, and were able to suggest possible distortions of the SiO$_4$ tetrahedron that would give rise to the proper sort of crystal field. Here we must content ourselves with a probable picture in general outline only -- the gadolinium favors sites in the soda-rich regions of the glass, probably in the spaces left when the sodium ion complexes combine into groups.
The $\text{Gd}^{3+}$ ion was placed in a wide variety of soda-silica glasses and studied by electron spin resonance. As the microwave frequency was varied from 5.4 to 38 Ghz the ESR spectra changed remarkably, but almost no changes occurred with variations in sample composition. The frequency dependence was interpreted with the spin Hamiltonian

$$\mathcal{H} = g_0 \mu_B \mathbf{H} \cdot \mathbf{S} + D(S_x^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2)$$

and $D$ and $E$ were determined to be 2.06 and 0.62 Ghz, respectively.

It was concluded that the $\text{Gd}^{3+}$ ion probably goes into the glass in soda-rich regions, where it experiences a more uniform crystalline electric field, in spaces left in the structure between the 6 or 8 coordinated sodium ion complexes as they formed groups to make up the region. When no soda was present, the $\text{Gd}^{3+}$ ion experienced a wider range of distorted surroundings as it fit into spaces between the structural $\text{SiO}_4$ tetrahedra.
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A. Energy Level Diagrams

The exact calculation was done for the interval $0 \leq \lambda \leq 1/3$. Figures 20 through 26 present the energy level schemes obtained when the Zeeman field is taken in the $x$, $y$, and $z$ directions as defined by Equation 39, and for $\lambda = 0.0$, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.33.
Figure 20. The energy levels of Equation 33 for $E/D = 0.0$
Figure 21. The energy levels of Equation 33 for $E/D = 0.05$
Figure 22. The energy levels of Equation 33 for $E/D = 0.10$
Figure 23. The energy levels of Equation 33 for $E/D = 0.15$
Figure 24. The energy levels of Equation 33 for E/D = 0.20
Figure 25. The energy levels of Equation 33 for $E/D = 0.25$
Figure 26. The energy levels of Equation 33 for $E/D = 0.333$
B. Calculations for \( \lambda = 0.30 \)

Table 5 gives the results of the crystal field strength, effective \( g \) value, and transition probability calculations which were used to produce Figure 17. The graphs were plotted for \( g_0/g \) on the vertical axis and \( D/h\nu \) on the horizontal axis.
Table 5. Results of calculations for $\lambda = 0.30$

<table>
<thead>
<tr>
<th>Transition</th>
<th>$D/\beta H$</th>
<th>$g$</th>
<th>$P$</th>
<th>$D/g\beta H$</th>
<th>$g_0/g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
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<td>4.6</td>
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<td>0.6</td>
<td>0.246</td>
<td>0.702</td>
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<td>0.6</td>
<td>0.235</td>
<td>0.588</td>
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<td>4.01</td>
<td>4.9</td>
<td>0.6</td>
<td>0.224</td>
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<td>4.66</td>
<td>4.8</td>
<td>0.6</td>
<td>0.215</td>
<td>0.429</td>
</tr>
<tr>
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<td>5.32</td>
<td>4.6</td>
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C. Strong Crystal Field Calculations

Table 6 tabulates the results of the strong CEF calculation. The range $0 \leq \lambda \leq 1/3$ produces all physically distinct possibilities, and $S = 7/2$. The energies $E$ are in units of $3\hbar$. The eigenvector coefficients for the crystal field levels are $A$, $B$, $C$ and $D$. The effective $g$ values are $g_x$, $g_y$ and $g_z$. 
Table 6. Strong crystal field energy levels, eigenvector coefficients, and effective g values

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>E</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
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<td>0.000</td>
<td>0.000</td>
<td>10.000</td>
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<td>0.00000</td>
<td>0.000</td>
<td>8.000</td>
<td>6.000</td>
</tr>
<tr>
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<td>0.00000</td>
<td>0.00000</td>
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<td>0.02292</td>
<td>0.00074</td>
<td>0.00004</td>
<td>0.001</td>
<td>0.001</td>
<td>13.996</td>
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<td>-0.00021</td>
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<td>0.05589</td>
<td>0.99842</td>
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<td>2.01550</td>
<td>2.824</td>
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<td>5.736</td>
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<tr>
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<td>0.98175</td>
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<td>$B$</td>
<td>$C$</td>
<td>$D$</td>
<td>$\varepsilon_x$</td>
<td>$\varepsilon_y$</td>
<td>$\varepsilon_z$</td>
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<td>-------</td>
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<td>13.781</td>
<td>0.180</td>
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</table>
D. Computer Programs

The programs for the exact g value calculation and for the strong CEF calculation were written in FORTRAN IV and executed on an IBM 360/50 system. The only special routine used is EIGEN, which produces the eigenvalues and eigenvectors of a real symmetric matrix, and which is a standard IBM -- routine.
C THIS PROGRAM IS DESIGNED TO DIAGONALIZE EXACTLY 3 HAMILTONIANS AND THUS
C COMPUTE THE G VALUES IN THE X, Y, AND Z DIRECTIONS. THE HAMILTONIANS ARE
C
C HX = G0*B*H*SZ - 1/3DS(S+1) + DSZ**2 + 1/4(D-E)(S+S- + S-S+ + 1/4(D+E)(S+S+ + S-S+))
C
C HY = G0*B*H*SZ - 1/3DS(S+1) + DSZ**2 + 1/4(D+E)(S+S+ + S-S+ + 1/4(D-E)(S+S+ + S-S+))
C
C HZ = G0*B*H*SZ - 1/3DS(S+1) + DSZ**2 + 1/4(D-E)(S+S+ + S-S+)
C
C HX AND HY ARE GOTTEN FROM HZ BY ROTATION AXES AND RELABELING. NOTE
C THAT THERE ARE NO TERMS IN THE FIRST OFF-DIAGONAL POSITION, AND HENCE NO
C COMPLEX MATRIX ELEMENTS, SO THAT AN EXACT SOLUTION RESULTS FROM EIGEN.
C REDEFINE D = D/BH AND E = E/BH SO HV = FREQUENCY = GBH IS IN UNITS OF
C BH AND THEN G = DIFFERENCE OF ENERGY EIGENVALUES. G VALUES FOR THE
C X, Y, Z DIRECTIONS FOR 1 GAMMA, 2 GAMMA AND 3 GAMMA TRANSITIONS ARE
C COMPUTED FOR EACH CHOICE OF D AND E. THE PROGRAM INPUT CARDS GIVE THE
C LIMITS ON D AND E, AND THEIR INTERVAL. IF GRAPHS ARE USED, THEN GRAPH
C LABELS MUST ALSO BE READ IN, UNDER THE FORMAT(2OA4).
C TO USE THIS PROGRAM, 1 DATA CARD IS NEEDED, ON WHICH YOU PUT THE
C LOWER AND UPPER LIMITS FOR E/BH, THE INCREMENT DELTA, AND LAMBDA = E/D.
C THE FORMAT IS (3F10.5). THE PROGRAM THEN DOES THE X, Y, Z HAMILTONIANS FOR
C ESTART<E/BH<ELIMIT IN INTERVALS OF DELTA, AND KEEPS LAMBDA CONSTANT.
C
C REAR IN MIND THAT LAMBDA CAN BE
C RESTRICTED 0<OR = LAMBDA<OR = 1/3 TO PRODUCE ALL THE DIFFERENT CASES
C POSSIBLE.
C
C DIMENSION EX(IO),EY(10),EZ(10),GLX(10),GLY(10),GLZ(10),G2X(10),
C D G2Y(10),G2Z(10),G3X(10),G3Y(10),G3Z(10), E(250),HX(36),
C D HY(36),HZ(36),XLX(8),XLY(8),XLZ(8),XLY(8),XLZ(8),XLY(8),
C XXY(8),XYZ(8),YXX(8),YXZ(8),YXY(8),YXZ(8),YXX(8),YXZ(8),
C YYX(8),YXY(8),XYY(8),YXX(8),YYX(8),XYY(8),YXX(8),YYX(8),
C D P1X(10),P2X(10),P3X(10),P1Y(10),P2Y(10),P3Y(10),P1Z(10),
C D P2Z(10),P3Z(10),V(8,8)
C D XL(5),YL(5),GL(5),DL(5)
C REAL LAMBDA
C COMMON W(18)
C 1000 READ(1,1)ESTART,ELIMIT,DELTA,LAMBDA
C 1 FORMAT(4F10.5)
C WRITE(3,2)
C 2 FORMAT(20X,ESTART,4X,ELIMIT,4X,DELTA,5X,LAMBDA)
C WRITE(3,1)ESTART,ELIMIT,DELTA,LAMBDA
C NE = ABS((ELIMIT-ESTART)/DELTA) + 1
C DO 4 J1=1,NE
C EXX(J1) = 0
C EXY(J1) = 0
C EXY(J1) = 0
C EZX(J1) = 0
4 EIZ(J1) = 0
DO 5 J1 = 1, 10
EX(J1) = 0
EY(J1) = 0
EZ(J1) = 0
G1X(J1) = 0
G1Y(J1) = 0
G1Z(J1) = 0
G2X(J1) = 0
G2Y(J1) = 0
G2Z(J1) = 0
G3X(J1) = 0
G3Y(J1) = 0
G3Z(J1) = 0
5 G3Z(J1) = 0
DO 6 J1 = 1, 8
P1X(J1) = 0
P2X(J1) = 0
P3X(J1) = 0
P1Y(J1) = 0
P2Y(J1) = 0
P3Y(J1) = 0
P1Z(J1) = 0
P2Z(J1) = 0
P3Z(J1) = 0
X1X(J1) = 0
X1Y(J1) = 0
X1Z(J1) = 0
X2X(J1) = 0
X2Y(J1) = 0
X2Z(J1) = 0
X3X(J1) = 0
X3Y(J1) = 0
X3Z(J1) = 0
Y1X(J1) = 0
Y1Y(J1) = 0
Y1Z(J1) = 0
Y2X(J1) = 0
Y2Y(J1) = 0
Y2Z(J1) = 0
Y3X(J1) = 0
Y3Y(J1) = 0
Y3Z(J1) = 0
6 Y3Z(J1) = 0
DO 200 I = 1, NE
E(I) = ESTART + (I-1)*DELTAL
D = E(I)/LAMBDAL
DO 3 K1 = 1, 36
HX(K1) = 0
HY(K1) = 0
HZ(K1) = 0
C SET UP THE MATRIX(BY COLUMNS) FOR THE X-DIRECTION HAMILTONIAN
HX(1) = 7. - 3.5*D + 10.5*E(I)
HX(3) = 5. - 0.5*D + 1.5*E(I)
HX(4) = 2.29129*D + E(I)
HX(6) = 3. + 1.5*D - 4.5*E(I)
HX(8) = 3.35410*D + E(I)
HX(10) = 1. + 2.5*D - 7.5*E(I)
HX(13) = 3.87298*D + E(I)
HX(15) = -1. + 2.5*D - 7.5*E(I)
\[ \begin{align*}
\text{HX}(19) &= 3.87298*10^3 + E(I) \\
\text{HX}(21) &= -3.35410*10^3 + 1.5*E(I) \\
\text{HX}(26) &= -5.5*E(I) + 1.5*E(I) \\
\text{HX}(34) &= 2.29129*10^3 - 5.5*E(I) \\
\text{HX}(36) &= -7.3*E(I) + 10.5*E(I)
\end{align*} \]

CALL EIGEN(HX,V,8,0)

EX(1) = HX(1)
EX(2) = HX(3)
EX(3) = HX(6)
EX(4) = HX(10)
EX(5) = HX(15)
EX(6) = HX(21)
EX(7) = HX(28)
EX(8) = HX(36)

DO 50 K = 1,8
N1 = 8*(I-1) + K
EXX(N1) = EX(K)
WRITE(3,39)((V(I3,J3),J3 = 1,8),I3 = 1,8)

CALCULATE 1,2 AND 3 GAMMA PROBABILITIES P1X,P2X,P3X.

N = 0
NN1 = 7
NN2 = 1
CALL ZILCH(N,NN1,NN2,V)

N = 7
NN1 = 6
NN2 = 2
CALL ZILCH(N,NN1,NN2,V)

N = 13
NN1 = 5
NN2 = 3
CALL ZILCH(N,NN1,NN2,V)

DO 30 K = 1,7
30 P1X(K) = W(K)
DO 31 K = 1,6
31 P2X(K) = W(K+7)
DO 32 K = 1,5
32 P3X(K) = W(K+13)

FOR THE Y-DIRECTION

\[ \begin{align*}
\text{HY}(1) &= 7.3*E(I) - 10.5*E(I) \\
\text{HY}(3) &= 5.3*E(I) - 1.5*E(I) \\
\text{HY}(4) &= -2.29129*10^3 - E(I) \\
\text{HY}(6) &= 3.35410*10^3 + 4.5*E(I) \\
\text{HY}(8) &= -3.35410*10^3 - E(I) \\
\text{HY}(10) &= 1.3*E(I) + 7.5*E(I) \\
\text{HY}(13) &= -3.87298*10^3 - E(I) \\
\text{HY}(15) &= -1.3*E(I) + 7.5*E(I) \\
\text{HY}(19) &= -3.87298*10^3 - E(I) \\
\text{HY}(21) &= -3.3*E(I) + 4.5*E(I) \\
\text{HY}(26) &= -3.3*E(I) - E(I)
\end{align*} \]
HY(28) = -5. - 0.5*D -1.5*E(I)
HY(34) = -2.9129*D -E(I))
HY(36) = -7. -3.5*D -10.5*E(I)

CALL EIGEN(HY,V,8,0)
EY(1) = HY(1)
EY(2) = HY(3)
EY(3) = HY(6)
EY(4) = HY(10)
EY(5) = HY(15)
EY(6) = HY(21)
EY(7) = HY(28)
EY(8) = HY(36)
DO 51 K = 1,8
N1 = 8*(I-1) + K
EYX(N1) = EY(K)
51 EYX(N1) = 0
WRITE(3,69)((V(I,J),J = 1,8),I = 1,8)
69 FORMAT(8 E14.6)

C

C CALCULATE 1,2 AND 3 GAMMA PROBABILITIES P1Y,P2Y,P3Y.
N=0
NN1=7
NN2=1
CALL ZILCH(N,NN1,NN2,V)

C

C FOR THE Z-DIRECTION
HZ(1) = 7.0 - 7.*D
HZ(3) = 5. - D
HZ(4) = 4.58258*E(I)
HZ(6) = 3. - 3.*D
HZ(8) = 6.70821*E(I)
HZ(10) = 1. - 5.*D
HZ(13) = 7.74596*E(I)
HZ(15) = -1. - 5.*D
HZ(19) = 7.74596*E(I)
HZ(21) = -3. - 3.*D
HZ(26) = 6.70821*E(I)
HZ(28) = -5. + D
HZ(34) = 4.58258*E(I)
CALL EIGEN(HZ,V,8,0)
EZ(1) = HZ(1)
EZ(2) = HZ(3)
EZ(3) = HZ(6)
EZ(4) = HZ(10)
EZ(5) = HZ(15)
EZ(6) = HZ(21)
EZ(7) = HZ(28)
EZ(8) = HZ(36)
DO 52 K = 1,8
   N1 = 8*(I-1) + K
   EZX(N1) = EZ(K)
   EZY(N1) = 0
WRITE(3,79)((V(I3,J3),I3 = 1,8,J3 = 1,8)
79 FORMAT(32 EIGENVECTORS/8E14/.6) )

C CALCULATE 1,2 AND 3 GAMMA PROBABILITIES P1Z,P2Z,P3Z.
N=0
NN1=7
NN2=1
CALL ZILCH(N,NN1,NN2,V)

C
N=7
NN1=6
NN2=2
CALL ZILCH(N,NN1,NN2,V)

C
N=13
NN1=5
NN2=3
CALL ZILCH(N,NN1,NN2,V)

C
DO 36 K=1,7
   36 P1Z(K) = W(K)
DO 37 K=1,6
   37 P2Z(K) = W(K+7)
DO 38 K=1,5
   38 P3Z(K) = W(K+13)

C CALCULATE THE G VALUES FOR 1 GAMMA TRANSITIONS.
DO 7 K = 1,7
   G1X(K) = EX(K) - EX(K+1)
   G1Y(K) = EY(K) - EY(K+1)
   G1Z(K) = EZ(K) - EZ(K+1)
   X1X(K) = D /G1X(K)
   Y1X(K) = 2.0/G1X(K)
   X1Y(K) = D /G1Y(K)
   Y1Y(K) = 2.0/G1Y(K)
   X1Z(K) = D /G1Z(K)
   Y1Z(K) = 2.0/G1Z(K)
7 Y1Z(K) = 2.0/G1Z(K)

C CALCULATE THE G VALUE FOR 2 GAMMA TRANSITIONS.
DO 9 K = 1,6
   G2X(K) = EX(K) - EX(K+2)
   G2Y(K) = EY(K) - EY(K+2)
   G2Z(K) = EZ(K) - EZ(K+2)
X2X(K) = 0 /G2X(K)
Y2X(K) = 2.0/G2X(K)
X2Y(K) = 0 /G2Y(K)
Y2Y(K) = 2.0/G2Y(K)
X2Z(K) = 0 /G2Z(K)
Y2Z(K) = 2.0/G2Z(K)

C CALCULATE THE G VALUES FOR 3 GAMMA TRANSITIONS
DO 11 K = 1,5

G3X(K) = EX(K) - EX(K+3)
G3Y(K) = EY(K) - EY(K+3)
G3Z(K) = EZ(K) - EZ(K+3)
X3X(K) = 0 /G3X(K)
Y3X(K) = 2.0/G3X(K)
X3Y(K) = 0 /G3Y(K)
Y3Y(K) = 2.0/G3Y(K)
X3Z(K) = 0 /G3Z(K)
Y3Z(K) = 2.0/G3Z(K)

WRITE(3,17)

FORMAT(20A4)
READ(1,25)XL,YL,GL,OL
CALL GRAPH(NPTS,EXX,EXY,3,7,20.0,10.0,2.0,-20.0,0.5,0.0,XL,YL,GL,
C GOD
C READ(1,25)XL,YL,GL,OL

WRITE(3,17)

CONTINUE
C THE FOLLOWING CARDS WILL GIVE YOU ENERGY LEVEL GRAPHS. DIMENSION.
C NPTS = 8*NE
C 25 FORMAT(20A4)
C READ(1,25)XL,YL,GL,DL
C CALL GRAPH(NPTS,EXX,EXY,3,7,20.0,10.0,2.0,-20.0,0.5,0.0,XL,YL,GL,
C DL)
C READ(1,25)XL,YL,GL,DL
CALL GRAPH(NPTS,EYX,EYY,3,7,20.0,10.0,2.0,-20.0,0.5,0.0,XL,YL,GL,
        GDL)
READ(1,25)XL,YL,GL,D
CALL GRAPH(NPTS,EZX,EZY,3,7,20.0,10.0,2.0,-20.0,0.5,0.0,XL,YL,GL,
        GDL)
GO TO 1000
END
SUBROUTINE ZILCH(N,NN1,NN2,V)
C
C N1 AND N2 ARE THE LEVELS BETWEEN WHICH THE TRANSITION TAKES PLACE
C V IS THE MATRIX OF EIGENVECTORS.
C
DIMENSION V(8,8)
COMMON W(18)
DO 58 N1=1,NN1
     N2=N1+NN2
SPLUS=2.64575*(V(1,N1)*V(2,N2)+V(7,N1)*V(8,N2))
     S +3.46410*(V(2,N1)*V(3,N2)+V(6,N1)*V(7,N2))
     S +3.87298*(V(3,N1)*V(4,N2)+V(5,N1)*V(6,N2))
     S +4.0*V(4,N1)*V(5,N2)
SMINUS=2.64575*(V(2,N1)*V(1,N2)+V(8,N1)*V(7,N2))
     S +3.46410*(V(3,N1)*V(2,N2)+V(7,N1)*V(6,N2))
     S +3.87298*(V(4,N1)*V(3,N2)+V(6,N1)*V(5,N2))
     S +4.0*V(5,N1)*V(4,N2)
N3=N+N1
W(N3)=SPLUS**2 + SMINUS**2
58 CONTINUE
RETURN
END
//LKD.SYSLIB DD DSNAME=SYS1.FORTLIB,DISP=OLD
// DD DSNAME=SYS1.MATHLIB,DISP=OLD
//DD SYSIN DD *
  0.0  0.20  0.005  0.05
  0.0  0.40  0.01  0.10
/\
STRONG CRYSTAL FIELD GVALUE PROGRAM

This program is a one-shot deal to calculate all the possible gx, gy, and gz values associated with the Hamiltonian:

\[ H = D(SZ*2 - 1/3S(S + 1)) + E(SX*2 - SY*2) + \text{GOBH} \]

in the strong crystal field approximation. The equation is put in units of \( D \) and \( \Lambda = E/D \) so that the program solves the eigenvalue problem exactly.

Then the wave functions of \( H_0 \) are used in equations derived from perturbation theory to calculate the \( G \) values. The spin is specifically \( S = 7/2 \) and the 8x8 matrix is factored into 2 4x4 matrices which give the same set of 4 eigenvalues, i.e., we have a 2 fold spin degeneracy left in each level of \( H_0 \). The application of \( \text{GOBH} \)'s splits this degeneracy and the \( G \) values are calculated by setting this energy splitting equal to \( \text{GOBH} \) (x, y, or z direction). Wickman (J. Chem. Physics Vol. 42, 2110(1965)) has shown that \( \Lambda \) can be restricted to \( 0 < \Lambda < \frac{1}{3} \) to generate all the possible \( G \) values.

This range exhausts all + and - values of \( D \) and all ratios \( E/D \) needed. (\( E \) is greater or equal zero) the A, B, C, D refer to coefficients of the basis set which makes up the wavefunction of \( H_0 \). The only input cards are the graph labels.

```
REAL LAMBDA(101)
DIMENSION H(10),V(4,4),E(4),GX(4,101),GY(4,101),
GZ(4,101)
D X(5),Y(5),G(5),L(5),GX(101),GY(101),GZ(101),
DO 100 J = 1,10
DO 100 J = 1,10
HO = 7.0
H(2) = LAMBDA(I) * 5.0258
H(3) = -3.0
H(4) = 0
H(5) = LAMBDA(I) * 4.74596
H(6) = -5.0
H(7) = 0
H(8) = 0
H(9) = -LAMBDA(I) * 6.70821
H(10) = 1.0
DO 12 J1 = 1,10
DO 12 J2 = 1,10
V(J1,J2) = 0
CALL EIGEN(H,V,4,0)
DO 15 J = 1,14
```

200 FORMAT(20A4)
WRITE(3,3)
3 FORMAT(5I4,9X,4A4,9X,2A4,9X,2A4,9X,2A4,9X,2A4,9X,2A4)
ZERO = 0
DO 100 I = 1,35
IF(I-35)6,5,5
LAMBDA(I) = 0.33333
GO TO 7
6 LAMBDA(I) = ZERO + (I-1)*0.01
7 DO 10 J = 1,10
10 H(I,J) = 0
H(I) = 7.0
H(2) = LAMBDA(I) * 4.53258
H(3) = -3.0
H(4) = 0
H(5) = LAMBDA(I) * 7.74596
H(6) = -5.0
H(7) = 0
H(8) = 0
H(9) = -LAMBDA(I) * 6.70821
H(10) = 1.0
DO 12 J1 = 1,10
DO 12 J2 = 1,10
V(J1,J2) = 0
CALL EIGEN(H,V,4,0)
DO 15 J = 1,14
15 \( E(1) = 0 \)
\( E(1) = H(1) \)
\( E(2) = H(3) \)
\( E(3) = H(6) \)
\( E(4) = H(10) \)
WRITE(3,16)
16 FORMAT(3E16.10,2E11.5,3F10.5,3F8.3)

DO 20 K = 1,4
GX(K,I) = 4.0*ABS(2.64575*Vd,K)*V(4,K) + 3.87298*V(2,K)*V(3,K) + 
G 3.46410*V(2,K)*V(4,K) + 2.0*V(3,K)**2
GY(K,I) = 4.0*ABS(2.64575*Vd,K)*V(4,K) + 3.87298*V(2,K)*V(3,K) - 
G 3.46410*V(2,K)*V(4,K) - 2.0*V(3,K)**2
GZ(K,I) = 2.0*ABS(7.0*Vd,K)**2 + 3.0*V(2,K)**2 - V(3,K)**2

20 WRITE(3,1)LAMBDAtI),EtK),Vd,K),V(2,K),V(3,K),V(4,K),GX(K,I),
W GY(K,I),G2(I,K) __ 
1 FORMAT(F6.2,F11.5,4F10.5,3F8.3)
GX1(I) = GX(1,I)
GY1(I) = GY(1,I)
GZ1(I) = GZ(1,I)
GX2(I) = GX(2,I)
GY2(I) = GY(2,I)
GZ2(I) = GZ(2,I)
GX3(I) = GX(3,I)
GY3(I) = GY(3,I)
GZ3(I) = GZ(3,I)
GX4(I) = GX(4,I)
GY4(I) = GY(4,I)
GZ4(I) = GZ(4,I)

100 CONTINUE
READ (1,200)XL,YL,GL,DL
CALL GRAPH(35,LAMBDA,GX1,1,101,7.0,5.0,0.05,0.0,0.0,0,OL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GY1,2,101,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(35,LAMBDA,GZ1,3,101,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GX2,1,101,7.0,5.0,0.05,0.0,0.0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GY2,2,101,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GZ2,3,101,0,0,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(35,LAMBDA,GX3,1,101,7.0,5.0,0.05,0.0,0.0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GY3,2,101,0,0,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GZ3,3,101,0,0,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(35,LAMBDA,GX4,1,101,7.0,5.0,0.05,0.0,0.0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GY4,2,101,0,0,0,0,0,0,0,0,0,0,0,0,DL)
READ (1,200)DL
CALL GRAPH(101,LAMBDA,GZ4,3,101,0,0,0,0,0,0,0,0,0,0,0,0,0,DL)
STOP
END
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<th>GX1</th>
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