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THE EFFECTS OF STRONG VIBRONIC COUPLING ON
THE ELECTRON PARAMAGNETIC RESONANCE SPECTRA
OF D(3) AND D(4) IONS IN ALKALINE-EARTH
FLUORIDES.

RICE UNIVERSITY, PH.D., 1979
RICE UNIVERSITY

The Effects of Strong Vibronic Coupling on the Electron Paramagnetic Resonance Spectra of $d^3$ and $d^4$ Ions in Alkaline Earth Fluorides

by

Rudy Lester Prater

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

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HOUSTON, TEXAS

May, 1979
ABSTRACT

The Effects of Strong Vibronic Coupling on the Electron Paramagnetic Resonance Spectra of \( d^3 \) and \( d^4 \) Ions in Alkaline Earth Fluorides

by

Rudy Lester Prater

The influence of the Jahn-Teller Effect on the electron paramagnetic resonance of the orbital triplet states of various \( d^3 \) and \( d^4 \) ions in alkaline earth fluorides has been studied. Two new centers are reported, the \( Cr^{3+} \) ion in \( SrF_2 \) and the \( Cr^{2+} \) ion in \( SrF_2 \).

The spectra of the \( Cr^{3+} \) ion in alkaline earth fluorides are explained using a Spin Hamiltonian with \( S = \frac{3}{2} \) that has axial symmetry about \((111)\) axes. The Spin Hamiltonian parameters for \( SrF_2:Cr^{3+}, g_||, g_\perp\), and the zero field splitting parameter, \( D \), have been determined by measuring the effective \( g \)-values at frequencies near 9 GHz and 35 GHz. Similar spectra have also been observed for systems with isoelectronic impurities, \( CaF_2:Cr^{3+}, CdF_2:Cr^{3+}, CaF_2:V^{2+}, \) and \( SrF_2:V^{2+} \). The same parameters, which have been reported by other workers for these systems, have been remeasured so that comparisons can be made. The observed transition in all these systems is seen at 77K and 4.2K; the states involved in this transition are not sufficiently
populated at 1.3K. The symmetry of these systems is thought to arise from vibronic coupling of the triply degenerate ground electronic state with a triply degenerate vibrational mode.

The Cr$^{2+}$ ion in the eightfold coordination of the alkaline earth fluorides also has a triply degenerate ground electronic state. The spectra of this ion in SrF$_2$, CdF$_2$, and CaF$_2$ are explained with a Spin Hamiltonian with $S = 2$, which includes a dominant axial zero field term with its axis along the (110) directions of the crystal, a second order nonaxial zero field term and a fourth order zero field term with cubic symmetry. Two transitions are observed at the two frequencies, 9 GHz and 35 GHz. The transition between the $M_s = \pm 2$ states is observed at 1.3K and 4.2K. The transition between the $M_s = \pm 1$ states is observed only at 4.2K. No signal is observed from this ion at 77K. The significance of these data arises from the fact that, although every indication is that the symmetry of this center is due to a spontaneous distortion, distortions along the (110) axes are not predicted by theories of the Jahn-Teller Effect which include only the linear and harmonic vibronic coupling terms. These data represent a more complete experimental definition of these defects aimed at helping to explain the discrepancy between this theory and these observations.
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I. Introduction

Many of the marvels of the modern technological world rely on devices made from very pure materials that contain very low levels of carefully controlled impurities which modify the electronic, magnetic, or optical properties of the material in a desirable fashion. The success of these devices has contributed to the interest of solid state physicists in obtaining a complete understanding of the interactions which occur between an impurity and its crystalline host. The work in this thesis represents an attempt to learn more about the modifications of the electronic energy levels of an impurity which occur when the impurity atom is located in the environment of a crystalline host rather than in the isotropic environment characteristic of a free ion. Furthermore, the influence of the impurity on the crystal immediately surrounding it can be deduced from the modifications in the impurity's electronic states.

The initial step in theoretical calculations which describe electronic states in molecules and solids is to use the Born-Oppenheimer Approximation\(^1\) to separate the description of the motion of the nuclei from the description of the behavior of the electrons. The validity of this approximation relies on the fact that the nuclei are massive compared to the electrons and will respond only to an
average field produced by the faster moving, lighter electrons. The electrons, however, will move in a field produced by the essentially stationary nuclei. In 1937, ten years after the work of Born and Oppenheimer, H. A. Jahn and E. Teller published a paper which discussed an interesting exception to the separation of the electronic behavior and the vibrational motion of the nuclei which the Born-Oppenheimer Approximation described. This exception is now known as the Jahn-Teller Effect and an essential feature of it is that there is no longer this independence of the motion of the nuclei from the orbital state of the electrons. As originally put, the Jahn-Teller Theorem states that:

All nonlinear nuclear configurations are therefore unstable for an orbitally degenerate electronic state. \((2)\)

In other words, the orbitally degenerate electronic state will not be observed in a (geometrically) nonlinear configuration that is stable; if the system is in a nonlinear configuration which allows orbital degeneracy, any slight change in the configuration that lifts the degeneracy will lead to an arrangement of the nuclei that is more stable and that leaves the electronic state nondegenerate. They proved the theorem using group theoretical arguments and systematically demonstrated its validity for all possible symmetries. No comments were made about the magnitude of
the effect although the distinct implication of a static distortion was present.

Two general types of Jahn-Teller Effects have been studied since the formulation of the theorem. First, the static Jahn-Teller Effect is observed when a static distortion permanently lowers the symmetry of the configuration of the nuclei around the ion and thus removes the orbital degeneracy. The simplest case occurs when an ion with an orbital doublet state is located in a site that originally has cubic or octahedral symmetry. The nuclei of the neighboring atoms will be rearranged by the coupling to the degenerate electronic state and a spontaneous tetragonal distortion (along the $\langle 100 \rangle$ direction) will be observed. Spectra from the ion will not exhibit the isotropic behavior of the cubic site, but will show the anisotropic characteristics of a site with tetragonal symmetry.

The second type of effect, the dynamic Jahn-Teller Effect, is observed when the barriers between the distortions are low enough so that the system continually moves from one distorted configuration to another. The anisotropic characteristics of the static effect are no longer observed; the spectrum of such a system regains the isotropic characteristics of a system with no Jahn-Teller Effect. However, the effects of the coupling of the electronic state to the vibrational motion of the nuclei are not invisible; as the system moves constantly from one distorted configuration to
another, the electronic state changes in a correlated manner. The details of this behavior for orbital doublets can be found elsewhere\(^3\) but the essence is that the rotational motion of the electrons in their orbits can be thought of as hindered by the tie with the nuclei, and the interactions which involve the angular momentum of the electronic state are reduced from the magnitude they would have if there were no dynamic effect. This behavior and its relation to the spectra of orbital triplets will be discussed shortly, but first, some nomenclature should be introduced.

Twenty years after the original paper by Jahn and Teller was published, a series of papers by Moffitt and Liehr,\(^4\) Moffitt and Thorson,\(^5\) and Longuet-Higgins et al.,\(^6\) redeveloped the problem in a manner that emphasized the coupling between the vibrational states and the electronic states of the system. They coined the word "vibronic" to describe the results of this coupling. Using the ideas developed in their work, the electronic degeneracy is replaced by a vibronic degeneracy. Each static distortion corresponds to a different vibronic state so the double electronic degeneracy of the orbital doublet is converted to a triple vibronic degeneracy when the static effect creates the possibility of three symmetrically equivalent tetragonal distortions. The vibronic ground state for the dynamic effect is a vibronic doublet rather than a vibronic triplet but it can be described using linear
combinations of these vibronic states to form vibronic states that are descriptive of this extreme of coupling strengths. The theoretical framework they developed has broadened the implications of the Jahn-Teller Effect. Not only did it set the stage for the discovery of the dynamic effects by Ham in 1965,\(^{(7)}\) but it has become apparent that other phenomena can be explained very elegantly using the theoretical tools that were originally developed to explain the coupling of orbitally degenerate states to the vibrational motion of the nuclei. Some topics which are currently being investigated in this manner are studies of off-center and paraelastic defects, and diffusion of hydrogen in metals.

Prior to Ham's paper, Öpik and Pryce\(^{(8)}\) had succeeded in diagonalizing the vibronic Hamiltonian which described orbital triplet states but only at values of the energy which are stationary points with respect to the distortion coordinates. Their analysis predicted static distortions along either (100) axes or (111) axes depending on whether the orbital triplet coupled primarily to doubly degenerate vibrational modes or to triply degenerate vibrational modes. Ham's work, however, was motivated by observations of electron paramagnetic resonance spectra of the orbital triplet ground states of \(\text{Cr}^0\), \(\text{Mn}^+\), \(\text{Mn}^0\), and \(\text{Fe}^+\) at tetrahedrally coordinated interstitial sites in silicon.\(^{(9)}\)

The spectra were isotropic but the effective g-values were
shifted strongly from the values expected if there were no vibronic coupling. While the effects of covalency generally cause a g-shift, the observed shift was too large to be accounted for in this fashion. The data could be explained by a "quenching" of the contribution of the orbital angular momentum to the effective g-value; this "quenching" originates in the coupling of the orbital triplet to the vibrational motion of the ion's neighbors.

Many experimental techniques have been used to study the effects of vibronic coupling. One of the more popular methods has been to study the optical absorption and emission spectra. If structure is resolved, it is sometimes observed to differ radically from the expected vibrational structure and attempts are then made to explain the spectra in terms of the vibronic interactions. Raman spectroscopy has been used on a few systems\(^\text{10,11}\) and shows much potential for revealing the complicated vibronic structure that is not always resolved with absorption and emission techniques. Other optical data of current interest are the anomalous emission spectra of thallium-like impurities in alkali halides.\(^\text{12}\) Excitation in a single optical absorption band results in fluorescent emission in two bands. Current explanations focus on the possible existence in the excited orbitally degenerate states of either of two different distortion symmetries at a given site. The optical data are a challenge to interpret
unambiguously; if a complicated spectrum is observed, it must be determined whether the ground state or the excited state is responsible for the unusual features. Then, a great variety of phenomena can influence the spectra which can easily contain a minimal amount of information. Sturges' review,\(^{(13)}\) although ten years old, is an excellent discussion of the influence of vibronic coupling in optical spectra.

Another very productive technique for studying vibronic coupling effects is electron paramagnetic resonance (EPR), the technique used for the work in this thesis. The technique is a particular form of microwave spectroscopy which uses the application of a magnetic field to split the spin states of a ground manifold of electronic states until transitions between the states are observed which absorb microwave photons. These states can also be influenced by the electric fields which are produced by the rest of the atoms in the solid. An analysis of the magnitude of the magnetic field and its orientation with respect to the crystalline axes when resonance is achieved can provide valuable insight to the influence of the rest of the atoms in a solid on the ground state of the impurity. An excellent review was written by Ham\(^{(14)}\) which describes the influence of vibronic coupling on EPR spectra in general.

The understanding of the effects of vibronic coupling on the EPR of orbital triplets is still at a very early
stage. The first systematic study of tetragonal distortions was published in 1974 by Vallin and Watkins,\(^{(15)}\) a study of the Cr\(^{2+}\) ion in II-VI compounds. Several instances of trigonal or \langle111\rangle\) distortions have been reported\(^{(16-21)}\) but no systematic study has been made prior to this work. The Ham Effect for orbital triplets has been studied in four systems. Besides the interstitial transition metals in silicon which led Ham to the discovery of the effect, he has studied Fe\(^{2+}\) in MgO\(^{(22)}\) and similar spectra have been observed in CaO:Fe\(^{2+}\),\(^{(23)}\) and K\(_{2}\)FeF\(_{6}\) :Fe\(^{2+}\).\(^{(24)}\) The other systems in which dynamic effects have been studied are Cu\(^{2+}\) ions in ZnO,\(^{(25)}\) ZnS,\(^{(26)}\) CdS,\(^{(27)}\) and BeO\(^{(28)}\) as well as the ions Ti\(^{3+}\) and V\(^{4+}\) in Al\(_{2}\)O\(_{3}\).\(^{(29)}\)

Besides these studies of theoretically predicted behavior, there is another system that has been reported and studied as an example of vibronic coupling. The Cr\(^{2+}\) ion was observed by deWit, Reinberg, Holton, and Estle in 1964\(^{(30)}\) in CaF\(_{2}\) and CdF\(_{2}\). The EPR spectra displayed an axial symmetry about \langle110\rangle\) axes at low temperature. As the temperature was raised from 4.2K the spectra broadened and disappeared. Preliminary experiments were made with the application of uniaxial stress that indicated that even at the lowest temperatures the stress induced fast reorientations among the centers oriented along different \langle110\rangle\) directions. This behavior is expected if the anisotropy of the center is due to a distortion rather than an associated
defect. Since the theory outlined in Chapter II indicates that \(\langle 110 \rangle\) distortions should rarely if ever, be stable, a more complete experimental understanding of this \(\langle 110 \rangle\) distortion was one of the goals of this study.

One other possibility motivated the investigations in this thesis. The \(d^3\) ions, \(Cr^{3+}\) and \(V^{2+}\), in various alkaline earth fluorides exhibit \(\langle 111 \rangle\) distortions which imply a fourfold vibronic degeneracy. As discussed in Chapter II, it is possible that a tunneling splitting will split this vibronic quartet into a vibronic triplet and a vibronic singlet. The hope was that some unusual effects would be observed in some of these systems as a result of this splitting. Since there are six equivalent \(\langle 110 \rangle\) directions, the vibronic degeneracy of the other system discussed here, \(Cr^{2+}\) in alkaline earth fluorides, is a six-fold degeneracy. The fact that this system is not predicted by theory seems to imply that the likelihood would be great for a tunneling splitting to cause some unusual dynamic effects. These points will be discussed in greater detail in Chapter II.

After the theoretical discussion in Chapter II and the description of the experimental apparatus in Chapter III, a discussion of the Spin Hamiltonians will be found in Chapter IV. This chapter is a convenient theoretical stopping point between the more abstract theory of Chapter II and the experimental results of Chapters V and VI. Finally, Chapter V
will discuss the experimental results and analysis of the d^3 ions, Cr^{3+} and V^{2+} in SrF_2, CaF_2, and CdF_2, while Chapter VI will do the same for the d^4 ion, Cr^{2+}, in SrF_2, CdF_2, and CaF_2. Particular attention will be paid to the results from the SrF_2:Cr system since this impurity in this host has never been reported prior to this work.
II. Theory

A. Assumptions for the Solution of Iron Group Impurity Electronic Problems in Solids

During the last fifty years, much effort has been invested in the understanding of the electronic properties of isolated atoms and free ions. A fairly complete understanding of the grosser aspects of this problem has been obtained and some of the approximations involved serve as an excellent starting point for the study of iron group impurity electronic states in solids. The general program is to describe the effects of the impurity nucleus and impurity electrons on the electronic states; then, the effects of the incorporation of the atom in the solid lattice are considered as modifications to the free ion electronic structure. Care must be taken that each interaction is considered in order of decreasing interaction energy regardless of whether the interaction originates from the free ion approximations or the impurity-solid effects. Different impurities, the rare earths, for example, deviate from the scheme outlined below.

The Hamiltonian which describes the electronic states of a free iron group ion will contain three types of terms which are much larger than any other, (1) the kinetic energy term for each electron, (2) the radial potential energy term for each electron describing the
interaction with the nucleus, and (3) the inter-electron Coulomb potential energy terms. If the third set of terms is separated into a dominant radial part and a remnant non-radial contribution, the original N-electron problem becomes N one-electron problems which are modified by the non-radial remnant as a perturbation. Using the resulting single electron wave functions, the atomic configurations can be constructed. These configurations consist of an inner core of filled orbitals, an outer incomplete shell of valence electrons, and an incomplete inner shell of d electrons. About $10^4$ cm$^{-1}$ separates the energies of the lowest configurations, but a high degree of degeneracy remains.

The next strongest interaction which removes some of this degeneracy is usually one of three, either (1) the residual, non-radial component of the inter-electron interaction, (2) the crystal field, or (3) the spin-orbit interaction. In the transition groups, the magnitudes of these three interactions have been observed to have comparable values; they are usually applied in this sequence when describing iron group impurities. When the first term is included, the Russell-Saunders Coupling will couple the $\vec{s}_i$ of the d-shell electrons to each other and the $\vec{\lambda}_i$ to each other. The result is a set of atomic terms characterized by $\vec{S}$ and $\vec{L}$, the total spin and orbital angular momentum of the ion. The ground term can be determined using
Hund's Rules. For the \( d^3 \) ionic configuration of \( \text{Cr}^{3+} \) and \( \text{V}^{2+} \) discussed in this thesis, the ground term is \( ^4F \) while for the \( d^4 \) ionic configuration of \( \text{Cr}^{2+} \), the ground term is \( ^5D \). Since the terms are split in energy by \( 10^4 \) to \( 10^5 \) cm\(^{-1} \) compared to the energy of a 30 GHz photon, about 1 cm\(^{-1} \), the ground term is of primary interest to EPR spectroscopists. The excited terms will influence the properties of the ground term and should not be ignored in a complete calculation.

2) Influence of a Crystal Field on Free Ion Energy Levels

The crystal field approximation can be used to describe the effects of the presence of the other atoms in the solid on the atomic terms. While care should be taken that the picture of the crystal field as an electric field produced by the atoms in the lattice is not taken too seriously when the iron group impurities are considered (a ligand field is more appropriate), the crystal field does describe the symmetry characteristics of the interaction very effectively. As a result, it can serve as the basis for a phenomenological model which builds on one set of experimental measurements to help explain another set; for example, optical absorption data can be used to estimate parameters which explain EPR data.

Therefore, the restrictions of cubic, or lower, symmetry are imposed on the Hamiltonian which describes
the impurity's electronic states and on its eigenfunctions. The degeneracies which are allowed by symmetry can then be obtained as well as the relative energy differences between different energy levels which are split from the same free ion term. The largest splittings are often obtained from lowering the symmetry from spherical symmetry (the free ion symmetry group) to cubic symmetry, even when the crystal structure or ion site has lower symmetry. Then, the effects of symmetry elements which remove the cubic symmetry can be included as a perturbation when the magnitude of these effects is significant.

A cubic crystal field will split the $^4F$ term of the $d^3$ configurations of $\text{Cr}^{3+}$ and $\text{V}^{2+}$ into two orbital triplets, $^4T_2$ and $^4T_1$, and an orbital singlet, $^4A_2$, as indicated in Figure II-1a. If an electric field with cubic symmetry is assumed, a single parameter, $D_q$, will describe the relative energy differences of the three levels, as indicated. The sign of $D_q$ determines whether the $^4A_2$ or $^4T_1$ states are the lowest of the three while the magnitude of $D_q$ determines the overall magnitude of the splittings. In eight-fold coordination, the $d^3$ configuration produces the ground orbital triplet state of interest in this research. The same cubic crystal field will split the $^5D$ ground term of $\text{Cr}^{2+}$ into a doublet, $^5E$, and a triplet, $^5T_2$, as shown in Figure II-1b. Again, a single parameter, $D_q$, describes the splitting and its sign indicates whether
Figure II-1. Splittings of the Ground Terms of the
(a) d$^3$ and (b) d$^4$ Configurations in a Cubic Crystal Field
the doublet or triplet state is lowest in energy. For eight-fold coordination, the $d^4$ configuration produces the ground triplet, $^5T_2$.

A detailed theoretical discussion of the value of $Dq$ as well as the effects of spin-orbit coupling and the strong crystal field effects can be found in Abragam and Bleaney (31) as well as other sources. (32, 33)

3) The Cluster Approximation

Vibronic coupling theories describe a breakdown in the separation of the mathematical problems which describe the motion of the nuclei and the behavior of the electrons. Some method has to be formulated for including the effects of the movement of the nuclei in the electronic Hamiltonian. The number of nuclei in the solid is large and so the number of degrees of freedom will be great. When formulating theories to explain vibrational behavior, the concept of normal modes of oscillation of the crystal is usually used. Ideally, for a study of vibronic coupling, these normal modes of the crystal would be combined with terms that depend on the electronic states of the impurity to form a vibronic Hamiltonian. However, even if the phonon modes are classified according to their symmetry properties, the number of phonons that need to be included in a given term of the vibronic Hamiltonian is inconvenient. The Cluster Model assumes that a single mode of vibration of the cluster of atoms which immediately surround the
impurity is sufficient to describe the vibronic coupling effects which arise from all phonon modes with the same symmetry properties. This mode is usually thought of as a normal mode of the impurity's nearest neighbors, or the strongest coupling normal mode of that symmetry when there is more than one.

The primary justifications for the use of this model in the orbital triplet problem is that it works so well in attempts to describe the vibronic coupling effects of orbital doublets. The exact connection between the frequency, effective mass, and nuclear motions of the cluster normal modes and the same parameters of the real phonon modes of the crystal are not clear although attempts have been made to address this problem. Another question concerns the possibility that two modes with different frequencies but comparable coupling strengths might both influence the system's behavior. The most important problem initially, though, is a complete understanding of the effects of coupling to a single mode.

B. Forming the Vibronic Hamiltonian

1) Sketching the Problem

The object of the theory as stated in the previous section is to write a Hamiltonian which describes the influence of a change of position of the nuclei surrounding an impurity on the electronic states of the impurity. First, the restrictions which symmetry places on the form of
the Hamiltonian and the ramifications of these restrictions on the formation of each term will be discussed. Then, the symmetry characteristics and notation of the basis states, the operators, and the normal modes will be introduced. Finally, the terms of the Hamiltonian will be presented.

The crystallographic point group, $O_h$, is the group which describes the point symmetry of the cation site in the alkaline earth halides. Therefore, the basis states and operators used to describe the vibronic interactions will transform according to this group. For reference, the character table, multiplication table, compatibility table, and assorted coupling tables are reproduced in Tables II-1, II-2, II-3, and II-4. This development will be valid for any of the five cubic groups that allow the existence of orbital triplets with primarily notational variations.

2) Symmetry Requirements

The two requirements restricting the form of any Hamiltonian operator which describes a physical system are:

(i) The Hamiltonian must be Hermitian so that the eigenvalues (the energies) are real numbers.

(ii) The Hamiltonian must be invariant under the symmetry operations (both spatial and temporal) which apply to the physical system.
<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$E$</th>
<th>$E'$</th>
<th>$8C_2$</th>
<th>$8C_2'$</th>
<th>$3C_4$</th>
<th>$3C_4'$</th>
<th>$6C_4$</th>
<th>$6C_4'$</th>
<th>$l$</th>
<th>$T$</th>
<th>$8S_4$</th>
<th>$8S_4'$</th>
<th>$3σ_h$</th>
<th>$3σ_h'$</th>
<th>$6σ_d$</th>
<th>$6σ_d'$</th>
<th>Time</th>
<th>Inv.</th>
<th>Bases</th>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>R</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
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</tr>
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<td>-1</td>
<td>2</td>
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<td>2</td>
<td>-1</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>$(2x^2 - x^2 - y^2), \sqrt{3}(z^2 - y^2)$</td>
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</tr>
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<td>0</td>
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<td>1</td>
<td>1</td>
<td>-1</td>
<td>a</td>
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<td>-1</td>
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<td>-1</td>
<td>a</td>
<td>$x, x, x$</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>a</td>
<td>$\Gamma_1'^* \times \Gamma_1'^*$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>-1</td>
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<td>$x, x, x$</td>
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<tr>
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<td>-1</td>
<td>2</td>
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<td>-2</td>
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<td>1</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>a</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>a</td>
<td>$x, y, z$</td>
<td></td>
</tr>
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<td>-3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>a</td>
<td>$\Gamma_5 \times \Gamma_5$</td>
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11
Table II-2.

Multiplication Table for the Group $O_h^{(15)}$

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<th>$\Gamma_1$</th>
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<th>$\Gamma_3$</th>
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<th>$\Gamma_7$</th>
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<td>$\Gamma_4$</td>
<td>$\Gamma_5$</td>
<td>$\Gamma_6$</td>
<td>$\Gamma_7$</td>
<td>$\Gamma_8$</td>
<td>$\Gamma_1$</td>
</tr>
<tr>
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<td>$\Gamma_2$</td>
<td>$\Gamma_3$</td>
<td>$\Gamma_4$</td>
<td>$\Gamma_5$</td>
<td>$\Gamma_6$</td>
<td>$\Gamma_7$</td>
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<td>$\Gamma_3$</td>
<td>$\Gamma_4$</td>
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<td>$\Gamma_6$</td>
<td>$\Gamma_7$</td>
<td>$\Gamma_8$</td>
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<td>$\Gamma_3$</td>
<td>$\Gamma_4$</td>
<td>$\Gamma_5$</td>
<td>$\Gamma_6$</td>
<td>$\Gamma_7$</td>
<td>$\Gamma_8$</td>
<td>$\Gamma_1$</td>
</tr>
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<td>$\Gamma_2$</td>
<td>$\Gamma_3$</td>
<td>$\Gamma_4$</td>
<td>$\Gamma_5$</td>
<td>$\Gamma_6$</td>
<td>$\Gamma_7$</td>
<td>$\Gamma_8$</td>
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Table II-3.

Compatibility Table for $O_h$ and Several Lower Symmetry Groups

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$E$</th>
<th>$T$</th>
<th>$T'$</th>
<th>$E'$</th>
<th>$T''$</th>
<th>$E''$</th>
<th>$T'''$</th>
<th>$T'''$</th>
<th>$E'''$</th>
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<tbody>
<tr>
<td>$O$</td>
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<td>$T_2$</td>
<td>$T_3$</td>
<td>$E$</td>
<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
<tr>
<td>$T_h$</td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$T_3$</td>
<td>$E$</td>
<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
<tr>
<td>$T_d$</td>
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<td>$T_2$</td>
<td>$T_3$</td>
<td>$E$</td>
<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
<tr>
<td>$D_{th}$</td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$T_3$</td>
<td>$E$</td>
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<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
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<tr>
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<td>$T_2$</td>
<td>$T_3$</td>
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<td>$T_2'$</td>
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<td>$E'$</td>
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<td>$T_3$</td>
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<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
<tr>
<td>$C_{3v}$: $III_w$</td>
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<td>$T_2$</td>
<td>$T_3$</td>
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<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
<tr>
<td>$C_{4v}$: $E(2)$</td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$T_3$</td>
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<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
<tr>
<td>$C_{2v}$: $E(v)$</td>
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<td>$T_3$</td>
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<td>$E'$</td>
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<td>$T_3''$</td>
</tr>
<tr>
<td>$C_{2v}$: $E(w)$</td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$T_3$</td>
<td>$E$</td>
<td>$T_2'$</td>
<td>$T_3'$</td>
<td>$E'$</td>
<td>$T_2''$</td>
<td>$T_3''$</td>
</tr>
</tbody>
</table>
Table II-4.

Selected Coupling Tables for the Group $O_h^{(2s)}$

$\psi^j_i$ is the function that transforms like the $i^{th}$ partner of the $j^{th}$ irreducible representation. $u^j_i$ and $v^j_i$ are the basis functions whose products sum to form the $\psi^j_i$.

<table>
<thead>
<tr>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
<th>$u^j_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega^4$</td>
<td>-$\sqrt{3}$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\omega^4$</td>
<td>0</td>
<td>$\sqrt{2}$</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\omega^4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\omega^4$</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$\sqrt{2}$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\omega^4$</td>
<td>0</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$\sqrt{2}$</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\omega^4$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$u^j_i$ transforms as $3x^2 - r^2$

$u^j_i$ transforms as $\sqrt{2}(x^2 - y^2)$
It is sufficient to apply these criteria term by term to the Hamiltonian. Since the $\Gamma_1^+$ irreducible representation is the invariant in all of the crystallographic point groups, each term should transform like $\Gamma_1^+$. Since the vibronic Hamiltonian is formed from the product of a function of the vibrational coordinates with the electronic operators, the prescription for matching these is necessary. Since, in general, the product $\Gamma_i \otimes \Gamma_i$ contains $\Gamma_1^+$, it is necessary that the electronic operator of a given symmetry be coupled with a function of the nuclear coordinates having the same symmetry. For multicomponent irreducible representations, the partners can be coupled according to the coupling tables, usually matching terms that transform like each partner with each other as in a Cartesian scalar product.

3) The States

When the physical system is invariant under the symmetry operations of the group $O_h$, orbital triplet electronic states can only transform like one of the four three-dimensional irreducible representations, $\Gamma_4^+$, $\Gamma_4^-$, $\Gamma_5^+$, or $\Gamma_5^-$. Recalling from Section II.A.2 that the cubic field leaves a $^5T_2$ ($\Gamma_5^+$) state lowest for $Cr^{2+}$ and a $^4T_1$ ($\Gamma_4^+$) lowest for $Cr^{3+}$ and $V^{2+}$, these are then the triplet electronic states under consideration. If, in the multiplication tables and coupling tables the $\Gamma_1$ and $\Gamma_2$ irreducible representations replace each other as do the
\( \Gamma_4 \) and \( \Gamma_5 \) representations, the tables remain correct, so the two types of triplets will behave identically except for the switch of subscripts. Therefore, the formalism only has to be worked out for one of the triplets. The difference between the two is apparent when perturbation calculations with other states are attempted; this difference will be discussed in Section II.E.3.

Here, the theory will be worked out using the notation of a \( \Gamma_5^+ \) state which transforms like the polynomials, \( yz, zx, \) and \( xy \), and will be denoted by \( |\xi\rangle, |\eta\rangle \) and \( |\zeta\rangle \).

4) The Operators

Any operator which acts on this basis of three states can be formed from a linear combination of the nine elementary projection operators \(^{(36)} \) defined by the relation:

\[
P_{ij} = |i\rangle\langle j|
\]

(II-1)

However, it is often more convenient in a high symmetry situation to use nine linear combinations of the \( P_{ij} \) which have the symmetry characteristics of the problem. Since these are obtained from the direct product of the basis, the nine symmetrized operators obtained from \( \Gamma_5^+ \otimes \Gamma_5^+ = \Gamma_1^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_5^+ \) can be written down from the coupling tables, Table II-4. They are given in Table II-5.
Table II-5

The Nine Symmetrized Electronic Operators

for an Orbital Triplet in $O_h$

transforming like $\Gamma_1^+$ is:

$$\mathcal{O} = |\xi\rangle\langle\xi| + |\eta\rangle\langle\eta| + |\zeta\rangle\langle\zeta| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

transforming like $\Gamma_3^+$ are:

$$U_\theta = \frac{1}{2}(|\xi\rangle\langle\xi| + |\eta\rangle\langle\eta| - 2|\zeta\rangle\langle\zeta|) = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$U_\zeta = \frac{\sqrt{3}}{2}(|\xi\rangle\langle\xi| + |\eta\rangle\langle\eta|) = \begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

transforming like $\Gamma_4^+$ are:

$$U_x = i(|\eta\rangle\langle\zeta| - |\zeta\rangle\langle\eta|) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$U_y = i(|\zeta\rangle\langle\xi| - i|\xi\rangle\langle\zeta|) = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$$

$$U_z = i(|\xi\rangle\langle\eta| - |\eta\rangle\langle\xi|) = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

transforming like $\Gamma_5^+$ are:

$$U_\zeta^+ = -(|\eta\rangle\langle\zeta| + |\zeta\rangle\langle\eta|) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$
Table II-5 Continued

\[ U_\eta = - (|\xi\rangle\langle\xi| + |\bar{\xi}\rangle\langle\bar{\xi}|) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \]

\[ U_\zeta = - (|\bar{\xi}\rangle\langle\bar{\xi}| + |\eta\rangle\langle\eta|) = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]
5) The Modes

The electronic operators will be multiplied by combinations of the normal modes that have the appropriate transformation properties under the symmetry operations of the group. The normal modes are symmetrized combinations of displacements of the nuclei of the cluster. A general function of the normal modes can be written as a Taylor series expansion of all of the normal mode coordinates. The lower order terms of the expansion should produce the strongest physical effects. Therefore, the normal modes which couple linearly with the electronic operators will be the most important in stabilizing a particular distortion. Since the electronic operators transform like \( \Gamma_1^+ \), \( \Gamma_3^+ \), \( \Gamma_4^+ \) and \( \Gamma_5^+ \), only normal modes with these symmetries can couple linearly with an electronic operator to produce a vibronic term with the required \( \Gamma_1^+ \) symmetry. A \( \Gamma_1^+ \) mode is the breathing mode and affects all electronic levels equally since it does not change the symmetry of the site. It will be ignored. The \( \Gamma_4^+ \) electronic operators, when made Hermitian, are odd under time reversal symmetry and this would require that the \( \Gamma_4^+ \) normal mode be odd under time reversal in order for the product to be even. Since the displacement of nuclei is even under time reversal, the \( \Gamma_4^+ \) mode cannot be odd under time reversal and cannot couple. Hence, linear vibronic coupling can only occur for \( \Gamma_3^+ \) and \( \Gamma_5^+ \) normal modes when coupling to an orbital triplet.
The higher order terms can be classified according to irreducible representations using repeated direct products of the representations and the coupling tables can be used to write the polynomial forms used in the next section. Higher order combinations of normal modes that do not couple linearly to the electronic states should also be considered in a complete discussion. Except for a few specific higher order terms mentioned in Section II.C.3, the anharmonic and nonlinear terms, as these are known, will be ignored because their effects should be small compared to the effects of the linear and harmonic terms.

6) The Hamiltonian

Following the guidelines of the previous sections, the vibronic Hamiltonian for an orbital triplet state in the linear coupling and harmonic approximations is:

\[ \hat{\mathcal{H}}_V = \left[ \frac{1}{2} k_E (Q_\theta^2 + Q_\zeta^2) + \frac{1}{2} k_T (Q_\zeta^2 + Q_\eta^2 + Q_\eta^2) \right] \dot{Q} \]

\[ + V_E (Q_\theta U_\theta + Q_\zeta U_\zeta) + V_T (Q_\zeta U_\zeta + \eta U_\eta + \eta U_\eta) \]  \hspace{1cm} (II-2)

The parameters are:

- \( Q_\theta, Q_\zeta \) = the coordinates which transform as partners of the doubly degenerate vibrational mode.
- \( Q_\zeta, Q_\eta, Q_\eta \) = the coordinates which transform as partners of the triply degenerate vibrational mode.
- \( V_E, V_T \) = the linear Jahn-Teller coupling coefficients for the doublet and triplet vibrational modes, respectively.
\( k_E, k_T \) \( \equiv \) the force constant in the elastic energy terms for the doublet and triplet vibrational modes.

For a study of dynamic aspects of the problem, the kinetic energy terms must be included. They are:

\[
\kappa_{\text{K.E.}} = \left[ \frac{1}{2 \mu_E} \left( P_\theta^2 + P_z^2 \right) + \frac{1}{2 \mu_T} \left( P_\xi^2 + P_\eta^2 + P_z^2 \right) \right] Q
\]  

(II-3)

where the \( P_i \)'s are the conjugate momenta of the normal mode amplitudes, \( Q_i \), and the constants \( \mu_E \) and \( \mu_T \) are effective masses for the two vibrational modes.

Finally, the lowest order nonlinear and anharmonic combinations of \( \Gamma_3 \) and \( \Gamma_5 \) modes will be discussed. They take the form:

\[
\kappa_{\text{H.O.}} = \left[ v_2 Q_\theta (3 Q_z^2 - Q_\theta^2) + v_3 Q_\xi Q_\eta Q_z \right] + \left[ v_4 \left( 2 Q_z^2 - Q_\xi^2 - Q_\eta^2 \right) Q_\theta + \sqrt{3} Q_z (Q_z^2 - Q_\eta^2) \right] Q_\theta + \left[ v_5 \left( Q_z^2 - Q_\theta^2 \right) Q_\eta + 2 Q_\theta Q_z U_\xi \right] + \left[ v_6 \left( 2 Q_z^2 - Q_\xi^2 - Q_\eta^2 \right) U_\theta + \sqrt{3} (Q_z^2 - Q_\eta^2) U_\xi \right] + \left[ v_7 \left( Q_\xi U_\zeta + Q_\eta U_\eta + Q_z U_\xi \right) + v_8 \left( -Q_\theta + \sqrt{3} Q_z \right) Q_\xi U_\zeta - \left( Q_\theta + \sqrt{3} Q_z \right) Q_\eta U_\eta + 2 Q_\theta Q_z U_\zeta \right]
\]  

(II-4)

This equation is complex enough that exploring the limiting cases is time consuming, and not truly enlighten-
ing; results of a specific calculation which includes these terms will be discussed in Section II.C.3. The inclusion of other vibrational modes of the cluster, notably the off-center vibrational mode, will not be discussed.

In the following sections, solutions of the vibronic Hamiltonian will be discussed according to the many limiting cases and approximations which have been used.

C. Solving the Eigenvalue Problem for the Vibronic Hamiltonian - Static Effects

1) Öpik and Pryce Method for Finding Minima

The initial approach to solving the vibronic coupling problem was to investigate the results when the coupling terms in Equation II-2 dominated the kinetic energy terms. This is called the "strong coupling limit" and leads to the static distortions which most people associate with the Jahn-Teller Effect. The general approach is to determine the energies of the eigenstates as a function of the vibrational mode amplitudes, \( E_i(Q_1, \ldots, Q_n) \), and then, to locate the energy minima of these n-dimensional surfaces. As discovered by Öpik and Pryce in 1957,\(^8\) it is not necessary to be able to explicitly find \( E_i(Q_1, \ldots, Q_n) \); it is possible to locate the stationary points and then to determine the conditions
that make these points minima and maxima. Since the analytical method of solving the secular equation requires the solution of a cubic equation and the analytical form of \( E(Q_1, \ldots, Q_n) \) is not very revealing, the method of Öpik and Pryce will be sketched here.

The first step is to substitute the general expression for an eigenstate:

\[
|\psi\rangle = \alpha |\xi\rangle + \beta |\eta\rangle + \gamma |\zeta\rangle
\]

(II-5)

into the matrix element that gives the energy:

\[
\langle \psi | H_V | \psi \rangle = E \langle \psi | \psi \rangle = E
\]

(II-6)

This substitution gives:

\[
E = \frac{1}{2} k_E (Q_\eta^2 + Q_\epsilon^2) + \frac{1}{2} k_T (Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)
- \frac{1}{2} V_E \left[ Q_\eta (2\gamma^2 - \alpha^2 - \beta^2) + \sqrt{3} Q_\epsilon (\alpha^2 - \beta^2) \right]
- 2V_T (Q_\xi \beta \gamma + Q_\eta \gamma \alpha + Q_\zeta \alpha \beta)
\]

(II-7)

Now, the stationary points with respect to each \( Q_i \) are found by setting the partial derivative with respect to \( Q_i \) equal to zero. The results are conditions on the value of each \( Q_i \) at the stationary points:

\[
Q_\eta = \frac{V_E}{k_E} \left( 2\gamma^2 - \alpha^2 - \beta^2 \right)
\]

\[
Q_\epsilon = \frac{V_E}{k_E} \sqrt{3} (\alpha^2 - \beta^2)
\]

\[
Q_\xi = \frac{2V_T}{k_T} \beta \gamma
\]
\[ Q_{\eta} = \frac{2V_T}{k_T} \gamma \alpha \]
\[ Q_{\xi} = \frac{2V_T}{k_T} \alpha \beta \] (II-8)

To find the energy at the stationary points, substitute these values into equation (II-7) and some algebra yields:
\[ E = -\frac{V_E^2}{k_E} + \left( \frac{3V_E^2}{k_E} - \frac{2V_T^2}{k_T} \right) \left( \gamma^2 + \gamma^2 \alpha^2 + \alpha^2 \beta^2 \right) \] (II-9)

Now, implement the method of undetermined multipliers to determine \( \alpha, \beta, \) and \( \gamma. \) Since normalization gives:
\[ \alpha^2 + \beta^2 + \gamma^2 = 1 \] (II-10)
the partial derivative of the expression:
\[ E - \lambda (\alpha^2 + \beta^2 + \gamma^2 - 1) \] (II-11)
with respect to \( \alpha, \beta, \) and \( \gamma \) will be zero. Three equations must then be satisfied; they are:
\[ \alpha (\gamma^2 + \beta^2) B - \lambda \alpha = 0 \] (II-12a)
\[ \beta (\alpha^2 + \gamma^2) B - \lambda \beta = 0 \] (II-12b)
\[ \gamma (\alpha^2 + \beta^2) B - \lambda \gamma = 0 \] (II-12c)
with:
\[ B = \frac{3V_E^2}{k_E^2} - \frac{2V_T^2}{k_T^2} \] (II-13)
Each equation has two possible solutions:

\[ \alpha = 0 \quad \text{or} \quad \alpha^2 = 1 - \frac{1}{B} \lambda \]  \hspace{1cm} \text{(II-14a)}

\[ \beta = 0 \quad \text{or} \quad \beta^2 = 1 - \frac{1}{B} \lambda \]  \hspace{1cm} \text{(II-14b)}

\[ \gamma = 0 \quad \text{or} \quad \gamma^2 = 1 - \frac{1}{B} \lambda \]  \hspace{1cm} \text{(II-14c)}

Since these must be compatible with the normalization condition, equation (II-10), \( \alpha, \beta, \) and \( \gamma \) cannot all be zero. There are three categories of solutions, though, which correspond to whether one, two, or all three of \( \alpha, \beta, \) and \( \gamma \) are nonzero. These solutions for the energy and coordinates of stationary points are given in Table II-6.

2) The Minima

The question concerning the conditions for each of these to be either minima or other types of stationary points has yet to be discussed. Öpik and Pryce used a variational technique, but this development does not require that rigor. Note that, in equation (II-9) the quantity \( (\alpha^2 \beta^2 + \gamma^2 + \alpha^2 \gamma^2) \) is always non-negative taking the values of 0, \( \frac{1}{4}, \) and \( \frac{1}{3} \) for stationary points I, II and III respectively. Therefore, an examination of the coefficient, \( B, \) will indicate which of the stationary points will be lowest in energy.

(a) Tetragonal Distortions

For \( B > 0, \) the energies of the stationary points are:
Table II-6

Coordinates and Energies of Stationary Points of the Adiabatic Potential Energy Surface for Orbital Triplets

I. For $\alpha^2 = 1$, $\beta = \gamma = 0$ (and cyclic permutations)

The Jahn-Teller Energy is: $E_I = -\frac{V_E^2}{k_E}$

Typical Distortion coordinates are:

$Q_\theta = -\frac{1}{2} \frac{V_E}{k_E}$, $Q_\varepsilon = \frac{\sqrt{3}}{2} \frac{V_E}{k_E}$, $Q_\zeta = Q_\eta = Q_\xi = 0$

The Electronic State for this distortion will be:

$\psi = |\xi\rangle$

There are three pure tetragonal $(\langle 100 \rangle)$ distortions.

II. For $\alpha^2 = \beta^2 = \frac{1}{2}$, $\gamma = 0$ (and cyclic permutations)

The Jahn-Teller Energy is:

$E_{II} = -\frac{V_E^2}{k_E} + \frac{3}{4} \left( \frac{V_E^2}{k_E} - \frac{2V_T^2}{k_T} \right)$

Typical Distortion Coordinates are:

$Q_\theta = -\frac{1}{2} \frac{V_E}{k_E}$, $Q_\varepsilon = \frac{V_T}{k_T}$, $Q_\zeta = Q_\eta = 0$

The Typical Electronic State will have the form:

$\psi = \text{(constant)} \times (|\xi\rangle \pm |\eta\rangle)$

There are six orthorhombic $(\langle 110 \rangle)$ distortions.
Table II-6 Continued

III. For $\alpha^2 = \beta^2 = \gamma^2 = \frac{1}{3}$

The Jahn-Teller Energy is:

$$E_{III} = -\frac{V_E^2}{k_E} + \frac{1}{3}\left(\frac{3V_E^2}{k_E} - \frac{2V_T^2}{k_T}\right)$$

Distortion Coordinates are given by:

$$Q_\xi = m_{1i}\frac{2V_T}{3k_T}, \quad Q_\eta = m_{2i}\frac{2V_T}{3k_T}, \quad Q_\zeta = m_{3i}\frac{2V_T}{3k_T}$$

$Q_\theta = Q_\zeta = 0$

with the $m_{ij}$ given by:

<table>
<thead>
<tr>
<th>$i$</th>
<th>$m_{1i}$</th>
<th>$m_{2i}$</th>
<th>$m_{3i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The $i^{th}$ electronic state is:

$$\psi_i = m_{1i}|\xi\rangle + m_{2i}|\eta\rangle + m_{3i}|\zeta\rangle$$

There are four pure trigonal $(\langle 111\rangle)$ distortions.
I. \[ E = - \frac{V_E^2}{k_E} \]

II. \[ E = - \frac{1}{2} \frac{V_E^2}{k_E} - \frac{V_T^2}{2k_T} > - \frac{V_E^2}{k_E} \] (II-15)

III. \[ E = - \frac{2}{3} \frac{V_T^2}{k_T} > - \frac{V_E^2}{k_E} \]

where the inequalities are derived from the condition that \( B > 0 \). The tetragonal distortions which result are most often discussed as the limiting case when the orbital triplet couples only to \( Q_\theta \) and \( Q_\varepsilon \) and all other coupling is neglected. As indicated in Table II-6, the electronic states are not mixed by the vibronic coupling, only the energy of each state is affected. A configuration coordinate diagram, a plot of energy as a function of the vibrational coordinates, is composed of three disjoint paraboloids with each minimum corresponding to a tetragonal distortion along a different cubic axis. Since the paraboloids are disjoint, a unique electronic state is associated with each paraboloid and, hence, with each distortion. So, the adiabatic approximation is still applicable, and the vibronic states are each a product of an electronic state with a vibrational state, a two-dimensional harmonic oscillator state. The ground vibronic state is triply degenerate, composed of the lowest vibrational state in each of the three wells. Hence, the effect of the vibronic coupling is to change the degeneracy from an electronic degeneracy to a vibronic degeneracy.
(b) Trigonal Distortions

Similarly, for $B < 0$, the energies of the stationary points are:

\[ I. \quad E = - \frac{v_E^2}{k_E} > - \frac{2}{3} \frac{v_T^2}{k_T} \]

\[ II. \quad E = - \frac{1}{4} \frac{v_E^2}{k_E} - \frac{1}{2} \frac{v_T^2}{k_T} > - \frac{2}{3} \frac{v_T^2}{k_T} \quad \text{(II-16)} \]

\[ III. \quad E = - \frac{2v_T^2}{3k_T} \]

where, again, the inequalities are derived from the condition that $B < 0$. As a result, the type III or trigonal distortions will be lowest in energy. These distortions are also usually discussed as the limiting case where the orbital triplet couples exclusively to the vibrational triplet. A configuration coordinate diagram is impossible to display except, possibly, in a three dimensional projection. The most important feature it would indicate is that, in this case, the vibronic coupling causes considerable mixing of the three electronic states. Therefore, this case is more like the well known electronic doublet problem than case I. There cannot be a unique identification of an electronic state with a sheet in the configuration coordinate diagram as there is for the three disjoint paraboloids of the previous section. This is related to the fact that the vibronic ground state is now
a quadruplet. A vibronic singlet has the same energy as the ground vibronic triplet in the case of extreme linear coupling. This phenomenon will be discussed further in Section II.D.1. When the coupling is very strong, the adiabatic approximation will be approximately correct for the lowest vibronic levels; the lower vibronic eigenstates can be approximated by products of the electronic state for a given distortion and anisotropic three-dimensional harmonic oscillator vibrational states within the well. The reason that this description is approximate and breaks down for higher lying vibronic states and weaker vibronic couplings is that the particular mix of the three electronic states in the vibronic eigenstates is a function of the position in configuration coordinate space. As the vibrational excitation increases within the well, the system has an increased probability of occupying parts of the lowest sheet in configuration coordinate space that correspond to appreciably different mixes of the electronic states than the mix which is found at the minimum. This behavior is the root of the difficulties in understanding the trigonal Jahn-Teller distortions.
3) The Saddle Points

The third type of stationary point in Table II-6 corresponds to a \( \langle 110 \rangle \) distortion, a distortion which preserves the symmetry elements of the face diagonals of the cube. In the linear coupling and harmonic elastic energy approximations of Öpik and Pryce, these stationary points are always saddle points and never local minima. Mary O'Brien\(^{(37)}\) has studied the energy levels as a function of the five configuration coordinates of the complete orbital triplet problem and she demonstrated that, when \( B = 0 \), there will be a continuous two-dimensional sheet of minimum energy which contains all three types of stationary points. She discusses the possibility that, when the coupling parameters have values so that \( B \) is close to zero, the system could move around on this surface when the kinetic energy terms are included. Thus, dynamic effects might be observed which are similar to those found in the well known dynamic Jahn-Teller Effect for orbital doublets.

Another possibility is intriguing. If the coupling is equally strong to both types of modes so that \( B = 0 \), the nonlinear coupling terms or anharmonic elastic energy terms could conceivably be strong enough to warp the energy "trough" and cause the \( \langle 110 \rangle \) type of stationary points to be lower in energy than the other two types. Considerable work has been done which attempts to explain the existence
of (110) distortions. A paper by Muramatsu and Iida\(^{(38)}\) discusses the effects of terms quadratic in the triply degenerate vibrational mode only. They conclude that (110) distortions are possible but their analysis seems to depend on a substantial contribution from linear vibronic coupling to an excited electronic state which affects the ground state in second order perturbation theory.

Estle has done an unpublished calculation of the energy of the lowest adiabatic potential energy surface restricted to the O'Brien two-dimensional energy trough when the higher order contributions due to the anharmonic and nonlinear terms are small. He started with the Hamiltonian in equation II-2 and added the effects of the terms in equation II-4 as a perturbation of O'Brien's solution of equation II-2. These higher order terms can be classified as the lowest order nonlinear terms of the doubly degenerate mode,

\[
V_5\left[ (Q_\varphi^2 - Q_\vartheta^2)U_\varphi + 2Q_\varphi Q_\vartheta U_{\varphi\vartheta}\right]
\]

the triply degenerate mode,

\[
V_6\left[ (2Q_\varphi^2 - Q_\varpi^2 - Q_\varphi^2)U_\varphi + \sqrt{3}(Q_\varphi^2 - Q_\varpi^2)U_{\varphi\varpi}\right]
\]

\[
+ V_7[Q_\varphi Q_\varpi U_{\varphi\varpi} + Q_\vartheta Q_\varpi U_{\vartheta\varpi} + Q_\varphi Q_\vartheta U_{\varphi\vartheta}]
\]

and the nonlinear terms which include the effects of both types of modes linearly,
\[ V_g \left[ (-Q_\theta + \sqrt{3}Q_\phi)Q_\phi U_\phi - (Q_\theta + \sqrt{3}Q_\phi)Q_\phi U_\phi + 2Q_\theta Q_\phi U_\phi \right] \]

the lowest order anharmonic terms for the doubly degenerate mode,

\[ V_2 Q_\theta (3Q_\phi^2 - Q_\theta^2) \]

the triply degenerate mode,

\[ V_3 (Q_\phi^2 - Q_\phi Q_\theta) \]

and the lowest order anharmonic combination of both types of modes,

\[ V_4 \left\{ (2Q_\phi^2 - Q_\phi^2 - Q_\theta^2)Q_\theta + \sqrt{3} Q_\phi (Q_\phi^2 - Q_\theta^2) \right\} \]

Estle dropped terms from the secular equation which had quadratic or higher order dependence on the nonlinear and anharmonic coupling coefficients, the \( V_1 \). His result for the energy of the lowest energy surface in O'Brien's trough is:

\[
e = -1 + \alpha_2 - 2\alpha_5 + 3(-\sqrt{3} \alpha_3 + 6\alpha_7)g_6
\]

\[ + \frac{9}{2}(-\alpha_2 + 2\alpha_5) (g_4 - 3g_6) \quad (II-17) \]

\[ + (3\alpha_4 - 6\alpha_6 - 2\sqrt{3} \alpha_8) (g_4 - 9g_6) + (3 - 2\alpha_1) (1 - 3g_4) \]

where the energy and coupling coefficients are parameterized by (\( V = V_E = V_T \)): 
\[ e = \frac{E}{2v^2/k_T} \]
\[ \beta = \frac{k_E - k_T}{k_T} \]
\[ \alpha_1 = \frac{v_1}{v} \]
\[ \alpha_5 = \frac{2v_5}{k_T} \]
\[ \alpha_2 = \frac{4v_2}{k_T^2} \]
\[ \alpha_6 = \frac{2v_6}{k_T} \] \hspace{1cm} \text{(II-18)}
\[ \alpha_3 = \frac{4v_3}{k_T^2} \]
\[ \alpha_7 = \frac{2v_7}{k_T} \]
\[ \alpha_4 = \frac{4v_4}{k_T^2} \]
\[ \alpha_8 = \frac{2v_8}{k_T} \]

and the angular dependence is given by \( g_4 \) and \( g_6 \) which are written in terms of the direction cosines with respect to the cubic axes of the crystal as:

\[ g_4 = m^2 n^2 + n^2 l^2 + l^2 m^2 \]
\[ g_6 = l^2 m^2 n^2 \] \hspace{1cm} \text{(II-19)}

The primary assumption of this calculation can be stated as:

\[ \beta < e \quad , \quad \alpha_i < e \quad \quad i = 1 \text{ to } 8 \] \hspace{1cm} \text{(II-20)}

These results indicate that, when only terms first order in the nonlinear and anharmonic contributions are considered, there is no general region of configuration coordinate space in which a (110) symmetry distortion is stable. A stable orthorhombic distortion might be achieved if several of the coupling coefficients have very special values, but a small shift in any of these values should
stabilize a distortion with a different symmetry. It seems probable that the change in coupling strengths due to replacing the Ca ions with Sr ions in an alkaline earth fluoride host would be more than enough to shift these coefficients.

Bacci, Ranfagni et al. have published several papers which investigate the effects of including the nonlinear terms\(^{(39)}\) and the anharmonic terms\(^{(40)}\) separately. In the first paper, they considered only higher order terms proportional to \(V_5, V_6,\) and \(V_7\) of equation II-4, and, in the second paper, they considered only the higher order terms proportional to \(V_2\) and \(V_3\). They analytically found the distortion coordinates and energies for the stationary points. (The distortion coordinates given by Öpik and Pryce are modified slightly by the higher order terms which are considered in these papers.) Then, they plotted regions of configuration coordinate space where orthorhombic (\(\{110\}\)) distortions could occur, as well as simultaneous orthorhombic and tetragonal distortions.

Two points are bothersome about their analysis. First, the scales on their figures tend to be misleading. As can be seen in Figure II-2 the large shaded areas have most of their area when the higher order coupling parameters are the same magnitude as or larger than the linear or harmonic coupling coefficients, or, using Estle's notation, in the regions where the \(\alpha_i\)'s are greater than or
Domains for the existence of tetragonal (horizontal shading) and orthorhombic (vertical shading) minima in the plane. In the checkered area both kinds of minima exist.

Figure II-2. Ranges of Parameters for the Existence of Tetragonal and Orthorhombic Minima, $V_5$ vs. $k_E$ (from Bacci, et. al. (39))
equal to one. Physically, it seems that a twenty-five per cent contribution from nonlinear or anharmonic effects would be very substantial. When the regions of their figures which are near the origin are considered and the adjustable boundaries are determined by the minimal higher order contributions, the conditions for (110) distortions seem very restrictive. In fact, it looks as if these diagrams agree with Estle's calculation since, as the strength of the higher order coupling terms diminish, (and therefore Estle's approximation should be increasingly more realistic), the area of configuration coordinate space in which (110) distortions are stable seems to diminish to a line which corresponds to a very special set of values for the higher order coupling parameters.

The second bothersome point about the published analysis of Bacci, Ranfagni et al. is that they have not yet included both the nonlinear and anharmonic terms simultaneously. A more serious omission is the higher order terms which include linear effects of both types of modes, the terms in equation II-4 which are proportional to $V_4$ and $V_8$. They did include the interesting possibility that the breathing mode could have a strong influence on the problem, but the physical justification of the terms they choose to ignore is questionable.
D. Weak Coupling Phenomenon - Tunneling Models

1) Introduction to Tunneling Models

The previous section applies only to those situations when the Jahn-Teller coupling is so strong that the splitting of the electronic energy levels which it introduces is much larger than either the phonon kinetic energy, $\hbar \omega$, or the spin-orbit splittings. If the spin-orbit interaction is strong enough, it can quench the effects of vibronic coupling to the pure orbital states. It is possible that, after the effects of Russell-Saunders Coupling and the crystal field are included, the ground state is a four-fold degenerate set of states that are mixtures of the pure spin states with the pure orbital states. Jahn-Teller coupling with both doubly and triply degenerate modes can split this $G_{3/2}$ ($g^+$) state and produce distortions similar to those already discussed.\(^{(41)}\) A further discussion of the details of this possibility will not be given here.

It is possible that the Jahn-Teller coupling is too weak to cause a static distortion but strong enough to dominate the spin-orbit interaction. The effects which arise from this situation are termed "weak coupling effects," or dynamic effects. The important theoretical feature is that the problem can no longer be solved as an electronic problem; it must be worked out using vibronic states, that is, quantum mechanical states that depend both on the
electronic coordinates and the nuclear coordinates. The next sections will discuss the variation of the vibronic eigenstates as the system parameters change from the static configuration to the weak coupling extreme first for coupling to doubly degenerate modes and then for coupling to triply degenerate modes. Physically, this transformation can be pictured as occurring when the wells which create the static behavior get progressively shallower, or the barriers separating the wells get lower. As this occurs, quantum mechanical tunneling allows the system to hop from one distortion configuration to another. The end result is the situation where the average site symmetry which is observed is cubic even though the instantaneous symmetry is usually distorted. These models can be referred to as tunneling models.

The second important feature of these weak coupling schemes is the Ham Effect. The overlap of the vibrational wave functions causes an effective reduction of the angular momentum and other physical quantities; as Ham put it, these quantities are "quenched." These effects will be discussed, in each case, after the discussion of the vibronic eigenstates.
2) Weak Coupling to Doubly Degenerate Vibrational Modes

(a) Vibronic States

As mentioned in Section II.C.2, the configuration coordinate diagram consists of three wells, each identified with an unmixed electronic state. Inclusion of the kinetic energy terms of the Hamiltonian given in equation II-3 will lead to two dimensional harmonic oscillator states centered about the displaced minimum of each well. The vibronic states will then be Born-Oppenheimer products of the electronic state for that well and a two dimensional vibrational function which describes the motion of the system in that well:

\[ |\gamma_{in}\rangle = |i\rangle |n_\theta, n_\zeta\rangle , \quad i = \xi, \eta, \text{ or } \zeta \quad (II-21) \]

Even though the functional forms of the vibrational eigenstates will differ due to the different displacements of the minimum of each potential well, the quantum numbers, \( n_\theta \) and \( n_\zeta \), will be the same standard Hermite polynomial indices for each dimension of the simple harmonic oscillator in each well. If the vibrational frequency is defined from \( k_E = \omega_E \hbar \omega_E^2 \), the energy of a given vibronic state is:

\[ E = E_0 - E_{JT} + (n+1) \hbar \omega_E , \quad n = n_\theta + n_\zeta \quad (II-22) \]
where $E_o$ is the electronic energy of the ion in cubic symmetry and $E_{JT}$ is the Jahn-Teller stabilization energy, given in Table II-6. The three-fold vibronic degeneracy is readily apparent from the fact that, for any given level of vibrational excitation, there are vibronic states due to each of the three electronic states. A change in the strength of the vibronic coupling will not change any of this except the magnitude of $E_{JT}$; if the coupling is weaker, the distortion minima are just located closer to the origin in configuration coordinate space.

When the coupling approaches zero, the system behaves as if there is no vibronic coupling and the configuration coordinate diagram consists of three degenerate paraboloids with minima at the origin. This description is too simplistic though; there is actually a competition between the vibronic coupling and the spin-orbit coupling. The three paraboloids will never be exactly degenerate, not just because it is unreasonable to say that the vibronic coupling will be exactly zero, but because, if the vibronic coupling is weak enough, the spin orbit coupling will dominate the problem, the orbital states will be mixed with the spin states, and the problem should be reformulated. The physically interesting behavior that occurs in the intermediate weak coupling regime, that is, before the spin-orbit coupling dominates, will be discussed in the following section.
(b) Vibrational Overlap and Reduction Factors

Using the three degenerate vibronic ground states of the previous section, \( \eta_0, \xi_0, \) and \( \gamma_0, \) as basis states, an effective vibronic Hamiltonian can now be written which should describe the properties of the system. Since the overall symmetry of the vibronic system is cubic, the effective vibronic Hamiltonian will have the same form as an effective electronic Hamiltonian in \( O_h \) symmetry; it will be formed using the same symmetry considerations as outlined in Section II.B.2. The Hamiltonian will be composed of symmetrized operators constructed from the projection operators of the vibronic triplet rather than the electronic triplet; the vibronic operator that has the same matrix form as the electronic operator, \( U_i \), will be denoted by \( U_{gi} \). The vibronic operators will be multiplied by combinations of quantities, such as the magnetic field, strains, the electronic spin, and nuclear spin, which transform according to the irreducible representations of the cubic group. The combinations which are most likely to influence EPR spectra are discussed in Section II.E; they will be included collectively here and represented by the coefficient, \( f_i \), for the operator \( U_i \) or \( U_{gi} \). Now, rather than using the electronic effective Hamiltonian given by:

\[
K_{\text{elec}} = f_1 U_1 + f_2 U_2 + f_3 U_3 + f_4 U_4 + f_5 U_5 + f_6 U_6 + f_7 U_7 + f_8 U_8 + f_9 U_9 + f_{10} U_{10}
\]

(II-23(a))
the effective vibronic Hamiltonian:

\[ V_g = \sum f_i g + f_g g + f_u u + f_x x + f_y y + f_z z + f_u u + f_g g + f_u u + f_g g \]

\( (\text{II-23 (b)}) \)

must be used (the bar indicates a time reversal odd quantity). Since symmetry arguments alone are used to construct the \( f_i \), the form of the coefficients will not differ whether the Hamiltonian is electronic or vibronic. However, the magnitude of the coupling parameters which are implicit in each \( f_i \) is not necessarily the same. Using a generalization of the Wigner-Eckardt theorem appropriate for cubic symmetry, \( (42) \) the coupling coefficients in each Hamiltonian in equation \( \text{II-23} \) are related by a single parameter for each irreducible representation, which is known as a "reduction factor." Ham \( (7) \) showed that vibrational overlap is responsible for the magnitude of the reduction factors, since, if \( \mathcal{O}_A \) is an operator which operates only on electronic states:

\[ \langle i, n_g, n_z | \mathcal{O}_A | j, n'_g, n'_z \rangle = \langle i | \mathcal{O}_A | j \rangle \langle n_g n_z | n'_g n'_z \rangle \]

\( (\text{II-24}) \)

The first matrix element on the right is the matrix element of the effective electronic operator and the second matrix element represents the reduction factor which depends entirely on the overlap of the two vibrational wave functions. This general form applies to this case because the linear vibronic coupling causes no mixing of the electronic states; therefore, the simple Born-Oppenheimer
product of an electronic function times a vibrational function is correct for all coupling strengths.

Ham has given a more thorough discussion of theoretical predictions for the magnitudes of these factors. Generally, when coupling to doubly degenerate modes is considered exclusively, any $f_i$'s which transform like $\Gamma_4^+$ or $\Gamma_5^+$ will have identical reduction factors, for all coupling strengths. The reduction factors for both $\Gamma_4^+$ and $\Gamma_5^+$ symmetry interactions will approach zero as the coupling strength increases. The $f_i$'s which transform like $\Gamma_3^+$ will experience no reduction. If the reduction factors are defined by:

$$K(E) = -\langle g^\xi | U_\theta | g^\zeta \rangle \quad \text{for the } \Gamma_3^+ \text{ I.R.}$$

$$K(T_1) = i\langle g^\xi | U_z | g^\eta \rangle \quad \text{for the } \Gamma_4^+ \text{ I.R.} \quad (II-25)$$

$$K(T_2) = -\langle g^\xi | U_\xi | g^\eta \rangle \quad \text{for the } \Gamma_5^+ \text{ I.R.}$$

where $U_i$ is an electronic operator rather than the vibronic operator, then the vibronic Hamiltonian is:

$$V_g = f_\xi U_\xi + f_\eta U_\eta + f_\zeta U_\zeta$$

$$+ K(T_2)[\underline{f}_x U_g x + \underline{f}_y U_g y + \underline{f}_z U_g z + f_\eta U_g \gamma + f_\zeta U_g \zeta + f_\xi U_g \xi] \quad (II-26)$$

The $f_i$'s in this case are identical to the $f_i$'s which could be derived, in principle, from theory when vibronic coupling is ignored. The terms which contribute to each $f_i$ will be discussed in Section II.E.2.
3) Weak Coupling to Triply Degenerate Vibrational Modes

(a) Vibronic States

The case of vibronic coupling to triply degenerate vibrational modes is not as straightforward. However, some of the same general ideas can be applied. As discussed in Section II.C.2(b), if the potential wells are deep enough, that is, \( E_{JT} \gg \hbar \omega_T \), \( (k_T = \mu_T \omega_T^2) \), then the Hamiltonian which includes the kinetic energy term will lead to a series of harmonic oscillator-like states with the four distortion configurations as the equilibrium positions. The ground vibronic states are approximately given by a Born-Oppenheimer product of the electronic state given in Table II-6 for each well, and the vibrational state which defines the distortion:

\[
\psi_i = \frac{1}{\sqrt{3}} (m_{1i} \psi_{\xi_i} + m_{2i} \psi_{\eta_i} + m_{3i} \psi_{\zeta_i}) |Q_{\xi_i}^0, Q_{\eta_i}^0, Q_{\zeta_i}^0\rangle \quad (II-27)
\]

where \( m_{ji} \) refer to the coefficients appropriate to the \( i^{th} \) distortion in Table II-6 and the indices of the vibrational part of the wave function, \( Q_{\xi_i}^0 \), \( Q_{\eta_i}^0 \), \( Q_{\zeta_i}^0 \), are the coordinates in configuration coordinate space which define the equilibrium position of the \( i^{th} \) distortion. These basis functions will be referred to as the "distortion basis functions." This form is an approximation because the mixing of the three electronic states varies with the location in configuration coordinate space and the zero point
motion within the well can be enough to affect the approximation if the wells are not very deep. This overlap of the electronic wave function due to the vibrational motion will make the four vibronic states, \( \tilde{\psi}_1 \), nonorthogonal.

In the same approximation that these vibronic eigenstates are orthogonal, the energy of these vibronic states will be identical; the vibronic states in the limit of extreme strong coupling are vibronic quartets. The overall symmetry of the crystal, and, hence, the vibronic system, is still cubic so the vibronic states must transform according to the representations of the original symmetry, \( O_h \). Each distortion, however remains an invariant under the group operations of \( D_{3d} \); since quantities which are invariant and transform like \( \Gamma_1^+ \) in \( D_{3d} \) transform like \( \Gamma_1^+ \) and \( \Gamma_5^+ \) in \( O_h \), the vibronic quartet transforms like the reducible representation \( (\Gamma_1^+ + \Gamma_5^+) \). The approximate vibronic wave functions given in equation II-27 do not form the basis which explicitly shows this symmetry of the vibronic wave functions in \( O_h \). A basis that does is given by:

\[
\begin{align*}
\tilde{\psi}_\xi &= \frac{1}{2\lambda} \left( \tilde{\psi}_1 - \tilde{\psi}_2 + \tilde{\psi}_3 - \tilde{\psi}_4 \right) \\
\tilde{\psi}_\eta &= \frac{1}{2\lambda} \left( \tilde{\psi}_1 - \tilde{\psi}_2 - \tilde{\psi}_3 + \tilde{\psi}_4 \right) \\
\tilde{\psi}_\zeta &= \frac{1}{2\lambda} \left( \tilde{\psi}_1 + \tilde{\psi}_2 - \tilde{\psi}_3 - \tilde{\psi}_4 \right) \\
\tilde{\psi}_S &= \frac{1}{2\lambda} \left( \tilde{\psi}_1 + \tilde{\psi}_2 + \tilde{\psi}_3 + \tilde{\psi}_4 \right)
\end{align*}
\]
The constants, $\Lambda$ and $\Lambda'$, are the normalization constants which will differ from each other only to the extent that the distortion basis functions are not orthogonal. This set of basis states will be referred to as the "tunnelling basis functions" because they display the symmetry characteristics of the vibronic problem which are very important when the dynamic characteristics of the system are considered. When the vibronic coupling strength is reduced to zero, the first three of these vibronic states, which transform like the $\Gamma^+_5$ triplet, will be reduced to the Born-Oppenheimer product of the original electronic triplet states of the indicated symmetry with the ground vibrational functions of the cubic system. The Hamiltonian for the system can now be solved using either one of these two sets of vibronic basis states. The details and differences will be discussed in the next section when discussing vibrational overlap effects.

The final item of interest is the connection between the vibronic states in the ideal limits of no vibronic coupling (and no spin-orbit interaction) and extreme strong vibronic coupling. If the vibronic coupling terms are zero, then the Hamiltonian will have only elastic energy and kinetic energy terms. The configuration coordinate diagram will be a superposition of three-dimensional paraboloids for each electronic state with the minimum energy at the origin. The kinetic energy term will create
isotropic three-dimensional harmonic oscillator states within the wells. The symmetry properties of these states can be derived\(^{(43)}\) and the resulting correlation diagram is given in Figure II-3 as calculated by Caner and Engleman\(^{(44)}\) using numerical techniques.

(b) Vibrational Overlap and Reduction Factors

The construction of the vibronic Hamiltonian is more difficult in this approximation because of the existence of the quadruplet vibronic ground state. Rather than nine effective operators which have a matrix form identical to the electronic operators' matrix form, the use of four basis states implies that there is a possibility of sixteen vibronic operators in the Hamiltonian. Furthermore, the two equivalent sets of basis states discussed in the previous paragraphs confuse matters even more. The tunneling basis functions have the advantage that they are classified by their symmetry properties under the cubic group. When the values of the normalization coefficients, \(\Lambda\) and \(\Lambda'\), are correctly expressed, they form a basis which will describe the behavior of this vibronic system for any coupling strength. The distortion basis functions, on the other hand, are only a convenient approximation to the correct vibronic eigenfunctions which are justified by the fact that they make physical sense in the limit of strong coupling. The discussion of this section will demonstrate how they can also be useful in diagonalizing
increased coupling strength →

Figure II-3. Correlation Diagram of the Vibronic States for an Orbital Triplet Coupled to Triply Degenerate Vibrational Modes (from Caner and Engleman\(^{(44)}\))
The Hamiltonian in the limit of strong vibronic coupling. The initial step will be to define the sixteen vibronic operators using the tunneling basis by using the symmetry properties of the states. Then, the operators can be expressed in terms of the distortion basis. Several unusual steps will be taken that are justified only by the neatness of the end result, even though they seem plausible in retrospect.

If the tunneling basis is used, nine of the operators can be written immediately. The 3x3 matrix forms for operators which are formed from vibronic triplet states alone (\(U_{gg}', U_{gt}', U_{gt}, \bar{U}_{gy}, \bar{U}_{gz}, U_{g\bar{t}}, U_{g\bar{t}}, U_{g\bar{t}}', \bar{g} g\)) can be expanded to the nine appropriate 4x4 matrix forms which represent operators between the \(\Gamma_5^+\) states of the vibronic quadruplet by adding zeros along the row and column that involve the vibronic singlet state. To describe the effects which arise from including the vibronic singlet, seven additional operators are needed. A script "\(\mathcal{A}\)" will be used initially to distinguish operators which include the effects of the singlet. The operators are:

Transforming like \(\Gamma_1^+\) is:

\[
\mathcal{A}_{g1} = |g1\rangle\langle g1|
\]

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

(II-29)
transforming like $\Gamma_{5_3}^+$ is:

$$a_{g_3} = - [ |g\xi\rangle\langle g_1| + |g_1\rangle\langle g_\xi|]$$

$$= \begin{pmatrix}
0 & -1 & 0 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$

transforming like $\Gamma_{5_\eta}^+$ is:

$$a_{g_\eta} = - [ |g\eta\rangle\langle g_1| + |g_1\rangle\langle g_\eta|]$$

$$= \begin{pmatrix}
0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$

transforming like $\Gamma_{5_\zeta}^+$ is:

$$a_{g_\zeta} = - [ |g\zeta\rangle\langle g_1| + |g_1\rangle\langle g_\zeta|]$$

$$= \begin{pmatrix}
0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0
\end{pmatrix}$$

and three time reversal odd operators:

transforming like $\Gamma_{5_3}^+$ is:

$$\bar{a}_{g_3} = i[ |g\xi\rangle\langle g_1| - |g_1\rangle\langle g_\xi|]$$

$$= \begin{pmatrix}
0 & -i & 0 & 0 \\
+i & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$
transforming like $\Gamma_5^+$ is:

$$\overline{\alpha}_{g\eta} = i[|g\eta\rangle\langle g1| - |g1\rangle\langle g\eta|]$$

$$= \begin{pmatrix}
0 & 0 & -i & 0 \\
0 & 0 & 0 & 0 \\
i & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}$$

transforming like $\Gamma_5^+$ is:

$$\overline{\alpha}_{g\zeta} = i[|g\zeta\rangle\langle g1| - |g1\rangle\langle g\zeta|]$$

$$= \begin{pmatrix}
0 & 0 & 0 & -i \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
i & 0 & 0 & 0
\end{pmatrix}$$

The vibronic Hamiltonian with this tunneling basis is then:

$$V_{gt} = f_1 \hat{g} \hat{g}_{1} + f_1 \hat{g}_{1} \hat{g} + f_{\theta} \hat{g}_{\theta} \hat{g}_{\theta} + f_{\zeta} \hat{g}_{\zeta} \hat{g}_{\zeta}$$

$$+ \hat{g}_{x} \hat{g}_{x} \hat{g}_{x} + \hat{g}_{y} \hat{g}_{y} \hat{g}_{y} + \hat{g}_{z} \hat{g}_{z} \hat{g}_{z} + f_{\xi} \hat{g}_{\xi} \hat{g}_{\xi} + f_{\xi} \hat{g}_{\xi} \hat{g}_{\xi} + f_{\xi} \hat{g}_{\xi} \hat{g}_{\xi} \tag{II-30}$$

$$+ f_{\xi} \hat{g}_{g\xi} \hat{g}_{g\xi} + f_{\xi} \hat{g}_{g\xi} \hat{g}_{g\xi} + f_{\xi} \hat{g}_{g\xi} \hat{g}_{g\xi} + f_{\xi} \hat{g}_{g\xi} \hat{g}_{g\xi} + f_{\xi} \hat{g}_{g\xi} \hat{g}_{g\xi} + f_{\xi} \hat{g}_{g\xi} \hat{g}_{g\xi}$$

where the bar indicates the quantity is odd under time reversal and the primes are used to distinguish the $f_i$ which multiplies the operator that includes the effect of the vibronic singlet when there would otherwise be an ambiguity with an $f_i$ that multiplies another operator with the same symmetry. A change of basis states can be
performed using the relationship in equation II-28. The advantage of the distortion basis set is that it should isolate the terms which dominate in the strong coupling limit. This scheme works very well if symmetric and antisymmetric combinations of some pairs of the operators that have the same symmetry are used after the change of basis. This change seems appropriate since, in the strong coupling limit, the singlet is completely degenerate with the triplet and there is less reason to separate operators that do or do not include singlet effects. To identify the change, make the following change of notation when converting to the distortion basis set operators:

\begin{align*}
\text{tunneling} & \quad \text{distortion} \\
\text{basis} & \quad \text{basis} \\
\text{operators} & \quad \text{operators} \\
\mathcal{J}_g & + \mathcal{A}_{g_1} \\
\mathcal{A}_{g_1} & - \mathcal{J}_g \\
U_{g_i} & + \mathcal{A}_{g_i} \\
U_{g_i} & - \mathcal{A}_{g_i}
\end{align*}

After this change, the symmetric combinations of the tunneling operators, $\mathcal{J}_g$, $U_{g_1}$, $U_{g_2}$, and $U_{g_3}$, when written with the distortion basis functions with $\Lambda = \Lambda'$, are completely diagonal while the antisymmetric combinations of the tunneling operators, $\mathcal{A}_{g_1}$, $\mathcal{A}_{g_5}$, $\mathcal{A}_{g_7}$, and $\mathcal{A}_{g_5}$, when written with the distortion basis, have nothing but off-
diagonal elements. So far, it is not clear what combinations of \( f_i \) and \( f'_i \) should multiply the operators when the distortion basis functions are used, nor is it clear what the difference is between \( f_i \) and \( f'_i \). Since symmetry arguments are used to form the \( f_i \) coefficients which multiply a given operator and these symmetry arguments have nothing to do with anything other than the symmetry properties of the operator, then the only differences between the \( f_i \) and the \( f'_i \) will be a difference in the implied parameter which indicates the strength of the coupling of the \( f_i \) to the operator it multiplies. The difference between the \( f_i \) which would multiply a given operator and the \( f'_i \) which would multiply the other operator with the same symmetry could be represented by a constant factor which multiplied one of them. This constant factor serves the same function as the reduction factor which was defined in the previous section (II.D.1); it is a proportionality constant that relates the coefficients of operators that have the same symmetry properties. It is a matter of definition to absorb this constant into the reduction factors which relate the coefficients of the original electronic operators to the coefficients of the two vibronic operators. So, the vibronic Hamiltonian can be written with the reduction factors as:
\[ V_g = f_1 \mathcal{J}_g + f_1 K(I) A_{g_1} + K(E) \left[ f_g U_{g \theta} + f_g U_{\xi \xi} \right] \]

\[ + K(T_1) \left[ \frac{f g_x}{Y_{g_x}} + \frac{f g_y}{Y_{g_y}} + \frac{f g_z}{Y_{g_z}} \right] \]

\[ + K(T_2) \left[ f_5 U_{g_5} + f_\eta A_{g_\eta} + f_\zeta A_{g_\zeta} \right] \]

\[ + K'(T_2) \left[ f_5 A_{g_5} + f_\eta A_{g_\eta} + f_\zeta A_{g_\zeta} \right] \]

\[ + \frac{K(T_2)}{T_2} \left[ \frac{f g_5}{Y_{g_5}} + \frac{f g_\eta}{Y_{g_\eta}} + \frac{f g_\zeta}{Y_{g_\zeta}} \right] \]

(II-31)

When the matrix forms of \( \mathcal{J}_g \) and \( A_{g_1} \) are written with the distortion basis functions with \( \Lambda = \Lambda' \), \( \mathcal{J}_g \) has only diagonal matrix elements and will include the isotropic electronic interactions while \( A_{g_1} \) consists of only off-diagonal matrix elements. This \( A_{g_1} \) operator was formed from the difference of the two \( \Gamma_1^+ \) operators written with the tunneling basis and represents the splitting of the energies of the vibronic triplet and singlet which approaches zero when the vibronic coupling approaches the strong coupling limit. This fact implies that \( K(I) \) will go to zero in this limit. Furthermore, Ham has shown (7) that in the limit of strong coupling to triply degenerate vibrational modes, \( K(E) = K(T_1) = 0 \) and \( K(T_2) = \frac{2}{3} \). So, the vibronic Hamiltonian in this limit will become:

\[ V_{g_\xi} = f_1 \mathcal{J}_g + \frac{2}{3} \left[ f_5 U_{g_5} + f_\eta A_{g_\eta} + f_\zeta A_{g_\zeta} \right] \]

\[ + K'(T_2) \left[ f_5 A_{g_5} + f_\eta A_{g_\eta} + f_\zeta A_{g_\zeta} \right] \]

\[ + \frac{K(T_2)}{T_2} \left[ \frac{f g_5}{Y_{g_5}} + \frac{f g_\eta}{Y_{g_\eta}} + \frac{f g_\zeta}{Y_{g_\zeta}} \right] \]

(II-32)
The $\Gamma_3^+$ and $\Gamma_4^+$ operators have no nonzero diagonal elements when written in the "distortion" basis appropriate for strongest coupling, and share this property with the $\Gamma_5^+$ operators which are written above with the $K'(T_2)$ and $K(T_2)$ reduction factors. By the reasoning given by Ham, this implies that $K'(T_2)$ and $K(T_2)$ should also go to zero as the coupling strength increases. Therefore, the vibronic Hamiltonian in the strong coupling limit is written in matrix form as:

$$V_{gs} = \begin{pmatrix}
  f_1 - \frac{2}{3}(f_5 + f_\eta + f_\xi) & 0 & 0 & 0 \\
  0 & f_1 + \frac{2}{3}(-f_5 + f_\eta + f_\xi) & 0 & 0 \\
  0 & 0 & f_1 + \frac{2}{3}(f_5 + f_\eta - f_\xi) & 0 \\
  0 & 0 & 0 & f_1 + \frac{2}{3}(f_5 - f_\eta + f_\xi)
\end{pmatrix} \tag{II-33}$$

The effects of the external parameters, such as random internal strains, applied magnetic fields, and spin coordinates which combine in the $f_1$ coefficients, should now be considered for these four ground vibronic states to describe the behavior of the system. The strongest effects are often thought to arise from large random internal strains. Therefore, the effects of these will be discussed in Section II.D.5.
4) Weak Coupling to Both Doubly and Triply Degenerate Vibrational Modes

As the discussion of Section II.C.3 indicates, little is understood about comparable coupling to both types of vibrational modes. The weak coupling effects are no exception. According to the analysis of O'Brien\(^{(34)}\), the ground vibronic state when an orbital triplet is strongly coupled to both types of modes equally will always be an isolated triply degenerate state. The effects of the higher order terms on the vibronic states are unknown. If \(\langle 110 \rangle\) distortions are somehow stabilized, the fact that there are six equivalent symmetric \(\langle 110 \rangle\) distortions means that the ground vibronic state must be a sextet. Since the highest degeneracy for an irreducible representation in cubic symmetry is three-fold, the six-fold degenerate state must be a combination of states that transform like two or more irreducible representations, either \((\Gamma_1^+ + \Gamma_3^+ + \Gamma_5^+)\) or \((\Gamma_4^+ + \Gamma_5^+)\). The appropriate combination is not known without knowledge of the driving force of the distortion.

The effects of coupling to both types of modes on the reduction factors are also poorly understood. O'Brien's analysis reveals that the reduction factors in the limit of strong equal coupling to both types of modes will be:

\[
K(T_1) = 0 \\
K(T_2) = \frac{2}{5} \\
K(E) = \frac{2}{5}
\]  

\[(II-34)\]
Ham(7) simply mentions that in the weak coupling limit, both types of modes should be considered and the effects of each type of mode should be "roughly additive" in reducing the electronic interactions.

5) Strain Effects

The effects of random strains are the most important contributions to the coefficients, \( f_i \), of the vibronic Hamiltonian. The random internal stresses are described by the strain components which are defined by:

\[
e_{ij} = \frac{1}{2} \left( \frac{\partial \rho_i}{\partial x_j} + \frac{\partial \rho_j}{\partial x_i} \right), \quad i, j = 1, 2, 3 \quad (II-35)
\]

The \( x_i \) are distances along the three cubic axes and \( \rho_i \) represents the displacement of the lattice from the equilibrium positions. The \( e_{ij} \) are components of a symmetric strain tensor. Therefore, there are six independent components which can be combined to form six quantities which have symmetry properties of the cubic vibronic system. These will be:

\[
f_1 = \frac{1}{\sqrt{3}} \nu_1 (e_{xx} + e_{yy} + e_{zz}) = \nu_1 e_1
\]

\[
f_\theta = \frac{1}{\sqrt{6}} \nu_3 (2e_{zz} - e_{xx} - e_{yy}) = \nu_3 e_\theta
\]

\[
f_\epsilon = \frac{1}{\sqrt{2}} \nu_3 (e_{xx} - e_{yy}) = \nu_3 e_\epsilon
\]

\[
f_\zeta = \nu_5 e_{yz} = \nu_5 e_\zeta
\]

\[
f_\eta = \nu_5 e_{zx} = \nu_5 e_\eta
\]

\[
f_\zeta = \nu_5 e_{xy} = \nu_5 e_\zeta
\]

(II-36)
Substituting these values into the strong coupling vibronic Hamiltonian, equation II-33, gives:

\[
\begin{pmatrix}
    v_{g_1} e_1 - \frac{2}{3} v_5 (e_5^{e_5} + e_{\eta}^{e_{\eta}} + e_\zeta^{e_\zeta}) & 0 & 0 & 0 \\
    0 & v_{g_1} e_1 + \frac{2}{3} v_5 (e_5^{e_5} + e_{\eta}^{e_{\eta}} + e_\zeta^{e_\zeta}) & 0 & 0 \\
    0 & 0 & v_{g_1} e_1 + \frac{2}{3} v_5 (e_5^{e_5} - e_{\eta}^{e_{\eta}} - e_\zeta^{e_\zeta}) & 0 \\
    0 & 0 & 0 & v_{g_1} e_1 + \frac{2}{3} v_5 (e_5^{e_5} - e_{\eta}^{e_{\eta}} + e_\zeta^{e_\zeta})
\end{pmatrix}
\]  

(II-37)

The combinations of $e_5^{e_5}$, $e_{\eta}^{e_{\eta}}$, and $e_\zeta^{e_\zeta}$ in this Hamiltonian are the expressions which describe pure longitudinal strains along the (111) directions of the crystal. So, the random strains at any given site will split the energies of the four degenerate vibronic states. Since the strain remains fixed at any given site, the ion will remain in the lowest vibronic state unless excited to one of the other vibronic states either thermally or by some external influence that can cause the transition. The anisotropy of the rest of the interactions which are discussed in the next section and are included in the $f_i$ coefficients will be determined by the particular (111) axis which corresponds to the vibronic state which is lowest in energy.

The (111) distortion has been discussed here because it applies directly to some of the data presented in the thesis. Exactly the same behavior will occur for (100) distortions; the strains which are not longitudinal along
the $\langle 100 \rangle$ directions are quenched and the primary axes of anisotropy are $\langle 100 \rangle$ axes.

E. Influence of Vibronic Coupling on EPR Spectra

1) Spin Hamiltonians

Data from electron paramagnetic resonance experiments are often summarized in the form of a Spin Hamiltonian. Since microwave transitions are observed between spin states split by an applied magnetic field, the spin states derived from the lowest electronic or vibronic state are the primary states of interest. Spin states of higher electronic or vibronic states are not populated at reasonable temperatures. The effects of the excited states are observed in the magnitudes of the parameters of the Spin Hamiltonian. The construction of the Spin Hamiltonian forms from symmetry arguments and the measurement of the parameters will be discussed in Chapters IV, V, and VI. This section will be concerned with discussing the interactions that will be considered and, finally, with the derivation of the major Spin Hamiltonian parameter magnitudes for the $d^3$ problem from the theory presented in this chapter.
2) Interactions and Effects on EPR Spectra

(a) Quadratic Spin Terms

The first terms to consider are terms quadratic in the spin operator since these lead to zero-field splittings of the spin states which dominate the observed spectra. The spin, \( \vec{S} \), transforms in \( O_h \) like \( \Gamma_4^+ \). Since \( \Gamma_4^+ \otimes \Gamma_4^+ = \Gamma_1^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_5^+ \), the quadratic contributions to the \( f_i \) are:

\[
\begin{align*}
        f_1 &= A(S_x^2 + S_y^2 + S_z^2) = A(S(S+1)) = \text{constant} \\
        f_\theta &= B[3S_z^2 - S(S+1)] \\
        f_\xi &= B \sqrt{3} (S_x^2 - S_y^2) \\
        f_\zeta &= C(S_y S_z + S_z S_y) \\
        f_\eta &= C(S_x S_z + S_z S_x) \\
        f_\xi &= C(S_x S_y + S_y S_x)
\end{align*}
\]

The constants \( A, B, \) and \( C \) are to be determined either from theory as in the next section or from experiment as in Chapter V. The \( \Gamma_4^+ \) term has not been written here; the form of the spin operators, \( S_i S_j - \frac{1}{2} \vec{S}_{ij} \), reduces to a term linear in spin operators because of the commutation relations. The result is a term identical to the spin-orbit term discussed next.
(b) Spin-Orbit Interaction

The contribution linear in spin will couple only with the vibronic operators which have the same symmetry as an orbital p-state and are time reversal odd. Since $\vec{S}$ is odd under time reversal, the overall Hamiltonian term will be even. The form of the coefficients will be:

$$\vec{t}_x = \lambda_g S_x$$
$$\vec{t}_y = \lambda_g S_y$$
$$\vec{t}_z = \lambda_g S_z$$

The constant $\lambda_g$ is to be determined; the subscript is a reminder that this $\lambda$ is only tenuously related to the free ion spin-orbit coupling constant. These terms will include the reduction effects resulting from the vibronic coupling and can include effects arising from the influence of the excited states.

(c) Spin Zeeman Effects

The Spin Zeeman Effects are characterized by terms proportional to both $\vec{S}$ and $\vec{H}$ which both transform like $\Gamma_4^+$. Since the product of the two time reversal odd operators, $\vec{S}$ and $\vec{H}$, is even with respect to time reversal, the overall time reversal symmetry of the combination of these two with the time reversal odd vibronic operators, $\vec{U}_x$, $\vec{U}_y$, and $\vec{U}_z$ will be odd and this combination would not be a valid Hamiltonian term. The remaining coefficients for the Hamiltonian will be
\[ f_1 = g_1 \hat{\mathbf{S}} \cdot \hat{\mathbf{H}} \]
\[ f_3 = g_3 \hat{\mathbf{S}} \cdot (3\mathbf{S}_z \mathbf{H}_z - \mathbf{S} \cdot \mathbf{H}) \]
\[ f_5 = g_5 \hat{\mathbf{S}} \cdot \sqrt{3}(\mathbf{S}_x \mathbf{H}_x - \mathbf{S}_y \mathbf{H}_y) \]
\[ f_7 = g_7 \hat{\mathbf{S}} \cdot (\mathbf{S}_y \mathbf{H}_y + \mathbf{S}_z \mathbf{H}_z) \]
\[ f_9 = g_9 \hat{\mathbf{S}} \cdot (\mathbf{S}_x \mathbf{H}_x + \mathbf{S}_y \mathbf{H}_y) \]

The values of \( g_1, g_3, \) and \( g_5 \) are to be determined. The inclusion of the Zeeman terms, including the Orbital Zeeman Term discussed next, is necessary for an EPR problem because the variation of the energy levels under an applied field allows the magnetic field and microwave frequency to be set so that resonance will be observed.

(d) Orbital Zeeman Effects

The magnetic field, a time reversal odd quantity that transforms like \( \Gamma_4^+ \) can couple linearly to the \( \Gamma_4^+ \) operators. The appropriate coefficients can be written:

\[ \bar{f}_x = g_L \hat{\mathbf{S}} \cdot \mathbf{H}_x \]
\[ \bar{f}_y = g_L \hat{\mathbf{S}} \cdot \mathbf{H}_y \]
\[ \bar{f}_z = g_L \hat{\mathbf{S}} \cdot \mathbf{H}_z \]

where \( g_L \) is the undetermined constant for this interaction and \( \hat{\mathbf{S}} \) is the Bohr magneton.
(e) Hyperfine Structure

The last two interactions of interest involve nuclear spins. First, the hyperfine terms involve the coupling of the electronic spin, $\vec{S}$, with the magnetic moment of the impurity nucleus, $\vec{I}$. The coefficients are:

$$f_1 = A_1 \vec{S} \cdot \vec{I}$$
$$f_0 = A_3 (3S_z I_z - \vec{I} \cdot \vec{S})$$
$$f_c = A_3 \sqrt{3} (I_x S_x - I_y S_y)$$
$$f_z = A_5 (I_y S_z + I_z S_y)$$
$$f_{\tau} = A_5 (I_x S_z + I_z S_x)$$
$$f_{\tau} = A_5 (I_z S_y + I_y S_x)$$

The parameters $A_1$, $A_3$, and $A_5$ are the undetermined constants. The combinations of $\vec{I}$ and $\vec{S}$ which transform like $\tau^+_4$ are not included in this list because they are not time reversal odd, a requirement for the $f_x$, $f_y$, and $f_z$ coefficients.

(f) Superhyperfine Interaction

When the nearest neighbor nuclei have a nuclear spin, $\vec{I}_i$, these can couple to the impurity spin, $\vec{S}$, and cause splittings of the observed lines. These splittings may or may not be resolvable. A distortion of the local environment will make some of the nearest neighbors inequivalent to others and this can sometimes be observed in the EPR spectra.
In the alkaline earth fluorides, there are eight nearest neighbors each with a spin of one half. The nuclear spin will transform like $\Gamma_4^+$ and the sites of the nearest neighbors will transform into each other like $(\Gamma_1^+ + \Gamma_2^- + \Gamma_4^- + \Gamma_5^+)$. So, the eight fluorine sites times the three spin components at each site will produce twenty-four linear combinations of nuclear spin components which can be written to show their transformation properties under the operations of $O_h$ and then combined either directly with the vibronic operators or coupled to $\vec{S}$ to form the coefficients of the operators. No attempt has been made to sort this large set of terms to predict the exact effects that each would induce. In Chapters V and VI, the superhyperfine structure will be discussed when it arises using more intuitive arguments.

3) Determination of Coefficients

The goal of this chapter is to relate the theory of the Jahn-Teller Effect to the experimental data described in later chapters. This goal cannot be accomplished in rigorous detail, but a general idea of the connection will be discussed in these concluding paragraphs. The first step will be to describe a calculation for values of the coefficients, $f_i$, of the electronic Hamiltonian before vibronic coupling effects are included. These values will be derived using perturbation theory from the physical
interactions which are most likely to play a role, the Zeeman Effect and the Spin Orbit Interaction. Then, the modification of these results due to the vibronic coupling will be discussed to indicate a possible source of the anisotropy which is observed.

The discussion will be restricted to the case of strong vibronic coupling to a triply degenerate vibrational mode which leads to the (111) distortions which are observed for the $d^3$ ions discussed in Chapter V. The (110) distortions of the $d^4$ ions discussed in Chapter VI will be ignored in this section due to the lack of a theory of vibronic coupling which predicts a stable distortion of this symmetry. It seems likely that an analogous procedure should be applicable once the vibronic problems are solved. In Chapter IV, the Spin Hamiltonian for the $d^3$ ions will be discussed. The Spin Hamiltonian formalism is particularly suited for conveniently summarizing the results of electron paramagnetic resonance experiments. The three parameters which are used to describe the spectra in Chapter V (neglecting nuclear magnetic moments) are the zero field splitting parameter, D, which is an indication of the strength of the axially directed interactions of the crystal environment with the spin, and the two components of the effective $g$-tensor of the Zeeman Effect, $g_\parallel$ and $g_\perp$. For the data discussed in this thesis, the dominant term is the one describing the zero-field splitting.
(a) Perturbation Theory in a Cubic Crystal Field

When the electronic problem is considered before the effects of vibronic coupling are included, the excited triplet and singlet states which are split from the same \(4\Gamma\) term as the ground electronic triplet state will influence the ground states via second order matrix elements of the Spin-Orbit and Zeeman interactions. A perturbation calculation is outlined in Appendix A which shows the effects of these interactions to second order on the three \(d\) electrons in a \(T_1\) ground state with a degenerate triplet \((T_2\rangle\) state excited by an energy \(8 D_g (\equiv \Delta)\) and an \(A_2\) singlet at an energy of \(16 D_g\) above the ground state. The result of this calculation is the electronic Hamiltonian in equation II-23(a) with the \(f_i\) coefficients expressed using the parameters, \(\lambda, \Delta,\) and \(g_e\) which are measurable in other experiments. The appendix demonstrates a general method which derives values for the phenomenological parameters introduced in Section II.E.2.

One major omission is made in this calculation. It is very possible that the lowest free ion term, a \(4\Pi\) term, is split from the ground state by an amount comparable to the splittings considered in this calculation. Since the \(4\Pi\) term transforms like a \(4T_1\) state in cubic symmetry, there will be an interaction with this state that has not been included.
When the effects of vibronic coupling to a triply degenerate vibrational mode are introduced, the electronic interactions which transform like \( \Gamma_3^+ \) and \( \Gamma_4^+ \) are quenched until their effectiveness approaches zero in the limit of strongest coupling. The \( \Gamma_1^+ \) electronic interactions are not quenched and the \( \Gamma_5^+ \) electronic interactions are partially quenched to the limiting value of two thirds the unquenched magnitude as discussed in Section II.D.3(b). In the strong coupling limit, the expression for the Zeeman and Quadratic Spin terms of the Hamiltonian can be found by combining equation II-33 and the results of Appendix A to get:

\[
\chi_Y = \left[ (g_e - \frac{5\lambda}{\Delta}) \hat{s} (\hat{S} \cdot \hat{S}) - \frac{5\lambda^2}{2\Delta} \hat{S} \cdot \hat{S} \right] Q_g \\
+ \frac{2}{3} \left\{ - \frac{15\lambda}{4\Delta} \hat{s} (H_{zY} S_Y + H_{zZ} S_Z) - \frac{15\lambda^2}{8\Delta} (S_Y S_Z + S_Z S_Y) \right\} U_{gx} \\
+ \frac{2}{3} \left\{ - \frac{15\lambda}{4\Delta} \hat{s} (H_{zX} S_X + H_{zZ} S_Z) - \frac{15\lambda^2}{8\Delta} (S_X S_Z + S_Z S_X) \right\} U_{gy} \\
+ \frac{2}{3} \left\{ - \frac{15\lambda}{4\Delta} \hat{s} (H_{zY} S_Y + H_{zX} S_X) - \frac{15\lambda^2}{8\Delta} (S_Y S_X + S_X S_Y) \right\} U_{gz}
\]

(II-38)

The random strains will have the effect of depressing the energy of one of the vibronic states relative to the others as described in Section II.D.5. As a result, the ground state will be a vibronic singlet and the Hamiltonian can be written as a Spin Hamiltonian of the form:
\[ \kappa_s = \left( g_e - \frac{5\lambda}{2\Delta} \right) \beta \hat{H} \cdot \vec{S} - \frac{5\lambda^2}{2\Delta} \vec{S} \cdot \vec{S} \]

\[ + \frac{5\lambda}{2\Delta} \beta (H_z S_y + H_y S_z + H_z S_x + H_x S_y + H_y S_z) \]  \( \text{(II-39)} \)

\[ + \frac{5\lambda^2}{4\Delta} (S_y S_z + S_z S_y + S_x S_z + S_z S_x + S_x S_y + S_y S_x) \]

This is the specific form when the distortion is along the [111] axis of the crystal. Now, if the coordinate system is redefined so that the z-axis is along the [111] direction, the y-axis is along the [110] direction, and the x-axis is perpendicular to these two, this Spin Hamiltonian can be rewritten as:

\[ \kappa_s = \left( g_e - \frac{5\lambda}{2\Delta} \right) \beta \hat{H} \cdot \vec{S} - \frac{5\lambda^2}{2\Delta} \vec{S}^2 \]

\[ + \frac{5\lambda}{2\Delta} \beta (3H_z S_y - \vec{H} \cdot \vec{S}) + \frac{5\lambda^2}{4\Delta} (3S_z^2 - \vec{S} \cdot \vec{S}) \]  \( \text{(II-40)} \)

Comparing this equation to equation IV-2 gives the expression for the parameters:

\[ g_{||} = g_e \]

\[ g_{\perp} = g_e - \frac{15\lambda}{2\Delta} \]  \( \text{(II-41)} \)

\[ D = + \frac{5\lambda^2}{4\Delta} \]

This calculation should indicate the general behavior which is expected from this system. However, one important feature has been left out. This feature will be discussed in the next section.
(b) Perturbation Theory in a Distorted Configuration

Some further insight should be gained by studying the admittedly idealized case of strongest vibronic coupling. Assume that the system is strictly frozen into position in configuration coordinate space and that the vibrational motions within the well in configuration coordinate space are strictly independent of the electronic state appropriate for that distortion. The energy levels will then be a set of excited vibrational levels associated with each electronic state. Two electronic states will each have an energy of \( \frac{3}{2} E_{JT} \) above the ground state and wave functions which are orthogonal to the ground state but composed of linear combinations of the original triplet electronic states. The excited vibrational states will have no effect on the ground state because all of the vibrational wave functions are orthogonal to the ground vibrational wave function; the matrix elements of any electronic interaction between the vibrationally excited states and the ground state are zero. The states that are closest in energy and will therefore have the strongest effect on the ground state will be the two excited electronic states. The second order perturbation effects of the Spin-Orbit and Zeeman interactions are derived in Appendix B. The results give an expression for the zero field parameter, \( D \), and the effective g-values in terms of experimental parameters that can be compared more easily to other measurements:
\[ D = \frac{3\lambda^2}{2E_{JT}} = \frac{3\lambda^2}{2V_T^2/k_T} \]

\[ g_{||} = g_e \quad (II-42) \]

\[ g_{\perp} = g_e - \frac{2\lambda}{E_{JT}} \]

The expression for \( D \) is qualitatively the same as the expression Ham gives in his 1965 paper\(^7\) for the zero field splitting arising from a static \((100)\) Jahn-Teller distortion when an orbital triplet couples only to a doubly degenerate vibrational mode. He obtains the expression as the limiting case of his "enhancement factors," the constants which describe the enhancement which arises from a second order interaction with the excited vibronic states due to the vibronic coupling. It seems that the particular assumptions made to allow the calculation in Appendix B just form a method for selecting out the vibronic states which will interact in the limiting case. Physically, it would be expected that a system with stronger vibronic coupling would have a more stable and more strongly interacting distortion, and, as a result, both the Jahn-Teller energy and the axial crystal field splitting of the spin states, \( D \), would be greater. Obviously, \( D \) can be small enough that no anisotropy is observed, the Jahn-Teller coupling is weak, and the system is described by the dynamic theory. If the coupling strength could be increased, the anisotropy would presumably appear and, for increasing coupling strengths,
it would become more pronounced. This behavior should be reflected in the value of $D$. This behavior is not apparent in the dependence of the zero field splitting on the Jahn-Teller energy which is derived with these calculations. They do demonstrate that, as the Jahn-Teller energy increases, the excited electronic states will have a decreasing influence on the ground state. The calculations also demonstrate that an axial zero field splitting should occur and that the mechanism for creating the splitting is probably a second order effect which arises from the electronic overlap of the excited vibronic states. The final comparison of these calculated values with the experimental results will be deferred to Chapter V and the conclusions.
III. Experimental Techniques

A. Sample Selection and Preparation

1) Ions of Interest

Three factors guided the selection of the ions for this study, the availability of an orbital triplet state, the likelihood of appreciable vibronic coupling and the spin degeneracy which would be encountered. The requirement that unpaired electrons be present so that paramagnetic effects would be seen restricts the selection of ions to the transition metal groups or the rare earth groups. When atoms from these groups are substituted for the cations in a diamagnetic, insulating crystal, the outer 4s, 5s or 6s electrons of the impurity ion participate in bonding leaving the inner d electrons or f electrons free to cause the crystal to exhibit paramagnetic behavior. The iron, palladium and platinum groups are more likely to give stronger vibronic coupling than the rare earth groups because the interaction of the stronger nuclear charge, even including the screening effects of the core electrons, cause f electrons both to occupy orbits closer to the nucleus and to be influenced less by the rest of the crystal relative to the d electrons. Thus, the unpaired d electrons of the transition metals will be more sensitive to the effects of a local distortion. Of the three transition metal groups, the iron group is of greater interest because it will have smaller spin-orbit interactions than
the palladium or platinum groups. As indicated in Chapter II, the competition between vibronic coupling effects and spin-orbit effects is critical and not always well defined. By restricting the study to iron group impurities, the influence of the spin-orbit interaction on the system is minimized and the influence of the vibronic coupling is maximized.

The possible degeneracies which would be expected from the ground states of iron group impurities in cubic symmetry are given in Table III-1. Derivation of these entries can be found elsewhere.\(^{(45,46)}\) The degeneracy of the ground state will depend on the coordination of the impurity site, and the strength of the cubic crystal field relative to the strength of the electron-electron interaction. The coordination numbers for a cubic site may be 4, for the site at the center of a tetrahedron of nearest neighbors, 6, for the site of the center of an octahedron, 8, for the site at the center of a cube, or 12, for the site at the center of a dodecahedron. The crystal field strength is denoted by weak or strong, referring to the strength of the crystal field relative to the competing electron-electron interaction. The most likely case for iron group ions is the weak coupling case. Strong coupling is more likely to occur when the ion has a larger charge than the ion it replaces.

The final consideration in the selection of the ion for study is the spin of the ground state. Ideally, an ion
Table III-1
Orbital and Spin Degeneracies for Iron Group Ions
Orbital Degeneracies (and Spin)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ions</th>
<th>Weak Field</th>
<th></th>
<th>Strong Field</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Coordination</td>
<td>6(S)</td>
<td>4,8,12(S)</td>
<td>Coordination</td>
</tr>
<tr>
<td>d&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Sc&lt;sup&gt;2+&lt;/sup&gt;,Ti&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>3 (½)</td>
<td>2 (½)</td>
<td>3 (½)</td>
<td>2 (½)</td>
</tr>
<tr>
<td>d&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Ti&lt;sup&gt;2+&lt;/sup&gt;,V&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>3 (1)</td>
<td>1 (1)</td>
<td>3 (1)</td>
<td>1 (1)</td>
</tr>
<tr>
<td>d&lt;sup&gt;3&lt;/sup&gt;</td>
<td>V&lt;sup&gt;2+&lt;/sup&gt;,Cr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1 (3/2)</td>
<td>3 (3/2)</td>
<td>1 (3/2)</td>
<td>2 (½)</td>
</tr>
<tr>
<td>d&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Cr&lt;sup&gt;2+&lt;/sup&gt;,Mn&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>2 (2)</td>
<td>3 (2)</td>
<td>3 (1)</td>
<td>1 (0)</td>
</tr>
<tr>
<td>d&lt;sup&gt;5&lt;/sup&gt;</td>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt;,Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1 (5/2)</td>
<td>1 (5/2)</td>
<td>3 (½)</td>
<td>3 (½)</td>
</tr>
<tr>
<td>d&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;,Co&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>3 (2)</td>
<td>2 (2)</td>
<td>1 (0)</td>
<td>3 (1)</td>
</tr>
<tr>
<td>d&lt;sup&gt;7&lt;/sup&gt;</td>
<td>Co&lt;sup&gt;2+&lt;/sup&gt;,Ni&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>3 (3/2)</td>
<td>1 (3/2)</td>
<td>2 (½)</td>
<td>1 (3/2)</td>
</tr>
<tr>
<td>d&lt;sup&gt;8&lt;/sup&gt;</td>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;,Cu&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1 (1)</td>
<td>3 (1)</td>
<td>1 (1)</td>
<td>3 (1)</td>
</tr>
<tr>
<td>d&lt;sup&gt;9&lt;/sup&gt;</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;,Ni&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>2 (½)</td>
<td>3 (½)</td>
<td>2 (½)</td>
<td>3 (½)</td>
</tr>
</tbody>
</table>
with a spin of one-half would be studied so that only one transition between the two levels could be observed. Also, an odd half integral spin is preferred since Kramers' Theorem\(^{(47)}\) shows that there must be a two-fold degeneracy when the applied magnetic field is zero. Therefore, increasing the applied field will cause the two levels to split until resonance is observed. Attempts to study the EPR of Cu\(^{2+}\) in alkaline earth halides were unsuccessful as were the attempts to study the next lowest spin case of Ni\(^{2+}\).\(^{(43)}\) Considerations outlined in the next paragraphs restricted the search to eight-fold coordinated sites and the remaining ions with triplet orbital states do not have such low spins. The merit of Cr\(^{3+}\), V\(^{2+}\), and Cr\(^{2+}\) was that signals had been seen from these ions that weren't completely understood\(^{(30)}\); both the \(\langle 111 \rangle\) and \(\langle 110 \rangle\) symmetry distortions have a vibronic degeneracy greater than the original electronic degeneracy. The hope was that, if the vibronic degeneracy was not perfect, dynamic effects would be observed. Furthermore, the mystery of stable \(\langle 110 \rangle\) distortions seemed to require a better experimental understanding of the distortion. Finally, it was possible in this study to observe the signals in more hosts than had previously been observed.
2) Hosts of Interest

The primary considerations for selection of a host crystal for this study are both physical and practical. The lattice structure must be cubic since only the cubic groups allow triply degenerate orbital states. The practical considerations are availability and the ability to incorporate the impurity of interest into the lattice.

In the initial phases of this work, unsuccessful attempts were made to diffuse copper and chromium into several of the alkaline earth fluorides using techniques available in the laboratory. These attempts dictated the choice of alkaline earth halides over the alkaline earth chalcogenides and the perovskites because the melting points of the fluorides are considerably lower. The alkaline earth fluorides are also more readily obtainable in single crystal form due both to the greater ease in growing the crystals and greater demand for such materials for other applications.

(3) Source of Samples

The samples discussed here were all grown by Walter Hargreaves at Optovac. Transition metals tend to be excluded from the lattice during growth, but he found that reasonable impurity concentrations could be obtained by including larger concentrations of the impurity in the melt than would be desirable in the final crystal and growing the crystals in a hydrogen fluoride atmosphere.
The initial dopant concentrations (in the melt) for the samples used in this study are given in Table III-2. In the initial stages of the study, attempts were made to measure the dopant concentrations using Proton Induced X-Ray Fluorescence. The technique and results are described elsewhere.\(^{(43)}\) Generally, the only reliable information which was obtained was that the dopant was present in samples in which the EPR for that ion was observed. When no EPR was observed, the results of this analysis were inconclusive.

4) Orientation of Samples

Sample orientation is a critical problem in studies such as this where the anisotropy of the data is a key factor in its interpretation. Three types of information were used to determine sample orientation. First, in all alkaline earth halides but CdF\(_2\), good single crystals will have \{111\} cleavage planes. Any two \{111\} planes intersect along a \langle 110 \rangle axis. This information can be used as a guide for cutting the sample as well as for the initial X-ray diffraction pictures. Laue diffraction patterns were used as a check on the cleavage information and as a primary source of orientation for the CdF\(_2\) crystals. The technique is a common one described in many texts.\(^{(49,50,43)}\) An X-ray beam is aimed along an axis of the crystal. Bragg diffraction from different sets of Miller planes produces spots on a piece of photographic film. The presence of
## Table III-2.

Initial Dopant Concentrations of Samples

<table>
<thead>
<tr>
<th>Host</th>
<th>Dopant</th>
<th>Initial Concentrations (mole %)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF₂</td>
<td>Cr</td>
<td>1.0</td>
<td>Optovac</td>
</tr>
<tr>
<td>CaF₂</td>
<td>Cr</td>
<td>0.25</td>
<td>Optovac</td>
</tr>
<tr>
<td>CdF₂</td>
<td>Cr³⁺</td>
<td>0.5</td>
<td>Optovac</td>
</tr>
<tr>
<td>CdF₂</td>
<td>Cr²⁺</td>
<td>&lt;1.0</td>
<td>Isomet</td>
</tr>
<tr>
<td>CaF₂</td>
<td>V</td>
<td>1.0</td>
<td>Optovac</td>
</tr>
<tr>
<td>SrF₂</td>
<td>V</td>
<td>1.0</td>
<td>Optovac</td>
</tr>
</tbody>
</table>
symmetry in the resulting photograph reveals any symmetry the incident beam axis might have. The crystal is then rotated (it is mounted on a goniometer with two perpendicular rotation directions) so that a high symmetry axis can be located. The data taken for this thesis were taken with the magnetic field rotating around a \(\langle 110\rangle\) axis of the sample, that is, in a \(\{110\}\) plane. The \(\{110\}\) planes are unique because they contain each of the three highest symmetry axes, the four-fold rotation axes along \(\langle 100\rangle\) directions, the three-fold rotation axes along \(\langle 111\rangle\) directions, and the two-fold rotation axes along the \(\langle 110\rangle\) directions.

(5) Cutting the Samples

Once the orientation of a \(\langle 110\rangle\) axis has been determined from the Laue photograph, the sample is remounted on the adjustable table of a Felker Di-Met (Model 8080) diamond saw. The initial position for orienting the sample before rotating so that the \(\langle 110\rangle\) axis is perpendicular to the saw blade is determined with the help of a dial indicator which measures slight deviations of the initial crystal face from the position which is parallel to the saw blade. In spite of the care taken in this procedure, orientation can only be expected to be within about two or three degrees.

The final crystal alignment and check on the orientation occurs when the EPR data are taken. Mounting the
crystal in the EPR apparatus can be done very consistently if enough care is taken. When the data indicate that alignment is too poor, the orientation in or on the sample holder can be modified to correct for small deviations. The limit of accuracy that can be achieved is probably about half a degree given an unlimited supply of patience, time, and liquid helium.

(6) Irradiation of Samples

Sample irradiation is used as a technique for changing the charge state of an impurity. The charge state can be changed by irradiation with either light of different wavelengths, X-rays, gamma rays, or possibly other sources. The best source depends on a variety of factors including the band gap of the host, the binding energies of the electrons on the various defects, and the stability of the defects. The primary technique used here was to irradiate the sample with X-rays from a target bombarded with 13 milliamps at 130 kilovolts. The irradiation was done using a Norelco MG 150 constant potential X-ray unit designed for industrial radiography. The sample is placed about 2.5 cm away from the window of a 150 kV Beryllium Window X-Ray Tube that can supply a 2.5 mm focus. The unit is well shielded with eighth inch thick lead sheet.

The length of the exposure time was varied from five minutes to four hours. The result of irradiating either CaF$_2$ or SrF$_2$ crystals in which Cr$^{2+}$ EPR signals alone had
been observed was to create both paramagnetic $\text{Cr}^+$ and $\text{Cr}^{3+}$ centers in the crystal. It was found that both of these charge states were observed after as little as five minutes of irradiation. The initial attempts to irradiate for periods of up to four hours created a considerable number of extraneous EPR signals. It was also observed that while the $\text{Cr}^{3+}$ signals could still be observed several weeks after irradiation, one year after irradiation they could not be observed. The $\text{Cr}^+$ signal, on the other hand, was still very apparent.
B. Electron Paramagnetic Resonance Spectrometer

1) Spectrometer Theory

A paramagnetic ion is one that has a permanent magnetic moment. An easy example is an ion with a single unpaired spin. The spin is one half and the projection of the spin along the $z$-axis can take two values, $M_s = +\frac{1}{2}$ or $M_s = -\frac{1}{2}$. If a magnetic field is applied to the free paramagnetic ion, the field defines the $z$-axis and the energy of the two spin states is split. If an electromagnetic field with the appropriate polarization is incident on the ion, a photon can be absorbed from the incident radiation which causes a transition between the spin states, but only when the magnetic field, $H$, and the radiation, at frequency $\nu$, satisfy the resonance condition:

$$h\nu = g\beta H$$  \hspace{1cm} (III-1)

The parameters $h$ and $\beta$ are Planck's constant and the Bohr magneton, respectively, and $g$ is the gyromagnetic ratio or effective $g$-value, a unitless number with a value which is usually within an order of magnitude of the $g$ value of the free electron, $g_e \approx 2$. In order to observe resonance from a free electron ($g \approx 2$) in an easily obtained laboratory magnetic field of about 3 kilogauss, the incident radiation must have a frequency near 9 GHz. This is the fundamental idea behind electron paramagnetic resonance.
In actual practice, the experiment is considerably more complex. First, rather than a free paramagnetic ion, these experiments are done on systems where the paramagnetic ion is in a crystal. Thus, the electric fields which the crystal produces will often influence the spin levels and the effective $g$-value must be considered as a function of the direction of the applied magnetic field relative to the crystalline axes. A second complexity arises from the deviations of ions from simple two spin level systems. More generally, a paramagnetic ion can have several spin states between which transitions can occur with different resonance conditions and transition probabilities. Furthermore, the existence of non-zero contributions of orbital angular momentum to the magnetic moment of the ion and the effects of higher excited electronic states on the ground states will cause the behavior of the effective $g$-value to vary widely for different ions in different locations in different hosts. It is convenient to describe the data in terms of an effective $g$-value derived from the resonance condition in equation III-1. Theory can then be developed with the intention of explaining the variation of the $g$-value with frequency and magnitude and direction of the applied magnetic field. The development of the theory to interface with experiment is developed in Chapters II and IV, and the connection will be made in the chapters on data and analysis.
The object of the experiment, therefore, is to measure the magnetic field and microwave frequency when power is absorbed from the incident radiation. It is convenient in practice to fix the microwave frequency at a very stable value and sweep the magnetic field while monitoring the power absorbed by the sample. In order to facilitate the separation of the signal from the noise, the applied magnetic field is modulated. As the field is swept through resonance, the power absorbed will be modulated at the same frequency. By using the frequency of the reference voltage which drives the modulation coils as a guide, the voltages, which are produced by the detectors and vary with the same frequency, can be selectively amplified and monitored to detect small changes in the power reflected from the cavity. By adjusting the phase of the microwave power which biases the detector relative to the power which is reflected from the cavity, two detection modes are possible. Detection of the absorption signal measures the change of the quality factor which occurs when the cavity is loaded differently. The cavity is loaded differently at resonance because the power absorbed by the sample causes the complex part of the susceptibility of the sample to change. The dispersion signal is measured when the change in the resonant frequency of the cavity is monitored; the dispersion signal is proportional to the real part of the sample susceptibility. Usually, the absorption signal is the signal which is recorded.
The final complication in these experiments is that the desired data must be taken at very low temperatures. The techniques for doing this are discussed in Section III.D.

The following sections will briefly summarize the characteristics of the particular spectrometers used in this study. More complete information on these spectrometers (43) and on the general operating features of EPR spectrometers (51, 52) can be found elsewhere.

2) Microwave Bridge Design Characteristics

Three major components handle the microwave radiation in the spectrometer, (1) the bridge, which includes the source of the radiation and guides the reflected power to the detectors, (2) the stalk, which guides the radiation from the bridge through the cryostat head to the cavity, and (3) the cavity, which contains the sample and, hence, the heart of the experiment. Resonance was studied in two frequency ranges and two microwave bridges were required, one to operate in the region near 9 GHz and the other to operate in the region near 35 GHz. Each is a standard homodyne reflection spectrometer bridge with balanced mixer detection. Figure III-1 gives the flow diagram for the 9 GHz spectrometer and Figure III-2 has the same for the 35 GHz spectrometer. The differences between these two spectrometers are primarily a matter of the details. The first major difference between the two will be discussed in Section III.B.3; diodes are used for
Figure III-1. Schematic Diagram of X-band Spectrometer
Figure III-2. Schematic Diagram of Ka-band Spectrometer
detection at 9 GHz and bolometers are used at 35 GHz. The other major difference is very important; at 9 GHz the microwave frequency is measured electronically through the waveguide to BNC converter while a wavemeter gives the best obtainable frequency measure at 35 GHz. At 9 GHz, the signal from the BNC connector is fed into a Hewlett-Packard Model 2590B Microwave Frequency Converter which mixes the microwave signal with the appropriate harmonic of an internally generated signal in the range of 240 to 390 MHz. This internally generated signal is tuned so that the difference between it and the input signal exactly matches a 30 MHz reference signal derived from an externally input 10 MHz standard. The 10 MHz standard is obtained from the standard in a Hewlett-Packard Model 5245L Electronic Counter which is also used with a Model 5253B Frequency Converter Plugin to measure the internally generated signal which has been locked onto the signal to be measured. A simple calculation gives the original microwave frequency to an accuracy of within 0.01 MHz. The frequencies near 35 GHz are too high to be measured with this equipment so the frequency was measured with a wavemeter that could be read to within 1 part in $10^5$.

Two separate cryogenic stalks were used with the two bridges. These are pictured in Figures III-3 and III-4. They are designed to form a vacuum seal at the top of the cryostat so that the helium bath can be pumped, allowing
Flange attaches to microwave bridge

o-ring seals to cryostat head

Figure III-3.
Stalk for X-Band Cylindrical Cavity

39\frac{1}{4}"

heat sheilds

Cavity
Sample Position
Figure III-4. Cryogenic Stalk for Ka-band Cylindrical Cavity
the sample temperature to be at temperatures as low as 1.3K. The second major object of the design was the use of heat shields and thin walled stainless steel waveguide to minimize both the heat transport down the stalk and the heat capacity of the apparatus. A Gordon coupler\(^{(53)}\) was used at the bottom of each stalk to allow impedance matching between the stalk and the cavity with control of the coupling from the top of the cryostat. Figure III-5 shows the design of the coupling assembly on both stalks.

The final piece of the microwave network is the cavity. The cavities used in this study were both TE\(_{011}\) cylindrical cavities. The design and dimensions of the cavities are shown in Figures III-6 and III-7.

3) Electronic Design Characteristics

There are three major electronic components in the spectrometer, the klystron power supply, the klystron stabilizer, and the lock-in amplifier.

The Varian V-153C 9 GHz klystron is powered by a Hewlett Packard Model 716B Klystron Power Supply. A klystron power supply is a very stable high voltage D.C. power supply that is designed to supply the beam voltage, reflector voltage, and heater current necessary for stable klystron operation. The klystron power output is about 200 milliwatts when the beam voltage is 250 volts, the beam current is 30 milliamperes and the reflector voltage is 190 volts. The klystron is mounted in a Narda Microline Model 58Z1 Klystron Cooler, a water flow cooling jacket.
Figure III-5. Schematic Drawing of Gordan Coupler Mechanism used with both X-band and Ka-band Systems
Figure III-6. TE_{011} Cylindrical Cavity for X-Band Spectrometer.
Figure III-7. TE_{011} Cavity Design. Operating frequency at 35 GHz. (unloaded)
The OKI 35V11 klystron used at 35 GHz requires voltages which are not available in the Hewlett-Packard supply so a Weinschel Engineering Model Z815B Universal Power Supply was used. It supplies a beam voltage of 1500 volts, a beam current of 20 milliamps and a reflector voltage of 250 volts with slightly less stability than the H.P. 716B. This klystron is air cooled with a small fan mounted on a separate base from the klystron.

The klystron stabilizer is a Teltronics Model KSLP Klystron Stabilizer. The reflector voltage is routed from the power supply through the KSLP and then to the klystron. The KSLP superposes a 70 KHz modulation on the DC reflector voltage. The output of a resonant cavity in the bridge is monitored by the KSLP so that the reflector voltage will be automatically corrected by the signal from a phase sensitive detector within the KSLP whenever the frequency of the klystron wanders from the resonance point of the reference cavity. The frequency stability achieved with this system is usually better than one part in $10^5$.

The lockin amplifier is the unit responsible for phase sensitive detection of the signal. A Princeton Applied Research Model 126 Lock-In Amplifier with a Model 118 Preamplifier is used at both frequencies. Operation of this amplifier with this preamp allows the detection of voltages with a frequency of 50 Hz to 5 KHz at levels of 50 mV to 10 V.
The reference voltage feeds to an 80 watt Lansing-Altec Model 1569A Linear Amplifier which produces an amplified signal in the modulation coils discussed in Section III.C.1. The coils produce an AC magnetic field superimposed on the slowly varying magnetic field. Thus, the microwave power which is absorbed by the sample as the field moves through resonance will be modulated as shown in Figure III-8. The detectors, which are discussed in the next section, then produce a signal voltage which is modulated at the selected frequency and which has an amplitude proportional to the slope of the power absorbed as a function of the sweeping magnetic field. The amplifier selectively amplifies the voltage it receives at the reference frequency. Then, the amplified signal is added to and subtracted from the reference signal with a relative phase that is set for maximum signal from the front panel. The output is a D.C. signal which can be amplified even further for output on a Hewlett-Packard Model 7005B X-Y Recorder as a function of magnetic field.

4) Detection

One of the most critical points in the spectrometer is the detection of the reflected power and conversion of this into a signal at the modulation frequency for input to the preamp. At 9 GHz, an optimum signal to noise ratio is obtained conveniently with diodes. The diodes used in the spectrometer for this study were Philco-Ford L 4164 A
Figure III-8. Schematic Diagram of Lockin Amplifier Output as a Function of Modulated Signal Input
back diodes. The primary noise sources in back diodes are $\frac{1}{f}$ noise and Johnson noise. The $\frac{1}{f}$ noise is decreased by increasing the frequency of the modulation, $f$. The modulation frequency was set at 3 to 3.5 kHz; a higher frequency modulation would be attenuated too much by the cavity. The Johnson noise of a resistor is thermal and increases with temperature. In diodes, the Johnson noise at a given temperature is increased by a constant factor from the value a resistor would have at that temperature. The constant factor is called the noise temperature. (51) The noise temperature can be used with the burnout rating and cw power rating to select acceptable diodes.

At 35 GHz, the experiment is done in a stainless steel dewar due to the decreased magnet gap which is required to reach the higher fields that are needed at these frequencies. As a result of the extra shielding from the dewar, the modulation frequency is reduced to 50 to 100 Hz. For a diode, the $\frac{1}{f}$ noise would be too great for sensitive operation and, therefore, bolometers, which don't have $\frac{1}{f}$ noise, are used. Bolometers are made of a thin metal wire which heats when microwave power is incident. The wire is biased with about 8 milliamps of current and the heating will cause the resistivity to change. As the resistivity changes, the voltage will change and this change will be proportional to the incident microwave power. Since the bolometer is essentially a resistive
element, the major source of noise is Johnson noise so bolometers are capable of being at least as sensitive as diodes if not more so. The bias circuit used to interface the bolometers with the preamp is shown in Figure III-9.

5) Sensitivity

The minimum number of detectable spins, called the "sensitivity" of the spectrometer, is an important characteristic especially when interpreting null results. A Varian Pitch probe standard is used to determine the sensitivity of the X-band spectrometer. About 4.3 cm of the probe (calibrated at $3 \times 10^{15}$ spins/cm) is inserted along the axis of the cylindrical 9 GHz cavity. The dewar is evacuated and the parameters of the spectrometer are set to a specific set of typical values. A typical calibration run is given in Figure III-10. The sensitivity from this run is found to be $6 \times 10^{12}$ spins/\text{gauss}. This procedure is repeated every few months and whenever a major change is made on the system so that any degradation of the measuring capability of the system will be known.

The Varian standard cannot be used in the 35 GHz system. In an attempt to get some idea of the sensitivity of this system, a closed quartz capillary containing DPPH was made and a sensitivity check run. This "standard" tended to load the TE$_{011}$ cavity too much, but the mode was found and the data taken at 35 GHz were compared with the signal from the same sample in the 9 GHz cavity. The
Figure III-9. Bolometer Blasting Circuit
Sensitivity $= 6 \times 10^{12}$ spins/gauss

Figure III-10. Typical Sensitivity Calibration Run
indication was that the 35 GHz system was about four times less sensitive than the 9 GHz system. Since the Q of the 35 GHz cavity generally shows much more improvement than the Q of the 9 GHz cavity when the temperature is lowered to 4.2K from room temperature, it is possible that the two spectrometers have comparable sensitivity.
C. Magnetic Fields

1) Modulation

The two spectrometers use modulating magnetic fields at different frequencies because of the differences in the response characteristics of the detectors as discussed in Section III.B.4.

The modulation in the 9 GHz spectrometer is run at 3 KHz with a pair of Varian modulation coils mounted on the cylindrical pole caps with a plastic cover which is attached to the face with non-magnetic screws. The coils have a resistance of 11Ω, an inductance of 4.3 mh when connected in series and the impedance is matched to the Altec linear amplifier using a set of capacitors mounted on a rotary switch. The current passing through the coils is measured using a Simpson meter and recorded as a measure of the modulation magnetic field. Hoffman(54) has calibrated the modulation amplitude as a function of the measured current and found that the peak-to-peak amplitude of the modulation is near 6 gauss when the current is one ampere. The pickup coil for this measurement is located inside the sample cavity in the evacuated dewar and everything is at room temperature. A decrease of 30% was observed when the cavity was cooled to 77K.

The low frequency modulation which is used with the 35 GHz spectrometer and with the NMR probe discussed in
Section III.C.4 is produced by the current in a pair of homemade coils originally built by Barksdale.(55) They are mounted around the outside rim of the cylindrical pole caps. The coils have a resistance of 21Ω and an RMS current of one amp produced a modulation field with a peak-to-peak amplitude near 20 gauss when Hoffman made his calibration curves.

2) DC Magnetic Field

The magnetic field for these experiments is supplied by a nine inch Varian V-HF 3400 electromagnet powered by a Varian V-FR2803 Mark I power supply. The pole caps are 9 inches in diameter with a gap of 4 inches when the 9 GHz spectrometer is run. The maximum obtainable field is ten kilogauss and the field homogeneity is $10^{-5}$ within a two inch diameter along the center of the gap at 3.3 kilogauss.

The 35 GHz spectrometer requires fields higher than ten kilogauss to observe a $g = 2$ resonance. A pair of tapered pole caps were purchased from Varian that allow the maximum field to reach eighteen kilogauss. The homogeneity of the field is $10^{-5}$ within a one inch diameter at the center of the gap which is 1.789 inches wide.
3) Hall Probe

The magnetic field is controlled and swept with a Varian Mark I Fieldial which uses a temperature compensated Hall probe to monitor the field. A field stability of 1 ppm can be achieved after one hour and the field is regulated to within 10 ppm for a 10% step change in line voltage. The Fieldial is calibrated within 0.2% and the sweep variation is within 0.5% of the indicated value. A potentiometer supplies a ramp voltage which is proportional to the fraction of the sweep range and this voltage is used to drive the x-axis of the x-y recorder. The field can be swept either up or down with a sweep range of 250 milligauss to 40 kilogauss and a sweep time of 0.5 minutes to 100 minutes. While the Fieldial is accurate enough for initial studies and surveys, the most accurate measurement of the magnetic field is made not with the Hall probe the Fieldial uses but with an NMR probe and gaussmeter which is discussed in the next section.

4) The NMR Gaussmeter

The most accurate measurements of the magnetic field have been obtained using a Model G-502 Precision NMR Gaussmeter purchased from the Magnion Division of Ventron Corporation. Since the oscillator is designed to sit as physically close to the probe as possible, the Model RD-50 Remote Controller is used to operate the unit. Four NMR probes are available to measure fields in the ranges
indicated in Table III-3. The red probe was found with a lead broken as the lead entered the epoxy so the epoxy case was scraped off to reveal a coil wrapped around a dumbbell shaped container which contains 0.08 cc of lithium and manganese chloride in water. The coil was removed and replaced with a coil formed from wire adjusted by trial and error to have the characteristics which are necessary for the circuit to resonate within the frequency range expected from the red probe. The sample and coil were wrapped in electrical tape to prevent unraveling. Even though the manufactured probes have been machined to make them thinner, it is not possible to place an NMR probe, the dewar, and the Field dial's Hall probe all along the central axis of the magnet gap. The Hall probe was moved away from the center of one face, the modulation coil was removed from that face, and the dewar still had to be positioned off the axis of rotation of the magnet. Thus, the range of angles which could be searched when the sample was in a fixed position was limited to between 40° and 50°. So that the NMR probes were within the cylinder of maximum homogeneity identified in the magnet specifications, only one probe was in the gap at any one time. The final difficulty discovered in the process of making these measurements occurred when it was observed that one of the g-shifts as a function of the microwave frequency from 9 GHz to 35 GHz was in the wrong direction. It was determined that the
Table III-3
Magnetic Field Ranges Measured by the Four NMR Probes

<table>
<thead>
<tr>
<th>Probe</th>
<th>Color</th>
<th>Proton Resonance Field Range (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td>Brown</td>
<td>341-702</td>
</tr>
<tr>
<td>122</td>
<td>Red</td>
<td>640-1330</td>
</tr>
<tr>
<td>123</td>
<td>Orange</td>
<td>1210-2600</td>
</tr>
<tr>
<td>124</td>
<td>Yellow</td>
<td>2582-6180</td>
</tr>
</tbody>
</table>
stainless steel dewar used for the 35 GHz measurements when the pole caps were on the magnet was causing a shift on the order of 30 gauss in the measured magnetic field. This problem was solved by machining an adapter for the head of the 9 GHz cryostat so that the 35 GHz stalk could be used in the glass dewar. Although the signals with $g_{\text{effective}} < 2.5$ could not be observed, the most important measurements were on transitions that could be observed below 10 kilogauss at 35 GHz.

The high frequency modulation of the EPR measurement wiped out the detection of the NMR signals and it was decided that the introduction of shielding was not very desirable. So, the field measurements were made by stopping the magnetic field sweep at the center of the resonance line, turning off the EPR modulation and turning on the NMR 60 Hz line voltage modulation to measure the field. Several sweeps were made in the same direction to check for stability and consistency and then the sweep was stopped at the desired point. The sweep range varied according to the linewidth from 10 gauss sweeps to 250 gauss sweeps. Data were taken sweeping in both directions over the same line and no significant difference was noted. As will be discussed in the chapters on data and analysis, the greatest error in most cases seemed to arise from determining the position of the center of the EPR absorption line. Once the sweeping field was stopped, the RF
frequency was varied until the proton resonance was observed on the scope display of the Gaussmeter Control. The modulation was decreased and phase adjusted so that the center of the signal occurred in the center of the screen. Then, the RF frequency was measured using the same frequency counter used in the 9 GHz frequency measurement and discussed in Section III.B.2. The microwave frequency was checked each time the EPR modulation was turned down so that the two frequencies were measured essentially simultaneously. The magnetic field is obtained from the RF frequency by multiplying the frequency by 234.865 gauss/Megahertz. The effective $g$-value at a given microwave frequency is given by:

$$g_{\text{effective}} = \frac{\hbar}{\beta K} \frac{\nu}{\Omega} = (3.04211) \times \frac{\nu\text{(in Gigahertz)}}{\Omega\text{(in Megahertz)}}$$  \hspace{1cm} (III-2)

with:

- $\hbar = 6.62620 \times 10^{-27}$ erg-sec
- $\beta = 9.27410 \times 10^{-21}$ erg/ gauss
- $K = 234.865$ gauss/Megahertz
- $\Omega = RF$ frequency of proton resonance
D. Cryogenics

1) Glass Dewars

Figure III-11 pictures the set of silvered glass dewars assembled for the 9 GHz spectrometer. The cavity is immersed in liquid helium in the center of the inner dewar. The vacuum space surrounding the inner dewar contains 5 to 10 torr of nitrogen gas which allows faster cooldown to nitrogen temperatures; when helium is transferred, this nitrogen freezes out and a hard vacuum is obtained for maximum insulation.

2) Stainless Steel Dewar

The higher fields required at 35 GHz necessitate the pole caps which leave a reduced magnet gap. The gap is too small, in fact, to use a glass dewar conveniently. The low thermal conductivity of stainless steel makes it ideal for use in fabricating a thin walled dewar to contain the helium bath for these experiments. Andonian Associates\(^{(57)}\) designed and manufactured the dewar used in this study. It is diagrammed in Figure III-12. In this dewar, the sample chamber is insulated by the helium reservoir. This allows the flow of helium into the sample chamber to be controlled. With the assistance of a heater, the temperature of the gas flowing from the capillary which connects the reservoir to the sample chamber can be controlled and adjusted from 4.2K to room temperature; liquid can be
Figure III-11. Glass Dewars Used with X-band Spectrometer
Figure III-12. Stainless Steel Dewars for 35 GHz Spectrometer
let into the sample chamber to create a bath around the cavity which is at 4.2K and the vapor pressure above the bath can be lowered with a pump to achieve temperatures below the $\lambda$ point.
IV. Spin Hamiltonians

An electron paramagnetic resonance experiment has the potential to provide a large amount of information which can be tedious to describe in detail. As a result, it is often convenient to communicate this information in a compact fashion using a Spin Hamiltonian. The Spin Hamiltonian describes the behavior of an idealized, isolated manifold of states so that the behavior of these states matches identically the behavior of the states observed in the experiment. This matching is accomplished by adjusting the values of the coefficients of the terms which have been derived using general physical principles and symmetry arguments. These parameters can be derived, at least in principle, from theory and this derivation would include the effects of the excited states and a more physical idea of the source of the values of the different parameters. A crude attempt at this has been discussed in the conclusion of Chapter II.

In the following sections, the Spin Hamiltonians which can be used to describe the data in the next two chapters are presented and expected properties of the transitions which should be observed are discussed. The reasoning will necessarily draw on some of the features of the data described in the following chapters.
A. The $S = \frac{3}{2}$ Spin Hamiltonian of the $d^3$ Ion

The $Cr^{3+}$ and $V^{2+}$ ions both have [Ar] $3d^3$ ground configurations with a spin of three halves. The manifold of states in the Spin Hamiltonian should have four states and up to six EPR transitions could be observed if there is one transition between each pair of the four states. The data consist of four lines but they behave like a single transition which originates from four equivalent sites with axial symmetry along the four $\langle 111 \rangle$ directions. This behavior is expected when a strong axial zero field term dominates the Zeeman interaction in the Spin Hamiltonian. The Spin Hamiltonian which includes the zero-field and lowest order Zeeman terms in axial symmetry for $S = \frac{3}{2}$ can be written:

$$\mathbf{H}_S = D[S_z^2 - \frac{1}{3} S(S+1)] + g_{||} \mu \mathbf{H} S_z + g_{\perp} \mathbf{\Delta} (\mathbf{H}_x S_x + \mathbf{H}_y S_y)$$

(IV-1)

The z-axis of this form will be one of the four $\langle 111 \rangle$ directions in the crystal and the x and y axes can be any two perpendicular axes in the plane which is perpendicular to the z-axis. The matrix expression for this Hamiltonian with the eigenstates ordered by the decreasing value of the z-component of angular momentum, $M_s$, is:
\[ \mathbf{K}_s = \begin{pmatrix} 
D + \frac{3}{2} g_\parallel \mathbf{\hat{H}} \cos \theta & \sqrt{3} g_\perp \mathbf{\hat{H}} \sin \theta & 0 & 0 \\
\sqrt{3} g_\perp \mathbf{\hat{H}} \sin \theta & -D + \frac{3}{2} g_\parallel \mathbf{\hat{H}} \cos \theta & g_\perp \mathbf{\hat{H}} \sin \theta & 0 \\
0 & g_\perp \mathbf{\hat{H}} \sin \theta & -D - \frac{3}{2} g_\parallel \mathbf{\hat{H}} \cos \theta & \sqrt{3} g_\perp \mathbf{\hat{H}} \sin \theta \\
0 & 0 & \sqrt{3} g_\perp \mathbf{\hat{H}} \sin \theta & D - \frac{3}{2} g_\parallel \mathbf{\hat{H}} \sin \theta 
\end{pmatrix} \]  

(IV-2)

The angle, \( \theta \), is the angle between the magnetic field, \( \mathbf{\hat{H}} \), and the \( z \)-axis. If the zero field splitting, \( 2D \), is much greater than \( g_\perp \mathbf{\hat{H}} \), then the four states are grouped into two doublets, one composed of the states with \( M_s = \pm \frac{1}{2} \) and the other composed of the states with \( M_s = \pm \frac{3}{2} \). The energies of the two doublets can be solved for separately in a manner discussed elsewhere.\(^{(45,46)} \) The energies for the four states are:

\[ E_{\pm \frac{1}{2}} = -D \pm \frac{3}{2} g_\parallel \mathbf{\hat{H}} \sqrt{g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta} \]  

(IV-3)

\[ E_{\pm \frac{3}{2}} = +D \pm \frac{3}{2} g_\parallel \mathbf{\hat{H}} \cos \theta \]  

(IV-4)

A plot of the energy of these two doublets as a function of magnetic field when the field is along the \( \langle \mathbf{111} \rangle \) axis and perpendicular to the \( \langle \mathbf{111} \rangle \) axis is given in Figure IV-1.

The EPR transitions within either doublet can be described by:

\[ h\nu = \mathbf{\hat{H}} \sqrt{g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta} \]  

(IV-5)

For the transition within the \( M_s = \pm \frac{1}{2} \) doublet, \( g_\parallel \) equals \( g_\parallel \) and \( g_\perp \) is \( 2g_\perp \) while within the \( M_s = \pm \frac{3}{2} \) doublet \( g_\parallel \) must be \( 3g_\perp \) and \( g_\perp \) is zero. Since \( g_\perp \) is zero, so is the intensity of the transition between the \( |M_s = \pm \frac{3}{2} \rangle \) state and the
Figure IV-1. Energy vs. Field Diagram for $S=\frac{3}{2}$ Spin Hamiltonian

(a) $H \parallel z$-axis and (b) $H \perp z$-axis
\(|M_s = -\frac{3}{2}\rangle\) state. The expression in equation IV-5 for the conditions of field and frequency at resonance has no explicit dependence on the zero field parameter, D, which characterizes the axial nature of the center (there is, however, an implicit axial character expressed by the difference between \(g_\|\) and \(g_\perp\)). The next section derives the dependence of the effective \(g\)-value on D.

2) Perturbation Theory and the Determination of D

As discussed in the concluding section of Chapter II, the zero field parameter, D, is related to the coupling parameters which are responsible for a Jahn-Teller distortion. Therefore, this information is one of the measurements which gives information about the vibronic coupling and can supply some indication of the coupling strength.

The Spin Hamiltonian in equation IV-1 can be rewritten as:

\[
\mathcal{H}_s = D\left[\frac{2}{3} - \frac{1}{3} S(S+1)\right] + g_\| \beta H z S_z + \frac{1}{2} g_\perp \beta (H_+ S_- + H_- S_+) \quad (IV-6)
\]

The terms in the Spin Hamiltonian which contain the raising and lowering operators, \(S_+\) and \(S_-\), are capable of mixing the states of the two doublets. When the microwave frequency is increased, the fields needed to achieve resonance are increased, some of the states of the two doublets get closer to each other and the influence of these states on each other is increased. The effects can be calculated using second order perturbation theory to derive a shift in the \(g\)-value as a function of frequency which depends on the
value of \( D \). The calculation can be found elsewhere\(^{43}\) and the results for the transition within the \( M_s = \pm \frac{1}{2} \) doublet can be expressed as:

\[
\eta' = \sqrt{g_{||}^2 \cos^2 \theta + (2g_\perp)^2 \sin^2 \theta - \frac{3}{4} \left\{ \frac{2g_{||}^2 \sin^2 \theta - 4g_\perp^2 \sin^2 \theta}{2} \right\} \left\{ \frac{2g_{||}^2 \cos^2 \theta - 4g_\perp^2 \sin^2 \theta}{2} \right\} \}
\]

\[(IV-7)\]

If \( g_{||} \) is approximately \( g_\perp \) in the last term, this result can be written in a simplified form\(^{58}\) for the effective \( g \)-value:

\[
geff = \sqrt{g_{||}^2 \cos^2 \theta + (2g_\perp)^2 \sin^2 \theta \left[ 1 - \frac{3}{2} \left( \frac{g_{||} \beta H}{2D} \right)^2 \frac{\sin^2 \theta (3 \sin^2 \theta - 1)}{3 \sin^2 \theta + 1} \right]}
\]

\[(IV-8)\]

Thus, by measuring the \( g \)-values at two widely separated frequencies, the value of the zero field splitting can be determined.

3) Temperature Dependence Information

The expression in equation IV-7 allows the determination of the magnitude of the zero field splitting, \( D \), but not its sign. The sign of \( D \) can be obtained from the variation of the line intensity as a function of temperature. In fact, a careful measurement of the temperature dependence of the line intensity can provide a value for the magnitude of \( D \) as well.
The source of the change in line intensity as a function of temperature is the change in the population distribution among the ground manifold of states that occurs when the temperature is raised. The number of electrons which are found in the state of energy $E_i$ at a temperature $T$ (the population), is given by the Boltzmann distribution (the ensemble of different centers is assumed to be non-interacting):

$$ P_{E_i} = \frac{\exp(-\frac{E_i}{kT})}{\sum_j \exp(-\frac{E_j}{kT})} N_{\text{Cr}^{3+}} $$ (IV-9)

where $N_{\text{Cr}^{3+}}$ is the number of $\text{Cr}^{3+}$ ions in the sample. The intensity of a line is proportional to the power absorbed which is proportional to the number of transitions within the sample at resonance. The number of transitions is related to the relative populations of the initial and final states, $P_{E_i}$ and $P_{E_f}$ respectively. The assumption is made that relaxation processes maintain the population at thermal equilibrium. The intensity will have the dependence:

$$ I_{\text{Cr}^{3+}} (T) \propto P_{E_i} - P_{E_f} $$ (IV-10)
and substituting from equation IV-9 gives:

\[
I_{\text{Cr}^{3+}}(T) \propto \left( \frac{\exp(-\frac{E_i}{kT}) - \exp(-\frac{E_f}{kT})}{\sum_j \exp(-\frac{E_j}{kT})} \right) N_{\text{Cr}^{3+}} \tag{IV-11}
\]

The absolute intensity is a difficult parameter to describe completely, but many of these difficulties are avoided if the measurement is of a relative line intensity. The intensity of a \(\text{Cr}^{3+}\) line measured relative to the intensity of a line from a Curie Law standard signal has compensated for the experimental difficulties of the absolute measurement. Therefore, the expression should be found for the temperature dependence of the ratio of the \(\text{Cr}^{3+}\) intensity to the intensity of a Curie Law standard. For a Curie Law standard, the intensity will have property that:

\[
I_{\text{Curie}}(T) \propto \frac{\exp(-\frac{1}{2} \frac{g\sigma h}{kT}) - \exp(+\frac{1}{2} \frac{g\sigma h}{kT})}{\exp(\frac{1}{2} \frac{g\sigma h}{kT}) + \exp(-\frac{1}{2} \frac{g\sigma h}{kT})} N_{\text{Curie}} \tag{IV-12}
\]

and, assuming that \(g\sigma h \ll kT\), this expression becomes:

\[
I_{\text{Curie}}(T) \propto \frac{g\sigma h}{kT} N_{\text{Curie}} \tag{IV-13}
\]

The \(\text{Cr}^{3+}\) ion has four states which are low enough in energy to be populated significantly at liquid helium temperatures.
As discussed earlier in this chapter, these four states are split into two doublets. Substituting the values of energy given in equations IV-3 and IV-4 (substituting $g$ for the square root) into the expression for the intensity of the transition between the $M_s = +\frac{1}{2}$ state and the $M_s = -\frac{1}{2}$ state obtained from equation IV-11, the intensity becomes:

\[
I_{\text{Cr}^{3+}(T)} \propto \frac{\left[ \exp\left(\frac{-D+\frac{1}{2}g\beta H}{kT}\right) - \exp\left(\frac{-D-\frac{1}{2}g\beta H}{kT}\right) \right] N_{\text{Cr}^{3+}}}{\exp\left(\frac{-D-\frac{1}{2}g\beta H}{kT}\right) + \exp\left(\frac{-D+\frac{1}{2}g\beta H}{kT}\right) + \exp\left(\frac{D-\frac{3}{2}g\beta H}{kT}\right) + \exp\left(\frac{D+\frac{3}{2}g\beta H}{kT}\right)}
\]

(IV-14)

The value of \(\exp\left(-\frac{D}{kT}\right)\) can be factored out of the numerator and the first two terms of the Taylor series expansion of the resulting exponents of the small numbers, \(\frac{g\beta H}{kT}\), will be kept to produce:

\[
\exp\left(\frac{-D}{kT}\right)\left[ 1 + \frac{1}{2}\frac{g\beta H}{kT} - \left(1 - \frac{1}{2}\frac{g\beta H}{kT}\right) \right] = \frac{g\beta H}{kT} \exp\left(-\frac{D}{kT}\right)
\]

(IV-15)

as the numerator. After manipulating the terms in the denominator in the same way, the intensity can be written as:

\[
I_{\text{Cr}^{3+}(T)} \propto \frac{\frac{g\beta H}{kT} \exp\left(-\frac{2D}{kT}\right)}{1 + \exp\left(-\frac{2D}{kT}\right)} N_{\text{Cr}^{3+}}
\]

(IV-16)

The ratio which can be measured is:
\[ R_{\text{Cr}^{3+}}(T) = \frac{\exp(-\frac{2D}{kT})}{1 + \exp(-\frac{2D}{kT})} \left( \frac{N_{\text{Cr}^{3+}}}{N_{\text{Curie}}} \right) \] (IV-17)

The constants \( N_{\text{Cr}^{3+}} \) and \( N_{\text{Curie}} \) are cancelled from the measurement when the ratio of this relative intensity at two different temperatures is considered:

\[ Q_{\text{Cr}^{3+}}(T_1, T_2) = \frac{\exp(-\frac{2D}{kT_1})}{\exp(-\frac{2D}{kT_2})} \left( \frac{1 + \exp(-\frac{2D}{kT_2})}{1 + \exp(-\frac{2D}{kT_1})} \right) \] (IV-18)

This expression can be used to give a value of the zero field splitting from the temperature dependence of the line intensity. Experimental considerations play a significant role in making a reliable measurement of the magnitude with this expression. A standard signal must be present that has the expected Curie Law temperature dependence. Frequently, such signals are easily saturated which can alter the line intensity and its variation with temperature. These effects are not so large that the information about the sign of the zero field splitting is lost and so, the sign is the most reliable information which is obtained. An ideal use of the temperature dependence information is as a consistency check on the g-shift measurement. While the line intensity relative to a Curie Law signal is not always feasible, the comparison of the \( \text{Cr}^{3+} \) line intensity relative to the \( \text{Cr}^{2+} \) line intensity should be reliable as a check when both problems
have been solved. The method for checking this information is to include the Boltzmann distribution in equation IV-9 in the computer calculations of the next section.

4) Diagonalizing the Hamiltonian - Isofrequency Plots

The ideal theoretical tool for analyzing a complicated EPR system in order to determine the extent of the detailed agreement of the experiment to theory is a device which, given values for the microwave frequency and the Spin Hamiltonian parameters, will produce the magnitude of the magnetic field where a resonance should be seen. If the calculation is repeated as the angle of the magnetic field is varied with respect to the crystalline axes, the result is an isofrequency plot of the angular dependence of the spectra. A computer program which would produce the field values for such a plot was written. The advantage of using this program for data analysis over the analytical expressions of the previous sections is that by diagonalizing the complete Spin Hamiltonian the eigenvectors of the states can be calculated which allows a calculation of the change in the line intensity as a function of the angle of the magnetic field.

The final Fortran Source program which produced the data for the isofrequency plots is given in Appendix C. The general method is to use the main program to set the parameters. A subroutine, SEARCH, is used to step through
the specified field range by a specified increment (usually 500 gauss or more). The Spin Hamiltonian is diagonalized at each step and a linear fit to the eigenvalues is constructed over each field increment by a subroutine called LINFIT. Then, these approximate linear expressions for the energy levels as a function of magnetic field are checked to determine if a resonance occurs within that range. If a resonance is indicated, an approximate value of the resonance magnetic field is computed from the linear approximations. The field increment is then reduced to a 50 gauss interval around this estimate and the linear fit is repeated over this interval to give a value with increased accuracy. The Hamiltonian is then diagonalized for this field value but this time the eigenvectors are also computed. The matrix element which is responsible for the intensity of the signal is computed using the subroutine INTENS and the relevant parameters are printed using the subroutine called OUTPUT.

The diagonalization is done using a very efficient library subroutine, EIGCH, which is written and maintained by IMSL.\(^{(59)}\) This subroutine uses the Givens-Householder reduction to a real tri-diagonal matrix\(^{(60)}\) and a standard algorithm, the QL algorithm, to find the eigenvalues and, optionally, the eigenvectors of a Hermitian matrix. The matrix is computed prior to diagonalization by a subroutine called AMATRIX. The subroutine structure has been used both
as a device for modular construction of the program as it developed and for ease in converting so that it can be used for the problem discussed in the last half of this chapter. A version of this program using Fortran single precision is sufficient if the line intensity calculation is not necessary, but double precision calculations are required for accurate eigenvectors.
B. The $S = 2$ Spin Hamiltonian of the $d^4$ Ion

The Cr$^{2+}$ ion has a [Ar]3$d^4$ ground configuration with a spin of two. A spin two system would have five energy levels and the potential for ten transitions between all possible pairs of these levels. An ion with an even number of electrons is a non-Kramers ion and, as a result, an electric field, such as the crystal field, can produce a large splitting of the spin states. Furthermore, these splittings are very sensitive to local variations in the electric field due to random strains and resonance lines of non-Kramers ions can be broadened beyond recognition. Therefore, it is no surprise when only four resonance lines are observed at 9 GHz with the magnetic field rotated in the (011) plane. The four lines have an angular variation which implies that the primary axis of quantization is along one of the six ⟨110⟩ axes. This strong axial symmetry is described by a Spin Hamiltonian with an axial zero field term that dominates the Zeeman interaction, as in equation IV-1 of the previous section. However, the z-axis is now defined as a ⟨110⟩ axis. The axial zero field term will split the five states of the $S = 2$ manifold into two doublets and a singlet, denoted by $M_S = \pm 2$, $M_S = \pm 1$, and $M_S = 0$ and pictured in Figure IV-2. The common $\Delta M_S = \pm 1$ magnetic dipole transitions can only be observed if $h\nu > D$. If $D \gg g\beta H$ and a transition is observed, it is between the
Figure IV-2. Energy vs. Field Diagram for S=2 Spin Hamiltonian
(a) $H \parallel z$-axis and (b) $H \perp z$-axis
states that compose one of the two doublets; the two states of each doublet are mixed with each other and a magnetic dipole transition with $\Delta M_S = 0$ can be observed. This mixing can occur when either non-axial zero field terms or higher order cubic and axial zero field terms are included in the Spin Hamiltonian. The Spin Hamiltonian used to analyze these data takes the form:

$$\kappa_S = D[S_z^2 - \frac{1}{3} S(S+1)] + g_{||} H_z S_z + \frac{1}{2} g_{\perp} S_z (H_+ S_- + H_- S_+)$$

$$+ \frac{1}{6} E (S_+^2 + S_-^2) + \frac{a}{48} (S_+^4 + S_-^4)$$

$$+ \frac{a}{120} [35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1)]$$

(IV-19)$$

$$+ \frac{F}{180} [35S_z^4 - 30S(S+1)S_z^2 + 25S_z^4 - 6S(S+1) + 3S^2(S+1)^2]$$

$$+ 4^{th} \text{ order non-axial terms}$$

The dominating term is the axial zero field term with coefficient, $D$. The next strongest terms will be the Zeeman terms, written with axial symmetry. The third line includes the two terms which mix the spin doublets in zero field; the term with the coefficient, $E$, describes the non-axial component of the crystal field while the term with the coefficient, $a$, is the fourth order zero field contribution to the cubic symmetry component of the crystal field. The term with the coefficient, $F$, is the fourth order contribution to the axial component of the crystal field. These last two terms, with coefficients of $\frac{a}{120}$ and
will shift the energy of the doublets relative to the singlet but by an amount very much smaller than the quadratic axial zero field term. Therefore, the effects of everything but the first three lines of equation IV-19 will be ignored. This step will be clearer after the discussion in Section IV.B.2.

The axial nature of the center described by equation IV-19 requires only that the z-axis be specified as a \langle 110 \rangle axis and the x- and y-axes be perpendicular. The inclusion of the quadratic non-axial term:

\[ \frac{1}{2}E(S_+^2 + S_-^2) = E(S_x^2 - S_y^2) \]  

(IV-20)

however, implies that these perpendicular axes are more critical, the correct definition of the principal axes will minimize the magnitude of E and the sign of E will depend on the convention for which axis is labeled x. For this analysis, it was decided to choose the axes to have the highest symmetry possible. The x-axis was chosen to be along a \langle 100 \rangle direction perpendicular to the z-axis and the y-axis is along the \langle 110 \rangle direction which is perpendicular to the other two and which forms a right handed coordinate system.
2) Perturbation Theory

The effects of the third line of equation IV-19 when applied as a perturbation to the solution of the eigenvalue problem which uses the first two lines will be discussed in this section. Using the identities:

\[ \frac{1}{2} E (S_+^2 + S_-^2) |\pm 2\rangle = 2\sqrt{3} E |0\rangle \]

\[ \frac{1}{2} E (S_+^2 + S_-^2) |\pm 1\rangle = 3E |\mp 1\rangle \]

\[ \frac{1}{2} E (S_+^2 + S_-^2) |0\rangle = 2\sqrt{3} E (|+2\rangle + |-2\rangle) \]

\[ \frac{a}{48} (S_+^4 + S_-^4) |\pm 2\rangle = \frac{a}{2} |\mp 2\rangle \quad \text{(IV-21)} \]

\[ \frac{a}{48} (S_+^4 + S_-^4) |0\rangle = 0 \]

\[ \frac{a}{48} (S_+^4 + S_-^4) |\pm 1\rangle = 0 \]

the first three lines of equation IV-19 can be written in the matrix form shown in Figure IV-3.

In the limit that \( \hbar \gamma, g \delta H \ll D \), this matrix is block diagonal, composed of the matrix elements between the \( M_S = \pm 1 \) states:

\[ \mathcal{H}_S (M_S = \pm 1) = \begin{pmatrix}
-D+g \delta H \cos \theta & 3E \\
3E & -D-g \delta H \cos \theta
\end{pmatrix} \quad \text{(IV-22)} \]

the matrix elements between the \( M_S = \pm 2 \) states:
\[ \chi_s = \begin{pmatrix} |+2\rangle & |+1\rangle & |0\rangle & |-1\rangle & |-2\rangle \\ 2g_{||} \beta H_{z} + 2D & g_{\perp} \beta H_{-} & 2\sqrt{3}E & 0 & \frac{a}{2} \\ g_{\perp} \beta H_{+} & g_{||} \beta H_{z} - D & \frac{3}{2} g_{\perp} \beta H_{-} & 3E & 0 \\ 2\sqrt{3}E & \frac{3}{2} g_{\perp} \beta H_{+} & -2D & \frac{3}{2} g_{\perp} \beta H_{-} & 2\sqrt{3}E \\ 0 & 3E & \frac{3}{2} g_{\perp} \beta H_{+} & -g_{||} \beta H_{z} - D & g_{\perp} \beta H_{-} \\ \frac{a}{2} & 0 & 2\sqrt{3}E & g_{\perp} \beta H_{+} & -2g_{||} \beta H_{z} + 2D \end{pmatrix} \]

Figure IV-3
\[ |+2\rangle \quad |-2\rangle \]
\[
\begin{pmatrix}
2D + 2g_\parallel \Phi \cos \theta & \frac{a}{2} \\
\frac{a}{2} & 2D - 2g_\parallel \Phi \cos \theta
\end{pmatrix}
\]
(IV-23)

and the diagonal element for \( M_s = 0 \):
\[
\langle 0 | \mathcal{H}_s | 0 \rangle = E_0 = -2D
\]
(IV-24)

Diagonalization of the 2x2 matrices gives the energies:

\[
E_{1S} = -D + \frac{1}{2} \sqrt{4g_\parallel \Phi^2 \cos^2 \theta + 36E^2}
\]

\[
E_{1A} = -D - \frac{1}{2} \sqrt{4g_\parallel \Phi^2 \cos^2 \theta + 36E^2}
\]
(IV-25)

\[
E_{2S} = 2D + \frac{1}{2} \sqrt{16g_\parallel \Phi^2 \cos^2 \theta + a^2}
\]

\[
E_{2A} = 2D - \frac{1}{2} \sqrt{16g_\parallel \Phi^2 \cos^2 \theta + a^2}
\]

There are two omissions in these results. First, there will be corrections to the \( |M_s| = 1 \) states that are on the order of \( \frac{g \Phi \sin \theta}{D} \) and corrections to the \( |M_s| = 2 \) states that are on the order of \( \frac{g \Phi \sin \theta}{3D} \). These corrections can be neglected as long as the approximation that \( g \Phi \ll D \) remains valid. Second, even at zero field, the term of the Hamiltonian which is proportional to \( E \) will mix the \( M_s = \pm 2 \) states with the \( M_s = 0 \) state via the
second order matrix elements of \(|+2\rangle\) and \(|-2\rangle\) with \(|0\rangle\).

The process can be viewed as the result of the addition of another term which has the form:

\[
\frac{E^2}{2} (s^2 + s^-^2) |0\rangle \langle 0| \frac{E^2}{2} (s^2 + s^-^2) = \frac{E^2}{160} (s^2 + s^-^2) |0\rangle \langle 0| (s^2 + s^-^2)
\]

(IV-26)

to the Hamiltonian which operates in the manifold of the \(M_s = \pm 2\) doublet alone. The detailed calculation which includes the second order effects can be found elsewhere. The result is a new set of values for \(E_{2S}\) and \(E_{2A}\):

\[
E_{2S} = 2D + \frac{9E^2}{2D} + \frac{1}{2} \sqrt{16g_{||}^2 s^2 H^2 \cos^2 \theta + (a + \frac{9E^2}{2D})^2}
\]

(IV-27)

\[
E_{2A} = 2D + \frac{9E^2}{2D} - \frac{1}{2} \sqrt{16g_{||}^2 s^2 H^2 \cos^2 \theta + (a + \frac{9E^2}{2D})^2}
\]

Using the values for \(E_{1S}\) and \(E_{1A}\) in equation IV-25 and the values for \(E_{2S}\) and \(E_{2A}\) in equation IV-27, the resonance condition for transitions within each doublet can be written as:

\[
hv = \sqrt{4g_{||}^2 s^2 H^2 \cos^2 \theta + 36E^2}
\]

(IV-28)

within the \(M_s = \pm 1\) doublet, and:

\[
hv = \sqrt{16g_{||}^2 s^2 H^2 \cos^2 \theta + (a + \frac{9E^2}{2D})^2}
\]

(IV-29)
within the $M_s = \pm 2$ doublet. These expressions conform to the general form for transitions within non-Kramers doublets:

$$g_{\text{effective}} = \sqrt{g'_\parallel^2 \cos^2 \theta + g'_\perp^2 \sin^2 \theta + \left(\frac{\Delta}{\Delta H}\right)^2}$$

with:

$$g'_\parallel = (\Delta M_s) g'_\parallel$$
$$g'_\perp = 0$$
$$\hbar \gamma = g_{\text{effective}} \frac{\Delta H}{\Delta}$$

For the $M_s = \pm 1$ transition:

$$\Delta M_s = 2$$

$$\Delta_1 = 6E$$

while for the $M_s = \pm 2$ transition:

$$\Delta M_s = 4$$

$$\Delta_2 = a + \frac{gE^2}{2D}$$

Using the expression in equation IV-29, the zero field splitting of the $M_s = \pm 2$ doublet, $\Delta_2$, can be measured by measuring the effective $g$-value at two different frequencies (fields); the $g$-value will shift more in one field than the other and that shift will give the value of $\Delta_2$ as described in Chapter VI. The same method can be used to determine $\Delta_1$, if that transition is observed at two frequencies.
The transition probability, which is proportional to the square of the matrix element of the microwave magnetic field terms of the Hamiltonian, will be given by the expression (43):  
\[ w_{ij} = \frac{\Delta^2}{(h\gamma)^2} \]  
(IV-33)

For the \( M_s = \pm 1 \) transition, this expression becomes:  
\[ w_{\pm 1} = \frac{36E^2}{(h\gamma)^2} \]  
(IV-34)

while for the \( M_s = \pm 2 \) doublet, it will be:  
\[ w_{\pm 2} = \frac{(a+\frac{9E^2}{2D})^2}{(h\gamma)^2} \]  
(IV-35)

Since these expressions arise from the \( H_{1z}S_z \) term of the Hamiltonian (\( H_1 \) is the microwave magnetic field), only the component of the microwave field along the \( \langle 110 \rangle \) axis of the center will contribute to the transition probability; these transitions are not observed when the microwave field is perpendicular to the \( z \)-axis. These expressions indicate the importance of this perturbation calculation; without the Spin Hamiltonian terms which are proportional to \( E \) and \( a \), there is no intensity to these resonance lines and they should be unobservable. Finally, measurements which determine whether the \( E \) term or the \( a \) term are primarily responsible for the initial observations of the transitions within the \( M_s = \pm 2 \) doublet can tell us
the extent of the non-axial character of the ion's surroundings thus giving a better picture of the nature of the (110) symmetry of the distortion.

3) Temperature Dependence Information

The expression in equation IV-29 will give the magnitude of $\Delta_2$, but not its sign. More of a problem, however, is that $\Delta_2$ not only has a dependence on $E$ and $a$, but also a dependence on the zero field splitting of the $S = 2$ quintet, $D$. The influence of $E$ and $a$ can be separated if the $M_s = \pm 1$ transition is observed since $\Delta_1$ depends only on $E$, but it is still necessary to have a value for $D$. Population effects can be used to determine the sign of $D$ and, with the same restrictions and reservations of Section IV.A.3, the magnitude of $D$.

The $Cr^{2+}$ signals observed in all three hosts display a signal from the $M_s = \pm 2$ doublet which is strongest at lower temperatures indicating that this doublet is lowest in energy and the sign of $D$ is negative.

Using the reasoning discussed in Section IV.A.3, the intensity of the $M_s = \pm 2$ transition in $Cr^{2+}$ can be written:

$$ I_{Cr^{2+}} \propto N_{Cr^{2+}} \frac{2g_{||}\beta H}{e kT} - \frac{-2g_{||}\beta H}{e kT} \frac{2g_{\perp}\beta H}{e kT} - \frac{-2g_{\perp}\beta H}{e kT} \frac{(g_{||}\beta H - 3D)}{e kT} + \frac{(g_{\perp}\beta H - 3D)}{e kT} + \frac{4D}{e kT} $$

(IV-36)

As before, if $g_\parallel \beta H \ll D$ and $g_{\perp} \beta H \ll kT$, then
\[ I_{Cr^{2+}} = 2 \left( \frac{2g_{\|} g_H}{kT} \right) \frac{N_{Cr^{2+}}}{2+2e} \left( \frac{-3D}{kT} \right) + \frac{-4D}{kT} \quad (IV-37) \]

The ratio of the intensity to a Curie Law standard is:

\[ R_{Cr^{2+}}(T) = \left( \frac{2N_{Cr^{2+}}}{N_{Curie}} \right) \frac{1}{1+e^{-\frac{-3D}{kT}} + \frac{-4D}{kT}} \quad (IV-38) \]

The value of D can be obtained by fitting the ratio of this value at two temperatures:

\[ Q_{Cr^{2+}}(T_1, T_2) = \frac{1+e^{-\frac{-3D}{kT_1}} + \frac{-4D}{kT_1}}{1+e^{-\frac{-3D}{kT_2}} + \frac{-4D}{kT_2}} \quad (IV-39) \]

to the experimental data.

The reliable application of these ideas to the data analysis is included in the next section where the intensity of the transition is calculated numerically and the effects of population shifts with temperature are included in the final values so that the relative intensity of the \( M_s = \pm 1 \) transition to the \( M_s = \pm 2 \) transition can be used to confirm the fit of the data to the parameters used in the calculation.
4) Isofrequency Plots

The original observations of Cr$^{2+}$ in CaF$_2$ and CdF$_2$ included the identification of the $M_s = \pm 2$ transition and no others. (30) When data were taken for this study, a line was observed in both systems near 4 kilogauss when the magnetic field was parallel to the [100] axis when the temperature reached 4.2K. When the same feature was observed in the SrF$_2$:Cr$^{2+}$ spectra, it seemed necessary to explain this line either in terms of the $S = 2$ Spin Hamiltonian or in terms of some vibronic coupling effect. The initial simple analysis using energy versus field diagrams proved to be insufficient to tell if this line could be explained using the Spin Hamiltonian. So, the program to produce isofrequency plots which was described in Section IV.A.4 was developed.

The architecture of the program which is reproduced in Appendix D is the same as the program described in Section IV.A.4. The change from the solutions of one system ($S = \frac{3}{2}$, $\langle 111 \rangle$ symmetry) to the other ($S = 2$, $\langle 110 \rangle$ symmetry) is done by changing the values of the dimension statements at the beginning of each program, substituting the correct subroutine for AMATRIX which sets up the matrix which is to be diagonalized, and changing the first data cards which read in the orientation of the coordinate axes for each center. The use of this program to understand the origin of the unusual line and to determine reasonable values for the parameters will be discussed in Chapter VI.
V. Data and Analysis; the $d^3$ Problem

A. Description of Samples

Electron paramagnetic resonance spectra have been observed and studied in six samples. One of these, a SrF$_2$ crystal with Cr impurities, produced the first EPR observations of the Cr$^{2+}$ and Cr$^{3+}$ ions in this particular host. These data will be the primary data presented in the next two chapters. The data from the other samples are presented to allow the comparison of the measured parameters as a function of crystalline host for each ion. For the $d^3$ problem presented in this chapter, the measured parameters can also be compared for two isoelectronic impurities with different ionic charge. Both of these comparisons are attempts to study the parameters as the vibronic coupling strength is varied.

All of the samples except the CdF$_2$ sample in which Cr$^{2+}$ was seen were obtained from Walter Hargreaves at Optovac, Inc.$^{(48)}$ The CdF$_2$ sample which had Cr$^{2+}$ ions was grown by Isomet. The amount of Cr in this sample is not known. The sample has a slight green tint and a yellow fluorescence when viewed under ultraviolet light. The Optovac samples were all grown using a Bridgman furnace with an HF atmosphere maintained during growth. The SrF$_2$:Cr sample was a translucent blue color when received and the Cr$^{2+}$ data presented in the next chapter were
obtained from the untreated sample. When the sample was irradiated with X-rays, the color changed to an olive green tint, and the Cr$^{3+}$ and Cr$^{+}$ charge states were observed. The initial chromium concentration in the melt before this crystal was grown was 1.0 mole %. The CaF$_2$:Cr sample was produced with an initial chromium concentration of 0.25 mole % in the melt. The CaF$_2$:Cr sample is initially clear and only Cr$^{2+}$ was observed in the untreated sample. Again, the irradiation produced the Cr$^{3+}$ and Cr$^{+}$ charge states and the sample acquired a clear blue color. The CdF$_2$:Cr sample which Optovac produced with a Cr concentration before crystal growth of 0.5 mole % is very green in color and only the Cr$^{3+}$ charge state was observed. Irradiation of this sample produced no indication of any other charge state.

The last two samples studied are CaF$_2$ and SrF$_2$ with vanadium impurities. The CaF$_2$:V sample was made with an initial vanadium concentration of 1.0 mole % and has a dark brown color. Both the $\langle 111 \rangle$ V$^{2+}$ signal and the isotropic signal which Zaripov et al.\textsuperscript{(18)} identified as V$^{3+}$ were observed in the untreated sample. The initial vanadium concentration in the SrF$_2$:V sample was also 1.0 mole % and this sample has a translucent brown color. Only the V$^{2+}$ charge state was observed in this sample. All of the samples contained enough Mn$^{2+}$ to be evident in the EPR at the normal incident power level of 0.1 milliwatt.
B. \textbf{SrF}_2:Cr\textsuperscript{3+}

Figure V-1 shows the angular dependence of the effective \( g \)-values in the (0\1\1) plane obtained from the electron paramagnetic resonance spectra of \textsuperscript{3+} ions in \textbf{SrF}_2. Since the extreme low \( g \)-value occurs when \( H \parallel [\text{1\1\1}] \), the extreme high \( g \)-value occurs when \( H \parallel [0\text{1\1}] \) (when \( H \) is perpendicular to two \( \langle \text{1\1\1} \rangle \) axes), and four resonance lines are observed in general, it can be concluded that these spectra arise from a center which has axial symmetry about the \( \langle \text{1\1\1} \rangle \) axes. The points in the figure give the experimental observations as a function of the angle, \( \theta \), from the \( [\text{1\0\0}] \) axis in the (0\1\1) plane. The line in the figure is calculated using the equation:

\[
\begin{align*}
g_{ei} &= \sqrt{g_{||}^2 \cos^2 \alpha_i + (2g_{\perp})^2 \sin^2 \alpha_i} \\
&\text{(V-1)}
\end{align*}
\]

where

\[
\alpha_i = \cos^{-1}[\sin \theta (\gamma \cos \Theta \sin \varphi) \sin \Theta_i \cos (\varphi_i - \varphi) \\
+ (\cos \Theta + \gamma \sin \Theta \sin \varphi) \cos \Theta_i] \\
&\text{(V-2)}
\]

is the angle between the magnetic field and the \( i^{th} \) \( \langle \text{1\1\1} \rangle \) axis which is defined by Figure V-2. This form is derived elsewhere.\(^{43}\) The angles \( \Theta, \varphi, \Theta_i, \) and \( \varphi_i \) are all standard spherical coordinates in the coordinate system where the \( x \)-axis is the \( [0\text{1\1}] \) axis, the \( y \)-axis is the \( [0\text{1\1}] \)
SrF$_2$:Cr$^{3+}$

Angular Dependence in (011) Plane

T = 4.2 K

v = 9.268 GHz

Figure V-1. Angular Dependence of SrF$_2$:Cr$^{3+}$ with Magnetic Field in the (011) Plane
Figure V-2. Four <111> Axes of a Cube, Labeled According to Table V-1.
axis about which the magnetic field is ideally rotated, and the z-axis is the [100] axis. The angle $\theta$ is the experimental parameter that gives the angle between the magnetic field and the [100] axis while $\Theta_i$ and $\varphi_i$ are the spherical coordinates for the $i^{th}$ axis given in Table V-1. As long as the alignment is perfect, the magnetic field is in the (0$\overline{1}$l) plane and $\varphi$ is zero. If the axis of rotation is tilted slightly from the (0$\overline{1}$l) axis, the non-zero value of $\varphi$ will be given by:

$$\varphi = \tan^{-1}(\delta + \gamma \cot\theta)$$  \hspace{1cm} (V-3)

The misalignment angles, $\gamma$ and $\delta$, are defined in Figure V-3. Equations V-2 and V-3 are good only for small $\gamma$ and $\delta$. The value of $\gamma$ is determined by adjusting its value until the splitting between $g_{e3}$ and $g_{e4}$ when $\theta = 0^\circ$ matches the experimental data. The value of $\delta$ can be obtained by matching the effective $g$-values when $\theta = 90^\circ$. Since, even when $\theta = 90^\circ$, the $g$-values are fairly insensitive to small changes in $\delta$, a more reliable value of $\delta$ can be obtained from the Cr$^{2+}$ spectra discussed in the next chapter.

Representative raw data for the three high symmetry axes in the (0$\overline{1}$l) plane are given in Figure V-4.

The data in this figure do not show the superhyperfine structure which was observed because the alignment is slightly off. The low field line when $H||[011]$ displays the five line pattern in Figure V-5. This is the only
Table V-1

Angles ($\theta_i$, $\varphi_i$) and Indices (i) for the Four \langle111\rangle Axes in Figure V-2

<table>
<thead>
<tr>
<th>Axis $i$</th>
<th>$\theta_i$</th>
<th>$\varphi_i$</th>
<th>Crystallographic Axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\cos^{-1} \frac{1}{3}$</td>
<td>0°</td>
<td>[11\bar{1}]</td>
</tr>
<tr>
<td>2</td>
<td>$180^\circ - \cos^{-1} \frac{1}{3}$</td>
<td>0°</td>
<td>[1\bar{1}1]</td>
</tr>
<tr>
<td>3</td>
<td>$\cos^{-1} \frac{1}{3}$</td>
<td>90°</td>
<td>[111]</td>
</tr>
<tr>
<td>4</td>
<td>$180^\circ - \cos^{-1} \frac{1}{3}$</td>
<td>90°</td>
<td>[\bar{1}11]</td>
</tr>
</tbody>
</table>
Figure V-3. Definition of the Misalignment Angles $\gamma$ and $\delta$
Figure V-4. Representative Data for SrF$_2$:Cr$^{3+}$ with Magnetic Field Along the Three High Symmetry Axes
SrF$_2$:Cr$^{3+}$
H∥[011]
ν = 9.4909 GHz
T = 77 K

Figure V-5. Superhyperfine Structure of SrF$_2$:Cr$^{3+}$ When the Magnetic Field is Perpendicular to the z-axis
orientation of the magnetic field with respect to the (111) axes in which the superhyperfine structure is resolved. Specifically, when the field is perpendicular to a (111) axis in a [110] plane and not along a (110) axis, the structure is not resolved in this fashion. The splitting between the components was measured on two separate occasions at 77K as 8.3 gauss. Once, the measurement was made at 4.2K with signal to noise that was not as good and the splitting was 8.8 gauss. The linewidth, measured peak-to-peak on the derivative line, was about 3.7 gauss at 77K. The width of the single line observed when \( H_\parallel [100] \) was about 22 gauss while the width of the line when \( H_\parallel [111] \) was about 13 gauss.

The data in Figure V-6 indicate that the transition which is observed is not between the lowest pair of states. Only after the temperature is high enough that the thermal energy, \( kT \), is comparable to or greater than the excitation energy of the two states of interest will these states be sufficiently populated that the transition between these states can be seen. This behavior is described in the Spin Hamiltonian of equation IV-1 by the zero-field splitting parameter, \( D \). The sign of \( D \) is negative if the \( |M_s| = \frac{1}{2} \) states are higher in energy than the \( |M_s| = \frac{3}{2} \) states. The change in intensity of the resonance signal as a function of temperature can be used to determine the magnitude of \( D \) as well. This technique has been employed
TEMPERATURE DEPENDENCE OF SrF$_2$:Cr$^{3+}$
AT 35 GHz WITH H || [100]

$T = 4.2 \text{K}$; $\nu = 34.242$

$T = 1.3 \text{K}$; $\nu = 34.103$

Figure V-6. Temperature Dependence of SrF$_2$:Cr$^{3+}$
for the Cr\textsuperscript{3+} signal in CaF\textsubscript{2}\textsuperscript{(43)} with questionable success. The key is to compare the Cr\textsuperscript{3+} intensity with a standard reference signal that displays the \( \frac{1}{T} \) Curie Law dependence of the intensity on temperature; the Mn\textsuperscript{2+} signal which is readily available in these samples and was used in the CaF\textsubscript{2}:Cr\textsuperscript{3+} study could be an appropriate standard except that the resonance signal has a tendency to saturate easily at the power levels used to observe the Cr\textsuperscript{3+}. If the signal is slightly saturated, the lineshape will not necessarily be affected, but the observed temperature dependence of the signal intensity will not be caused exclusively by the population changes which produce the Curie Law behavior. As a result the measurement will be inaccurate. The best value obtained from these data was a D of about -2.1\pm0.5 cm\textsuperscript{-1}.

Note that Figure V-6 is data taken at a much higher microwave frequency than the data in Figure V-4. The angular dependence of the effective g-values of Cr\textsuperscript{3+} in SrF\textsubscript{2} in the (0\bar{1}1) plane at the Ka band frequencies given in Figure V-7 looks identical to the angular dependence in Figure V-1, and equation V-1 can also be used to fit the data fairly successfully. Therefore, the \( |M_S| = \frac{1}{2} \) doublet remains fairly isolated from the \( |M_S| = \frac{3}{2} \) states even when the magnetic field has split the \( |M_S| = \frac{1}{2} \) states by the energy of the 35 GHz photon, about 1 cm\textsuperscript{-1}. Just as important is the fact that no transitions are observed between the \( |M_S| = \frac{1}{2} \) states and the \( |M_S| = \frac{3}{2} \) states. These
SrF$_2$: Cr$^{3+}$

$T = 4.2 \text{ K;} \quad \nu = 34.301 \text{ GHz}$

Angle Between $\uparrow$ and [100]

Figure V-7. Angular Dependence of Effective $g$-value of SrF$_2$:Cr$^{3+}$ at 35 GHz
observations imply a lower limit for the value of the zero-field splitting, 2D, which is greater than about 1.5 cm⁻¹.

A more precise value for D is available, however, by carefully measuring the effective g-values at two different frequencies (fields) and using equation IV-8 to calculate D from the shift in the g-value. The magnetic field at resonance was measured with the NMR probe for the most accurate determination since the g-shifts were expected to be not too much larger than the errors in some of the measurements (especially those in the next chapter). The magnetic field measurement was thus reduced to the measurement of a frequency. The other quantity which was needed with as much accuracy as possible was the microwave frequency. As described in Chapter III, the measurements near 9 GHz were made with the same counter and time base as the frequency measurement for the field while a wavemeter with decreased precision measured the frequency at 35 GHz.

The most difficult problem in making these measurements turned out to be assuring the accuracy of the results. When the initial measurements were completed, the g-shift of the Cr²⁺ data was in the wrong direction; the effective g-value near 35 GHz was greater than that near 9 GHz rather than the reverse. After investigation, it was decided that the "non-magnetic" stainless steel
dewar was disturbing the homogeneity of the field so that the probe located at the center of the pole face outside the dewar was measuring a field which was different than the field the sample experienced. The solution to this difficulty is to make the 35 GHz measurements in the same glass dewar which is used to make the 9 GHz measurements. This procedure restricts the magnetic field which can be obtained so that a g = 2 signal cannot be observed as a check, but the fields which needed to be accurately measured are all below the 10 kilogauss limit of the magnet with the glass dewars. (The glass dewar was used at 35 GHz for only the NMR field measurements.) Although no systematic errors seem very likely, there are three possible sources for systematic error. First, even though the resonant cavities were checked using standard samples, one of the two cavities might cause the magnetic field to differ at the sample site from the value measured at the probe. Second, the probe is located about 4 centimeters from the sample and an unanticipated variation of the field over this distance could create a systematic error whether the cavities played a role or not. Third, the calibration of the wavemeter for the Ka band frequency measurements could be off. There is no reason to suspect the existence of any systematic error since the measurements on different samples seem consistent and compare favorably with published values where comparisons are possible.
The experimental errors in the value of the effective g-value can come from several sources. There is an error of less than 1 part in $10^5$ in the determination of the NMR resonance frequency, an error of 1 part in $10^6$ in the determination of the X-band microwave frequency, and an error of about 5 parts in $10^5$ in the determination of the Ka-band microwave frequency. Therefore, the total uncertainty in the measurement of the effective g-value is about 1 part in $10^5$ at 9 GHz and about 5 parts in $10^5$ at 35 GHz.

The value of $D$ is obtained by taking the difference between the expression for the effective g-value in equation IV-8 at the two separate frequencies. The result can be solved for $D$. If the $u$ subscript refers to fields and g-values at the upper frequency and the $l$ subscript refers to the lower frequency, the expression can be written

$$D = \frac{H_u^2 - H_l^2}{\frac{3}{8} g_{el} - g_{eu}} \frac{2 g_{el}^2 \sin^2 \theta (3\sin^2 \theta - 1)}{3\sin^2 \theta + 1} \sqrt{g_{||}^2 \cos \theta + (2g_{\perp})^2 \sin^2 \theta}$$

(with $\theta_{l} = \theta_{u} = \theta$) (V-4)

If the quantity $(g_{||}^2 \cos^2 \theta + (2g_{\perp})^2 \sin^2 \theta)^{1/2}$ is replaced by the effective g-value at the angle, $\theta$, that is least affected by the g-shift, $g_{el}'$, equation V-4 can be rewritten as:

$$D = \frac{1}{2} g_{el} \sqrt{\frac{3}{2} g_{el} \frac{H_u^2 - H_l^2}{\frac{3}{8} g_{el} - g_{eu}} \frac{2 \sin^2 \theta (3\sin^2 \theta - 1)}{3\sin^2 \theta + 1}}$$

(V-5)

The best value for the zero-field splitting will be given by measurements made when the field is oriented so
that the g-shift as a function of frequency is greatest. The greatest g-shift will occur when the angle between the field and a given \(\langle 111\rangle\) axis is 90°. Data taken with the field oriented in this manner are given in Table V-2. The g-values are calculated from the NMR frequency, \(\Omega\), and the microwave frequency, \(\nu\), using:

\[
g_e = \frac{h \nu}{3 \Omega} \frac{1}{(234.865 \text{ gauss/MHz})} \tag{V-6}
\]

with

\[
h = 6.62620 \times 10^{-27} \text{ erg sec}
\]

\[
\beta = 9.27410 \times 10^{-21} \text{ erg/gauss} \tag{V-7}
\]

as the fundamental constants obtained from the latest study of fundamental constants in Reviews of Modern Physics. (62)

The value of \(D\) which is obtained from averaging all values obtained from the data in Table V-2 is 1.91 cm\(^{-1}\) with a standard deviation of 0.04 cm\(^{-1}\). The experimental errors in the field and frequency measurements propagate to give a value for the experimental error of \(D\) of 0.015 cm\(^{-1}\). The parameters, \(g_\parallel\) and \(g_\perp\), can be computed, \(g_\parallel\) from a direct measurement when \(H\parallel[111]\) and \(g_\perp\) from the data when \(H\parallel[011]\) after correcting for the shift due to \(D\). The results are given in Table V-3.
Table V-2

NMR Data for SrF$_2$:Cr$^{3+}$ Low Field Line with $\mathbf{H || [011]}$

<table>
<thead>
<tr>
<th>$g_e$</th>
<th>v (GHz)</th>
<th>T</th>
<th>$\delta$ (from Cr$^{2+}$ Data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9385</td>
<td>9.49088</td>
<td>77K</td>
<td>0°</td>
</tr>
<tr>
<td>3.9382</td>
<td>9.49086</td>
<td>77K</td>
<td>0°</td>
</tr>
<tr>
<td>3.9333</td>
<td>9.4775</td>
<td>77K</td>
<td>0°</td>
</tr>
<tr>
<td>3.9350</td>
<td>9.2690</td>
<td>4.2K</td>
<td>0°</td>
</tr>
<tr>
<td>3.8666</td>
<td>35.853</td>
<td>77K</td>
<td>1.08°</td>
</tr>
<tr>
<td>3.8713</td>
<td>35.859</td>
<td>77K</td>
<td></td>
</tr>
<tr>
<td>3.8722</td>
<td>35.079</td>
<td>4.2K</td>
<td></td>
</tr>
<tr>
<td>3.8701</td>
<td>34.960</td>
<td>1.3K</td>
<td>1.08°</td>
</tr>
</tbody>
</table>

Average of all possible values of D calculated from these data is 1.91 cm$^{-1}$ ($\sigma = 0.04$).
Table V-3

Results of Measurements on $d^3$ Ions

in Alkaline Earth Halides

<table>
<thead>
<tr>
<th>Host:Ion</th>
<th>$g_{jj}$</th>
<th>$g_{\perp}$</th>
<th>$A_{jj}$ (cm$^{-1}$)</th>
<th>$A_{\perp}$ (cm$^{-1}$) (effective)</th>
<th>$D$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF$_2$:Cr$^{3+}$</td>
<td>1.9655</td>
<td>1.970</td>
<td>--</td>
<td>--</td>
<td>-1.91</td>
</tr>
<tr>
<td>$\pm 0.0010$</td>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td></td>
<td>$\pm 0.005$</td>
<td></td>
</tr>
<tr>
<td>CaF$_2$:Cr$^{3+}$</td>
<td>1.965</td>
<td>1.971</td>
<td>--</td>
<td>--</td>
<td>-2.27</td>
</tr>
<tr>
<td>$\pm 0.005$</td>
<td>$\pm 0.01$</td>
<td>$\pm 0.005$</td>
<td></td>
<td></td>
<td>$\pm 0.05$</td>
</tr>
<tr>
<td>CdF$_2$:Cr$^{3+}$</td>
<td>1.965</td>
<td>1.973</td>
<td>--</td>
<td>--</td>
<td>-2.02</td>
</tr>
<tr>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td></td>
<td></td>
<td>$\pm 0.05$</td>
</tr>
<tr>
<td>CaF$_2$:V$^{2+}$</td>
<td>1.936</td>
<td>1.944</td>
<td>79.7(5) x$10^{-4}$</td>
<td>182.8(5) x$10^{-4}$</td>
<td>-1.52</td>
</tr>
<tr>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td></td>
<td>$\pm 0.05$</td>
<td></td>
</tr>
<tr>
<td>SrF$_2$:V$^{2+}$</td>
<td>1.944</td>
<td>1.942</td>
<td>85.1(5) x$10^{-4}$</td>
<td>179.4 x$10^{-4}$</td>
<td>-1.76</td>
</tr>
<tr>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td></td>
<td>$\pm 0.05$</td>
<td></td>
</tr>
</tbody>
</table>
C. Measurement of D for Other Systems

1) CaF$_2$:Cr$^{3+}$

The angular dependence of the effective g-values of the Cr$^{3+}$ ion in CaF$_2$ in the (011) plane is given in Figure V-8 and representative data for the three high symmetry axes are shown in Figure V-9. Figure V-10 shows that the only resolved superhyperfine structure observed in the spectra from this system is identical to that observed in SrF$_2$:Cr$^{3+}$. This figure is also the only definitive data which clearly show the hyperfine structure which arises from the Cr$^{53}$ isotope (I = $\frac{3}{2}$ and a natural abundance of 10.96%). The temperature and frequency dependence has the same characteristics as the SrF$_2$:Cr$^{3+}$ data and is discussed elsewhere.$^{43}$ The same analysis of the g-shift as a function of frequency can be done as discussed in the previous section and the results for g$_{\parallel}$, g$_{\perp}$, and D are given in Table V-3. One slight variation in the method for determining g$_{\parallel}$ was necessary since the Cr$^{3+}$ line which would provide a direct measurement of g$_{\parallel}$ when H$_{\parallel}$[111] was obscured by the intense Cr$^{+}$ line. Therefore, the value for g$_{\parallel}$ was obtained from the other well defined orientations once the values of g$_{\perp}$ and D had been calculated.
Figure V-8. Angular Dependence of the Effective g-value of CaF$_2$:Cr$^{3+}$
Figure V-9. Representative Data for CaF$_2$:Cr$^{3+}$ With Magnetic Field along the Three High Symmetry Axes
Figure V-10. Superhyperfine Structure and Fine Structure of the CaF$_2$:Cr$^{3+}$ Signal with the Magnetic Field Perpendicular to the [111] Axis and Along the [011] Axis

$\nu = 9.499 \text{ GHz}$

$T = 77 \text{ K}$

1725 Gauss
2) CdF$_2$:Cr$^{3+}$

Although the Cr$^{3+}$ ion was not observed after irradiating the CdF$_2$ sample in which Cr$^{2+}$ was observed, a separate sample did display signals which can be identified as Cr$^{3+}$. The angular dependence of the effective g-values of these data with the magnetic field in the (011) plane is shown in Figure V-11. Figure V-12 gives the data observed when the field was oriented along the three high symmetry axes in this plane. The superhyperfine structure of the CdF$_2$:Cr$^{3+}$ is also seen only when the magnetic field is oriented perpendicular to the z-axis of the center and along a $\langle 110 \rangle$ axis. Figure V-13 shows the superhyperfine structure for Cr$^{3+}$ in CdF$_2$. The splitting is 8.3 gauss and the peak-to-peak linewidth for each component is 4 gauss. The temperature and frequency dependence of these data were also the same as that observed for SrF$_2$:Cr$^{3+}$ and the data in Table V-3 were obtained in the same manner from the g-shift as a function of frequency.
CdF$_2$:Cr$^{3+}$
Angular Dependence in (011) Plane.

T = 4.2 K

\( \gamma = 33.85 \text{i GHz} \)

fit uses:
\( g_\parallel = 1.952 \)
\( g_\perp = 3.819 \)
\( \gamma = -5.01^\circ \)
\( \delta = 2.85^\circ \)

Figure V-11. Angular Dependence of CdF$_2$:Cr$^{3+}$ with Magnetic Field in (011) Plane
Figure V-12. Representative Data of CdF$_2$:Cr$^{3+}$ with Magnetic Field Along the Three High Symmetry Axes.
Figure V-13. Superhyperfine Structure of CdF$_2$:Cr$^{3+}$ When the Magnetic Field is Perpendicular to the z-axis
3) CaF$_2$:V$^{2+}$

The nuclear magnetic moment of the predominant isotope of vanadium, V$^{51}$, is $\frac{7}{2}$. The resultant eight line hyperfine structure clearly identifies the spectra as vanadium and complicates the analysis of these spectra. The angular dependence of the spectra when the magnetic field varies in the (011) plane is shown in Figure V-14. Figure V-15 has representative data from the three high symmetry directions in this plane.

The analysis of the measurements of the hyperfine line positions taken with the NMR probe is not a straightforward procedure. If the hyperfine term:

$$\vec{S} \cdot \vec{A} \cdot \vec{I}$$

is included in the Spin Hamiltonian in equation IV-1 as a perturbation to the Zero Field and Zeeman Terms, the high magnetic field approximation of the Breit-Rabi formula in axial symmetry which is derived in the appendix of Pake and Estle$^{(45)}$ will be applicable. The general expression for the magnetic field at resonance of the $\Delta M_S = \pm 1$, $\Delta M_I = 0$ transition is:

$$H = \frac{\hbar \gamma}{g \beta} - \frac{A}{g \beta} M_I - \frac{1}{2} n^2 (1-n^2) \frac{g' \gamma \beta}{4 g \beta A^2 \hbar} \frac{2 (A^2 - A_+^2)}{A^2} M^2_I$$

$$- \frac{1}{4} \frac{A_+^2 (A^2 + A_+^2)}{g \beta A^2 \hbar \gamma} \left[ I(I+1) - M^2_I \right]$$

(V-9)

with
Figure V-14. Angular Dependence of the Effective g-value of CaF$_2$:V$^{2+}$ with the Magnetic Field in the (011) Plane.
Figure V-15. Representative Data for CaF$_2$:V$^{2+}$ with Magnetic Field Along the Three High Symmetry Axes
\[ g^2 = g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta \]
\[ A^2 = A_\parallel^2 \cos^2 \theta + A_\perp^2 \sin^2 \theta \]  

(V-10)

\[ n = \cos \theta \]

\[ \theta = \text{angle between the magnetic field and the z-axis, a particular \langle111\rangle axis.} \]

The \( g \)-values used in this analysis will be the effective values of \( g_\parallel \) and \( g_\perp \) for the \( M_s = \pm \frac{1}{2} \) transition; \( g_\perp \) of this analysis is obtained by multiplying the value of \( g_\perp \) in Table V-3 by two. The calculation done here assumes that the problem is solved for an isolated \( S = \frac{1}{2} \) doublet; the effect of the \( M_s = \pm \frac{3}{2} \) states on the hyperfine structure is ignored. Therefore, the values of the perpendicular components of the \( g \) and \( A \) tensors will be about twice the parallel components. This factor of two is included in the entries for \( A_\perp \) in Table V-3 to emphasize this approach while the \( g_\perp \) values in Table V-3 do not include this factor. The two cases for which careful NMR measurements were made were when \( \theta = 0^\circ \) and \( \theta = 90^\circ \). When the field is aligned along the [111] axis, \( \theta = 0^\circ \) for the high field set of lines, and equation V-9 reduces to:

\[ H_{M_1} = \frac{\hbar \gamma}{g_\parallel \frac{1}{2}} - \frac{A_\parallel}{g_\parallel \frac{1}{2}} M_1 - \frac{1}{2} \frac{A_\perp^2}{g_\parallel \frac{1}{2} \hbar \sqrt{\gamma}} [I(I+1) - M_1^2] \]  

(V-11)

When the field is along the [011] axis, \( \theta = 90^\circ \) for the low field set of lines and equation V-9 reduces to:
\[ H_{M_l} = \frac{h\nu}{g'_l^2} - \frac{A_l}{g'_l^2} M_l - \frac{1}{2} \frac{(A_{||}^2 + A_{\perp}^2)}{g'_l^2 h\nu} [I(I+1) - M_l^2] \]  
\text{(V-12)}

Both of these expressions have a hyperfine independent term, the linear hyperfine term, and a correction term which is quadratic in the hyperfine splitting. The data which these equations should explain are given in Tables V-4 and V-5. The object is to determine the precise values for \( g_{||} \), \( A_{||} \), \( A_{\perp} \), and \( g_{\perp} \) at both frequencies. The latter will then give the value of \( D \) in the same manner as for \( \text{Cr}^{3+} \).

The first step is to get an initial value for \( A_{||} \) and \( A_{\perp} \) using the linear hyperfine terms. These can be used to calculate the second order terms which will shift the position of the average of the eight lines away from the field of resonance if there were no hyperfine interaction. The seven splittings between each adjacent pair of the eight lines can be averaged to give the value of \( A_{||} \) and \( A_{\perp} \) from:

\[ A_{||} = \Delta H_{\text{average}}(g'_l^2) \text{ from Table V-4} \]
\[ A_{\perp} = \Delta H_{\text{average}}(g'_l^2) \text{ from Table V-5} \]
\text{(V-13)}

Initially, the value for \( g_{||} \) and \( g_{\perp} \) in these expressions can be obtained by averaging the eight fields.

When the field is along the [011] axis, some of the hyperfine lines from the high field transition obscure the hyperfine lines of interest at 9 GHz; the lines are observable but an accurate measurement of their position is not
Table V-4

Measured Parameters for Hyperfine Lines of CaF$_2$:\textsuperscript{2+} with H||[111]

\[ T = 4.2 K \quad \nu = 9.2619 \text{ GHz} \]

| \( M_I \) | Magnetic Field | \( g_{||} \) |
|---|---|---|
| 7/2 | 3089.0 | 1.9358 |
| 5/2 | 3141.6 | 1.9356 |
| 3/2 | 3205.3 | 1.9359 |
| 1/2 | 3281.1 | 1.9361 |
| -1/2 | 3369.0 | 1.9362 |
| -3/2 | 3469.3 | 1.9361 |
| -5/2 | 3581.8 | 1.9359 |
| -7/2 | 3706.1 | 1.9358 |

Average \( 1.9359 \)

\( \sigma = 0.0002 \)
Table V-5

Measured Parameters for Hyperfine Lines of CaF$_2$:\textit{v}$^{2+}$
with $H \parallel [011]$ (field perpendicular to $<111>$ axis)

<table>
<thead>
<tr>
<th>$M_|$</th>
<th>Magnetic Field</th>
<th>$g_\perp$</th>
<th>$\nu$ = 9.2616 GHz</th>
<th>Magnetic Field</th>
<th>$g_\perp$</th>
<th>$\nu$ = 35.259 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>1346.8</td>
<td>3.8782</td>
<td>6321.9</td>
<td>3.7672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>1436.8</td>
<td>3.8789</td>
<td>6422.2</td>
<td>3.7676</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/2</td>
<td>1529.7</td>
<td>3.8812</td>
<td>6520.9</td>
<td>3.7695</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>1627.1</td>
<td>3.8810</td>
<td>6619.1</td>
<td>3.7722</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>1727.5</td>
<td>3.8820</td>
<td>6720</td>
<td>3.7738</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td>*</td>
<td>--</td>
<td>6817.6</td>
<td>3.7777</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>*</td>
<td>--</td>
<td>6921.7</td>
<td>3.7785</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-7/2</td>
<td>*</td>
<td>--</td>
<td>7028.5</td>
<td>3.7783</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average of $M_\| = \pm \frac{1}{2}$: 3.8815

$\sigma = 0.005$

*Accurate value cannot be measured due to overlap with other lines.
possible (see Figure V-15(c)). The 35 GHz data can be used
to give the value of the splitting since the average of
the splitting between the eight lines should be independent
of frequency. Then, equations V-11 and V-12 can be in-
verted to give expressions for \( g'_{||} \) and \( g'_{\perp} \). For example,
equation V-11 gives:

\[
g'_{||} = \frac{h\nu}{2\hbar M_I} - \frac{A_{||}}{2\hbar M_I} M_I - \frac{1}{2} \frac{A_{\perp}^2}{2\hbar M_I} \nu \left[ I(I+1)-M_I^2 \right] \quad (V-14)
\]

The value for \( g'_{||} \) and \( g'_{\perp} \) can be derived for each field
measurement. These eight values can be averaged to give
corrected values for \( g'_{||} \) and \( g'_{\perp} \) which can be used to correct
the values of \( A_{||} \) and \( A_{\perp} \). Using the corrected \( A_{||} \) and \( A_{\perp} \),
the g-values in Tables V-4 and V-5 were obtained.

Finally, the g-shift as a function of frequency can
be used in the same manner as before to give the parameters
for CaF\(_2\):V\(^{2+}\) given in Table V-3.

One other feature of these spectra must be mentioned.
Superhyperfine structure is observed only when the magnetic
field is aligned along the [111] axis. Each of the eight
hyperfine lines is split into three lines with relative
intensity of 1:2:1. This splitting is the result of an
interaction with two equivalent fluorine nearest neighbors,
previously those two along the distortion axis, that is
stronger than the interaction with the rest of the fluor-
ines. This structure is seen in better detail in Figure
V-16. The splitting between superhyperfine components is
Figure V-16. Superhyperfine Structure of CaF$_2$:V$^{2+}$ with the Magnetic Field Parallel to the z-axis.
24.0 \pm 0.5 \text{ gauss} \text{ and the peak-to-peak width of the lines is about } 15 \text{ gauss for the center line and 13 gauss for the two outside lines.}
4) \( \text{SrF}_2:V^{2+} \)

The angular dependence in the (0\(\bar{1}1\)) plane of the magnetic field values of the eight hyperfine components of \(V^{2+}\) in \(\text{SrF}_2\) is given in Figure V-17 and representative data from the three high symmetry directions is given in Figure V-18. The data are analyzed in exactly the same manner described in the previous section; the initial field measurements and effective g-values are given in Tables V-6 and V-7. The values for \(g'_1\) at the two frequencies are used in the same manner as the other \(d^3\) ions to determine the value of \(D\) in Table V-3.

The superhyperfine structure observed in the \(\text{SrF}_2:V^{2+}\) spectra has the same general features as the \(\text{CaF}_2:V^{2+}\) structure. It is resolved only when the field is oriented parallel to the [111] axis. The structure is shown in Figure V-19. The splitting is observed to be 16 gauss and the peak-to-peak width of the derivative line is about 5 gauss. These numbers are independent of temperature.

The \(\text{SrF}_2:V^{2+}\) data exhibited one anomalous feature that remains unexplained. Figure V-20 indicates the temperature dependence of the \(V^{2+}\) signal when \(H\parallel[111]\). The feature which is unusual is the large change in the intensity of the high field line compared to the low field lines. In Figure V-21 the same change is observed when \(H\parallel[011]\) and the temperature is varied from 4.2K to 1.3K. The linewidth
Figure V-17. Angular Dependence of the Effective $g$-value of SrF$_2$:V$^{2+}$ with the Magnetic Field in the (0\overline{1}I) Plane.
Figure V-18. Representative Data for SrF$_2$:V$^{2+}$ with the Magnetic Field along the Three High Symmetry Axes
Table V-6

Measured Parameters for Hyperfine Lines of SrF$_2$:V$^{2+}$ with H|[111]

| $M_I$   | Magnetic Field | $g'_{||}$  |
|---------|----------------|------------|
| 7/2     | 3135.0         | 1.9469     |
| 5/2     | 3201.5         | 1.9430     |
| 3/2     | 3273.8         | 1.9425     |
| 1/2     | 3356.2         | 1.9426     |
| -1/2    | 3449.0         | 1.9432     |
| -3/2    | 3552.0         | 1.9443     |
| -5/2    | 3666.2         | 1.9453     |
| -7/2    | 3791.5         | 1.9463     |
| Average |                | 1.9443     |

$\nu = 9.4888$ GHz

$\sigma = 0.0017$
Table V-7

Measured Parameters for Hyperfine Lines of SrF$_2$:V$^{2+}$
with $H_{||}[011]$ (field perpendicular to $<111>$ axis)

<table>
<thead>
<tr>
<th>$M_z$</th>
<th>Magnetic Field</th>
<th>$g_z$</th>
<th>Magnetic Field</th>
<th>$g_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>1355.0</td>
<td>3.8777</td>
<td>6438.0</td>
<td>3.7902</td>
</tr>
<tr>
<td>5/2</td>
<td>1443.4</td>
<td>3.8779</td>
<td>6534.1</td>
<td>3.7916</td>
</tr>
<tr>
<td>3/2</td>
<td>1535.4</td>
<td>3.8779</td>
<td>6631.4</td>
<td>3.7928</td>
</tr>
<tr>
<td>1/2</td>
<td>1631.1</td>
<td>3.8775</td>
<td>6729.9</td>
<td>3.7939</td>
</tr>
<tr>
<td>-1/2</td>
<td>1730.1</td>
<td>3.8776</td>
<td>6829.4</td>
<td>3.7948</td>
</tr>
<tr>
<td>-3/2</td>
<td>1833.0</td>
<td>3.8769</td>
<td>6929.2</td>
<td>3.7961</td>
</tr>
<tr>
<td>-5/2</td>
<td>*</td>
<td>--</td>
<td>7029.5</td>
<td>3.7976</td>
</tr>
<tr>
<td>-7/2</td>
<td>*</td>
<td>--</td>
<td>7131.7</td>
<td>3.7985</td>
</tr>
</tbody>
</table>

Average of center
four $\sigma = 0.0004$ $\sigma = 0.0014$

*Accurate value cannot be measured due to overlap with other lines.
Figure V-19. Superhyperfine Structure of SrF$_2$:V$^{2+}$ with the Magnetic Field Parallel to the z-axis.
Figure V-20. Temperature Dependence of SrF₂:V²⁺ with the Magnetic Field Parallel to [111]
SrF$_2$: V$^+$

(a) $T = 4.2 \, K$

$\nu = 9.2677 \, GHz$
Figure V-21. Temperature Dependence of SrF₂:V²⁺ with the Magnetic Field Parallel to [011]
does not vary in either instance. The intensity of a resonance line is ideally proportional to the square of the matrix element of the states of the transition with the microwave terms of the Hamiltonian and a variation of this sort is not to be expected. It is possible that some unusual experimental effect is the cause, perhaps the saturation of another defect. These ideas, however, remain speculations.
D. Correlation and Discussion of Data

The first question to be answered in a discussion of these measurements is the question of their validity. Table V-8 lists the previous measurements on these systems. Comparison of the g-values measured in this work, given in Table V-3, with the values in Table V-8 indicates that the measurements presented in this thesis agree very well in general with the measurements of other workers. A comparison of the values for the zero field splitting parameter, D, in both tables reveals a discrepancy; the measurements reported by Zaripov and his co-workers are consistently about 10% lower than the values reported here. The method Zaripov used to arrive at his values is not clearly explained in detail; a brief reference is made to measurements at 9 GHz and 40 GHz, but how these were used to arrive at a value for D is not clear. Indications are that any error is systematic since the variation is about 0.2 cm⁻¹ in the same direction in each system. Therefore, any changes in the value of the zero field splitting, 2D, as the host changes or as the charge of the ion changes should still be reflected in these measurements. As stated earlier, a study of the variation of D as a function of the charge state of the impurity (Y²⁺ vs. Cr³⁺) and as a function of the substituted cation (Ca²⁺, Cd²⁺, or Sr²⁺) should reveal some general trend of the behavior of the
### Table V-8

Previous Measurements on \( d^3 \) Ions in Alkaline Earth Fluorides

<table>
<thead>
<tr>
<th>System (Source)</th>
<th>( g_{\parallel} )</th>
<th>( g_{\perp} )</th>
<th>( D(\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CaF}_2:Cr^{3+}(a) )</td>
<td>1.961(5)</td>
<td>1.97(1)</td>
<td>-1.98(1)</td>
</tr>
<tr>
<td>( \text{CdF}_2:Cr^{3+}(b) )</td>
<td>1.966(5)</td>
<td>1.97(1)</td>
<td>-1.80(1)</td>
</tr>
<tr>
<td>( \text{SrF}_2:V^{2+}(c) )</td>
<td>1.927(5)</td>
<td>1.944(5)</td>
<td>-1.59(1)</td>
</tr>
<tr>
<td>( \text{CaF}_2:V^{2+}(b) )</td>
<td>1.935(5)</td>
<td>1.943(5)</td>
<td>-1.42(1)</td>
</tr>
<tr>
<td>( \text{CaF}_2:V^{2+}(d) )</td>
<td>1.9353(4)</td>
<td>1.941(1)</td>
<td>--</td>
</tr>
<tr>
<td>( \text{CdF}_2:V^{2+}(b) )</td>
<td>1.943(5)</td>
<td>1.955(5)</td>
<td>-1.45(1)</td>
</tr>
</tbody>
</table>


system as the vibronic coupling strength changes. The following discussion should convince the reader that the problem is considerably more complex than originally anticipated.

Table V-9 lists the systems studied with the ionic radii of the cations for each system, the energy of the lowest transverse optic mode of vibration, $E_{TO}$, and the values of D measured in this study. A comparison of the ionic radii of the impurity ion and the cation it replaces can give a rough indication of the relative strength of the influence of changes in the locations of nearest neighbors on the impurity's electronic state. The change of the ratio of the radii when the impurity is changed from $Cr^{3+}$ to $V^{2+}$ is significant but the change in D when the impurity is varied is much larger in CaF$_2$ than in SrF$_2$ so there seems to be no good correlation. The ratio of the ionic radii also varies for the same ion substantially in these two systems. On the other hand, using Zaripov's data for CdF$_2$:V$^{2+}$ and CaF$_2$:V$^{2+}$, the identical ratio corresponds to nearly identical zero field splittings. Again, it seems that any correlation between the change in the ratio of the ionic radius of the impurity to the radius of the substituted cation and the zero field splitting parameter which arises as a result of the vibronic coupling is not visible here in a reliable manner.
<table>
<thead>
<tr>
<th>System</th>
<th>$D$ (cm$^{-1}$) (from Table V-3)</th>
<th>Cation Ionic Radius (Å)</th>
<th>Energy of Lowest Transverse Optic Mode (cm$^{-1}$) ($E_{TO}$)</th>
<th>$\frac{E_{TO}}{D} \approx V_T^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF$_2$:Cr$^{3+}$</td>
<td>-1.91</td>
<td>1.12</td>
<td>225</td>
<td>118</td>
</tr>
<tr>
<td>CdF$_2$:Cr$^{3+}$</td>
<td>-2.02</td>
<td>0.97</td>
<td>224</td>
<td>111</td>
</tr>
<tr>
<td>CaF$_2$:Cr$^{3+}$</td>
<td>-2.27</td>
<td>0.99</td>
<td>267</td>
<td>118</td>
</tr>
<tr>
<td>CaF$_2$:V$^{2+}$</td>
<td>-1.52</td>
<td>0.99</td>
<td>267</td>
<td>176</td>
</tr>
<tr>
<td>SrF$_2$:V$^{2+}$</td>
<td>-1.76</td>
<td>1.12</td>
<td>225</td>
<td>128</td>
</tr>
</tbody>
</table>

The Cr$^{3+}$ ionic radius is 0.63Å.

The V$^{2+}$ ionic radius is 0.88Å.
The third column in Table V-9 gives the energy, \( E_{TO} \), of the lowest transverse optic phonon in the pure materials. This number should give an indication of the variation of the elastic coupling parameter, \( k_T \), as a function of different host materials. This information can be used with the expression in equation II-42:

\[
D = \frac{3\lambda^2}{2E_{JT}} \frac{3\lambda^2}{2V_T^2 / k_T}
\]

(II-42)

to get an idea of the variation of the linear vibronic coupling parameter, \( V_T \), as a function of host since the other parameter, the spin-orbit coupling parameter, \( \lambda \), should be fairly constant for a given impurity. The last column, then, is the ratio of \( E_{TO} \) divided by \( D \) which should be an indication of the value of \( V_T \). It is interesting to note that this analysis predicts that the vibronic coupling strength is nearly identical for \( \text{Cr}^{3+} \) in all three hosts, but seems to vary noticeably when \( \text{V}^{2+} \) is the impurity. The reason for behavior of this kind is not clear.

A pertinent question is whether the measured values for \( D \) are predicted by reasonable values for the parameters as measured in other systems or by other means. Combining the results of the two calculations discussed in the conclusions of Chapter II, equations II-41 and II-42 give:
\[ |D| = \frac{5\lambda_1^2}{4\Delta} + \frac{3\lambda_2^2}{2E_{JT}} \]  
(V-15)

The two values for \( \lambda \) are distinguished in this expression since the quenching of \( \lambda \) due to vibronic coupling may be different for the interactions between the three Jahn-Teller split states and the interactions between the ground state and the doublet split by the cubic crystal field. A reasonable value for \( E_{JT} \) can be obtained from the study of strong [100] distortions arising from \( \text{Cr}^{2+} \) in II-VI compounds; Vallin and Watkins\(^{(15)} \) give \( E_{JT} \approx 600 \text{ cm}^{-1} \). The free ion spin-orbit parameter for \( \text{Cr}^{3+} \) is given in Abragam and Bleaney\(^{(31)} \) as 91 \text{ cm}^{-1}.

Therefore, the second term in V-15 would have a value near 21 \text{ cm}^{-1}. If the value for the cubic crystal field splitting, \( \Delta \), is taken as 5,000 \text{ cm}^{-1}, the first term contributes 2 \text{ cm}^{-1} to \( D \). These values should be high because no quenching effects have been included. Vallin and Watkins discuss their results with no reference to vibronic quenching. Their results are reasonably explained by quenching which arises from covalency effects but they observe a large variation of \( D \) with host that is not observed here. The II-VI compounds should also be more strongly influenced by the effects of covalency. Therefore, their analysis provides no clue about the value of \( \lambda_1 \) or \( \lambda_2 \) after vibronic quenching effects are included. If both are decreased to one third of their original (free ion) values,
the value of $|D|$ approaches 2.2 cm$^{-1}$ which is in good
general agreement with these experimental values. It is
not clear whether this value, $K(T_1) \approx \frac{1}{3}$, is a reasonable
one.

There is a more definitive difference between the
observed spectra of the $V^{2+}$ ion and the spectra of the
$Cr^{3+}$ ion. The superhyperfine structure is radically dif-
ferent for the two ions but remains the same for each ion
in different hosts. The $V^{2+}$ ion only shows resolved super-
hyperfine structure when the magnetic field is along the
axis of symmetry of the center. It indicates an equal
interaction with two fluorine nuclei that is stronger than
the interaction with any other nuclei. The only pair of
nearest neighbor nuclei that are equivalent when the sym-
metry axis is a $\langle 111 \rangle$ axis is the pair that lies on that
axis; the other six nearest neighbor nuclei form a
separate equivalence group. So, the major component of
the superhyperfine interaction is the interaction between
the electronic state in the distorted crystal field and
the nuclei along the distortion axis. The $Cr^{3+}$ systems,
however, display resolved superhyperfine structure only
when the magnetic field is perpendicular to the distortion
axis and along a $\langle 110 \rangle$ axis. The structure indicates an
interaction with four equivalent F$^{19}$ nuclei. This struc-
ture is completely consistent with the axial symmetry of
the center; the electronic state interacts primarily with
four nuclei which do not lie on the axis of symmetry of the distortion. So the major component of the superhyperfine interaction is clearly not the same as that for the vanadium systems. Why these systems should differ is not clear; they are isoelectronic and the most obvious differences are their electronic charge and their ionic radii. What roles these factors play in determining the strength of the superhyperfine interactions will have to wait for further investigations.
VI. Data and Analysis; the $d^4$ Problem

A. SrF$_2$:Cr$^{2+}$

1) Description of Data and Initial Measurements

The SrF$_2$ sample in which the spectra of Cr$^{2+}$ ions were observed was described at the beginning of the previous chapter. With no treatment other than orientation of the boule using Laue diffraction, mounting of the sample using beeswax, and cutting with the diamond saw, the Cr$^{2+}$ signals were observed. An angular dependence in the (011) plane of the effective $g$-value is shown in Figure VI-1. The line is a fit generated by using the indicated values and equation V-1. The values for the angular coordinates of the $i$-th center, $\theta_i$ and $\varphi_i$, are given in Table VI-1 and the six (110) centers are shown in Figure VI-2. Figure VI-3 shows typical data when the magnetic field is parallel to the [100] axis at both operating frequencies. Note the line near 4.5 kilogauss in Figure VI-3(a); this is the line that was referred to in Chapter IV as an unexplained observation. It had to be observed in the Cr$^{2+}$ data from three different host crystals before it could be considered as arising from the same center. The data points at 5° and 10° in Figure VI-1 were then taken to determine the angular dependence of the line. It split, the two lines broadened, and eventually disappeared as the field was rotated away from the [100]
Figure VI-1. Angular dependence of SrF$_2$:Cr$^{2+}$ with Magnetic Field in (011) Plane
Table VI-1

Angles ($\theta_i, \varphi_i$) and Indices ($i$) for the Six $\langle 110 \rangle$
Axes in Figure V-3

<table>
<thead>
<tr>
<th>Axis $i$</th>
<th>$\theta_i$</th>
<th>$\varphi_i$</th>
<th>Crystallographic Axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135°</td>
<td>135°</td>
<td>[110]</td>
</tr>
<tr>
<td>2</td>
<td>45°</td>
<td>45°</td>
<td>[101]</td>
</tr>
<tr>
<td>3</td>
<td>45°</td>
<td>135°</td>
<td>[1\bar{1}0]</td>
</tr>
<tr>
<td>4</td>
<td>135°</td>
<td>45°</td>
<td>[10\bar{1}]</td>
</tr>
<tr>
<td>5</td>
<td>90°</td>
<td>0°</td>
<td>[011]</td>
</tr>
<tr>
<td>6</td>
<td>0°</td>
<td>90°</td>
<td>[0\bar{1}1]</td>
</tr>
</tbody>
</table>
Figure VI-2. Six ⟨110⟩ Axes of a Cube, Labeled According to Table VI-2.
Figure VI-3. Frequency Dependence of SrF$_2$:Cr$^{2+}$ with Magnetic Field along the [100] Axis
axis. Furthermore, the line was observed when the temperature was 4.2K and not when it was 1.3K. This behavior will be explained in the next section.

The superhyperfine structure of the SrF$_2$:Cr$^{2+}$ data when both the D.C. magnetic field and the microwave magnetic field are parallel to the [011] axis is shown in Figure VI-4. The five lines have a peak-to-peak linewidth of 6.8 gauss and each is about 12.5 gauss from the next line. The relative intensity of the five lines has the 1:4:6:4:1 pattern characteristic of an equal interaction with four fluorines each of which has a nuclear spin of one-half. It is not clear whether the four equivalent nuclei lie in a plane that contains the z-axis or in a plane perpendicular to the z-axis.

Figure VI-5 shows the angular dependence of the data taken with a microwave frequency near 35 GHz. The $M_s = \pm 2$ transition has been fit using the form in equation V-1 but the upper set of lines, the $M_s = \pm 1$ transition, cannot be fit very well with such a simple form. These lines can be fit much better using the isofrequency plot program discussed in the next section. Figure VI-6 shows typical data when the magnetic field is aligned along the [011] axis as well as the temperature dependence of that data. No signals were observed at either frequency from the Cr$^{2+}$ center at a temperature of 77K. No study was made of the temperature between 4.2K and 77K. As discussed in Chapter
Figure VI-4. Superhyperfine Structure of SrF$_2$:Cr$^{2+}$ with the D.C. and Microwave Magnetic Fields Both Parallel to the [110] Axis.
**Figure VI-5.** Angular Dependence of the Effective $g$-value of SrF$_2$:Cr$^{2+}$ with the Magnetic Field in the (0\bar{1}1) Plane
Figure VI-6. Temperature Dependence of SrF$_2$:Cr$^{2+}$ at 35 GHz with the Magnetic Field Parallel to the [011] Axis.
IV, the large increase in the intensity of the \( M_s = \pm 1 \) transition (labeled \( \Delta M_s = 2 \) in Figure VI-6) relative to the \( M_s = \pm 2 \) transition (\( \Delta M_s = 4 \)) when the temperature is raised from 1.3K to 4.2K occurs because, as the temperature increases, thermal excitations cause the excited \( M_s = \pm 1 \) states to be populated more thus increasing the probability that a transition between the two states could occur. The fact that the \( M_s = \pm 1 \) states are the excited states implies that the zero field splitting of the \( S = 2 \) quintet, \( D \), is negative. The data can also provide a very good measure of the magnitude of \( D \). The best data give a value for \( D \) of \( 2.19 \pm 0.01 \text{ cm}^{-1} \). This determination proves invaluable in the analysis of the next section.

The other important measurement which has been obtained has been the value of the zero-field splitting of the \( M_s = \pm 2 \) doublet, \( \Delta_2 \), which is calculated from the shift of the effective \( g \)-value as a function of frequency (field). Using equation IV-8, the value is:

\[
\Delta_2 = h \left[ \frac{g_L^2 - g_U^2}{2} \frac{1}{2} \left( \frac{1}{v_L} - \frac{1}{v_U} \right) \right]
\]

The subscripts, \( u \) and \( l \), refer to the indicated quantities at the upper and lower frequencies, respectively. The data in Table VI-2 were taken using the NMR probe to measure the magnetic field at resonance when the D.C. field was oriented along the [100] axis and the microwave magnetic field was
Table VI-2
Data for g-shift of SrF$_2$:Cr$^{2+}$ with H∥[100]

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Temperature</th>
<th>Measured $g_e$</th>
<th>Misalignment Angle ($\gamma$)</th>
<th>Corrected $g_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2689 GHz</td>
<td>4.2K</td>
<td>5.5537</td>
<td>4.8°</td>
<td>5.5931</td>
</tr>
<tr>
<td>35.039 GHz</td>
<td>4.2K</td>
<td>5.5193</td>
<td>3.5°</td>
<td>5.5398</td>
</tr>
<tr>
<td>34.918 GHz</td>
<td>1.3K</td>
<td>5.5191</td>
<td>3.6°</td>
<td>5.5401</td>
</tr>
</tbody>
</table>
perpendicular. An attempt was made to make the measurement when the sample was placed on the bottom of the cavity with the long axis directed radially. This sample configuration is used because then both the D.C. magnetic field and the microwave magnetic field can be aligned along the (110) axis which is nearly parallel to the long axis of the sample. The flaw in this measurement is that any rotation of the (110) axis which should be in the plane of the cavity base out of this plane will give a lower maximum g-value than the true measure of \( g \parallel \) which can be obtained when alignment is perfect and the D.C. field is rotated until the minimum field (i.e., maximum \( g \)) of the resonance is observed. The only check for this misalignment is a comparison to data taken at the crossover point when the D.C. field is along the [100] direction to see if a larger effective g-value is measured. If the \( H \parallel [100] \) measurement of \( g \) is larger, there still exists no method for determining the magnitude of the misalignment of the initial measurement. Therefore, the measurement when \( H \parallel [100] \) is a more accurate determination. Furthermore, the effects of misalignment can be corrected for when \( H \parallel [100] \).

There are four (110) directions that are neither perpendicular to the (0\( \bar{1} \)1) plane nor in the (0\( \bar{1} \)1) plane. The crossover when \( H \parallel [100] \) occurs because these four have the same value for \( \cos^2 \theta \) when the magnetic field is along the [100] axis (\( \theta \) is the angle between the field and the (110)
axis here). These four \( \langle 110 \rangle \) axes form two pairs of mirror images when reflected about the \( (0\bar{1}1) \) plane. As a result, when the D.C. field is in the \( (0\bar{1}1) \) plane, the value of \( \cos \theta \) for each \( \langle 110 \rangle \) direction is the same as for its mirror image and data taken with the field in this plane will generally consist of two lines each of which arises from two centers whose \( z \)-axis is related by reflection in this plane. The effect of a small misalignment of the sample so that the field is no longer rotated about an axis exactly parallel to the \( [0\bar{1}1] \) direction is to split these lines in the fashion observed in Figure VI-5. The orientation of the magnetic field when the crossing is observed is thus the orientation of the field in the misaligned plane which is closest to the \( [100] \) direction. The splitting between the two magnetic fields is a measure of the angle between the magnetic field and the \( [100] \) axis. The effective \( g \)-values for these two fields can be written as (\( \gamma \) is defined in Figure V-3):

\[
\begin{align*}
g_{e^+} &= g_\parallel \cos (\theta_c + \gamma) \\
g_{e^-} &= g_\parallel \cos (\theta_c - \gamma)
\end{align*}
\]

(VI-1)

The angle, \( \theta_c \), is the value of \( \theta \) for correct alignment. These expressions can be combined to find an expression for \( \gamma \). First, the trigonometric identities for the sum and difference of angles is used to give:
\[ g_{e^+} = g_{\parallel} (\cos \theta_c \cos \gamma \sin \theta_c \sin \gamma) \]  
\[ g_{e^-} = g_{\parallel} (\cos \theta_c \cos \gamma \sin \theta_c \sin \gamma) \]  
(VI-2)

Then, the difference of the two yields:

\[ g_{e^-} - g_{e^+} = 2g_{\parallel} \sin \theta_c \sin \gamma \]  
(VI-3)

and \( \gamma \) can be solved for to give:

\[ \gamma = \sin^{-1} \left( \frac{g_{e^-} - g_{e^+}}{2g_{\parallel} \sin \theta_c} \right) \]  
(VI-4)

This expression was used to give the values of \( \gamma \) in Table VI-2. The sum of the \( g \)-values gives:

\[ g_{e^+} + g_{e^-} = 2g_{\parallel} \cos \theta_c \cos \gamma \]  
(VI-5)

Using the approximation that \( \gamma \) is small, solving for \( g_{\parallel} \) gives the expression:

\[ g_{\parallel} \approx \frac{g_{e^+} + g_{e^-}}{2 \cos \theta_c} (1 + \frac{\gamma^2}{2}) \]  
(VI-6)

which is correct to second order in the misalignment angle, \( \gamma \). It is this expression which gives the corrected value for \( g_{\parallel} \) in Table VI-2 which is used in the subsequent analysis.

The 9 GHz measurement can be combined with the two 35 GHz measurements to give the values for \( \Delta_2 \) of \( 4.41 \times 10^{-2} \) cm\(^{-1}\) and \( 4.37 \times 10^{-2} \) cm\(^{-1}\) which average to a value:

\[ \Delta_2 = 4.39 \times 10^{-2} \text{ cm}^{-1} \]  
(VI-7)
This value will be used in the next section to determine \( E \) and \( a \).

2) Isofrequency Plots and Final Analysis

The final section of Chapter IV discussed the iso-frequency plot program which had to be developed to explain the behavior of the anomalous line observed at 9 GHz. The behavior of this line could not be explained in terms of any obvious transitions that exhibited the angular dependence indicative of a purely axial center aligned along \( \langle 110 \rangle \) axes. The angular dependence of the \( M_s = \pm 1 \) transition when \( E = 0 \) is given in Figure VI-7(a). The low field crossover when \( \mathbf{H} \) is along the \( [100] \) axis cannot be made to correspond to the field of the observed transition with any even slightly reasonable selection of parameters. The high field transition does not conform to the observed angular variation when the field is near the \( [100] \) axis; when \( E = 0 \), one of the two lines which split as the field is rotated away from the \( [100] \) axis should remain at the same field. The observations indicate that one line moves up in field as the other moves down in field as the orientation of the field is rotated farther from the \( [100] \) direction. Figure VI-7(b), however, solves the puzzle; \( E \) is not zero and, in fact, has the opposite sign as \( D \), given the convention for the choice of axis labels described in Chapter IV. The sign is obvious from the theoretical prediction in Figure VI-7(c), when the sign of \( E \) has been reversed.
Figure VI-7. Theoretical Isofrequency Plots of the $M_S = +1$ Transitions of an $S=2$ System with
(a) $E=0$, (b) $E=(-0.01)D$, (c) $E=(+0.01)D$
So, a method for fitting the values of the parameters has been found. First, the magnitude and sign of $D$ was determined from the temperature dependence of the $M_s = \pm 1$ transition relative to the $M_s = \pm 2$ transition at 35 GHz. Then, the shift of the effective $g$-value as a function of frequency gives a value for:

$$\Delta_2 = a + \frac{9E^2}{2D} \quad \text{(VI-8)}$$

Finally, different values of $E$ are entered into the iso-frequency plot program until the field value for the $M_s = \pm 1$ transition at 9 GHz which was accurately measured with the NMR probe is matched. For each value of $E$, $a$ is calculated so that $\Delta_2$ has the experimentally observed value. A fit is very easy to find. The position of the $M_s = \pm 1$ transition observed at 9 GHz is observed to be very sensitive to variations in the value of $E$; a variation of 1% shifts the predicted magnetic field by 10 gauss. Finally, the program can be run using parameters appropriate to the 35 GHz data. The predictions agree within 20 gauss with the data for the $\Delta M_s = \pm 1$ transitions which arise from centers not in the (011) plane. This represents an error of 0.1%. Recalling that these data could only be taken using the stainless steel dewar which was found to affect the magnetic field measurement, the agreement is better than can be expected. The results of this process are given in Table VI-3.
Table VI-3.

Measured Parameters for $d^4$ Ions ($Cr^{2+}$).

<table>
<thead>
<tr>
<th>Host:Ion</th>
<th>$g_{\parallel}$</th>
<th>$\Delta_2$ (cm$^{-1}$)</th>
<th>$D$ (cm$^{-1}$)</th>
<th>$E$ (cm$^{-1}$)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF$_2$:Cr$^{2+}$</td>
<td>1.957 +0.005</td>
<td>1.31 +0.01</td>
<td>-2.19 +0.01</td>
<td>+2.30 +0.02 x 10$^{-2}$</td>
<td>+4.18 +0.02 x 10$^{-2}$</td>
</tr>
<tr>
<td>CdF$_2$:Cr$^{2+}$</td>
<td>1.945 +0.005</td>
<td>1.26 +0.01</td>
<td>-2.60 +0.01</td>
<td>+2.94 +0.02 x 10$^{-2}$</td>
<td>+4.50 +0.02 x 10$^{-2}$</td>
</tr>
<tr>
<td>CaF$_2$:Cr$^{2+}$</td>
<td>1.950 +0.005</td>
<td>1.40 +0.05</td>
<td>&lt; -2.0</td>
<td>&lt; 1 x 10$^{-2}$</td>
<td>---</td>
</tr>
</tbody>
</table>
Finally, some comments should be made about the determination of other parameters in the $S = 2$ Spin Hamiltonian. First, in this calculation the value of $g_\parallel$ was assumed to be equal to $g_\perp$. The position of the $M_s = \pm 1$ resonance was found to be insensitive to a change in the value of $g_\parallel$ smaller than 5%. There is no reason to believe that a change of 5% or more would occur. Second, this analysis ignores the existence of both the fourth order axial and the fourth order non-axial zero field contributions to the Spin Hamiltonian. There are three reasons for neglecting these terms. They should be much smaller than the second order and even the fourth order cubic terms, they should influence the spectra in a very similar manner, and they will add two more parameters which would require at least that much more data to determine. Without the availability of better measurements on more transitions, pursuit of a more exact fit seems futile.
B. CdF$_2$:Cr$^{2+}$

1) Description of Data and Measurements

The angular dependence of the effective $g$-value when the magnetic field is rotated in the (011) plane at 9 GHz is given in Figure VI-8. Figure VI-9 includes typical data at 9 GHz when the field is aligned along the [100] and [011] directions. The new feature in this center is the observation when $H \parallel [011]$ of the $M_s = \pm 1$ line that would be isotropic if $E$ was zero. This line occurs at a field that is out of range of the data in Figure VI-9, but it is seen in Figure VI-11. This line moves down in field and broadens until it can no longer be observed as $H$ is rotated away from the [011] direction. The fact that it is seen at higher field when $H$ is along [011] than when $H$ is along [100] indicates that $E/D$ is negative as observed in Figure VI-7(b). Also of interest in Figure VI-9 is the observation of the $M_s = \pm 1$ lines just above 1750 gauss. The $M_s = \pm 1$ transitions which are due to the $\langle 110 \rangle$ directions which are oriented 45° from [100] are only seen at 9 GHz in this sample.

The most interesting feature of the CdF$_2$:Cr$^{2+}$ data is the observation of superhyperfine structure in both the $M_s = \pm 2$ and the $M_s = \pm 1$ transitions at 9 GHz as well as at 35 GHz. The observation (see Figure VI-9) of this structure in the $M_s = \pm 1$ transitions at all orientations of the $\langle 110 \rangle$
Figure VI-8. Angular Dependence of the Effective g-value of CdF$_2$:Cr$^{2+}$ with the Magnetic Field in the (0\bar{1}1) Plane
Figure VI-9. Representative Data for CdF$_2$:Cr$^{2+}$ with the Magnetic Field Along Two High Symmetry Axes at 9.267 GHz
axes when the field is along both the [100] and [011] directions is strong support for the explanation developed in the previous section of the source of the "anomalous" line observed at 9 GHz. Figure VI-10 shows the superhyperfine structure of the $M_\parallel = \pm 2$ transition when the field is nearly parallel to the [100] axis. The relative intensity of the lines has the 1:4:6:4:1 pattern expected from an interaction with four equivalent fluorine nearest neighbors. When the field is parallel to a ⟨110⟩ axis, the splitting between the superhyperfine lines is 16.0 gauss and the peak-to-peak linewidth is 4.5 gauss. Figure VI-11 shows the superhyperfine structure of the $M_\parallel = \pm 1$ transition at high field when $H\parallel[011]$. This line arises from the center which has the z-axis always perpendicular to the D.C. magnetic field and parallel to the microwave magnetic field. The fact that there are five lines with relative intensities of 1:4:6:4:1 indicates that the splitting still arises from an interaction with four equivalent nearest-neighbor fluorines and this is consistent with the orthorhombic symmetry of the ⟨110⟩ distortion. The lines are split by 9.0 gauss and the peak-to-peak linewidth is 4.5 gauss. The data on this line when $H\parallel[100]$ at 9 GHz also show superhyperfine structure but a clear picture of the structure could not be obtained. Two lines were crossing and each had structure that interfered with that of the other. When the field was rotated enough so that the
Figure VI-10. Superhyperfine Structure of the $M_s = \pm 2$ Transition of $\text{CdF}_2:Cr^{2+}$ at 9 GHz with the Magnetic Field near [100]
Figure VI-11. Superhyperfine Structure of the $M_S = \pm 1$ Transition of CdF$_2$:Cr$^{2+}$ with the Magnetic Field Along [011] but Perpendicular to the z-axis of the Center.
lines were clearly separated, the structure could not be resolved. Much effort would be needed to solve these problems since the sensitivity to misalignment seems to be severe.

Finally, Figure VI-12 shows the observation of superhyperfine structure at 35 GHz. This is the only case in which the structure is resolved for Cr\(^{2+}\) in alkaline earth fluorides at this frequency. It shows the same features as the 9 GHz data, the same relative intensity and splittings. No evidence was found which would require the inclusion in the Spin Hamiltonian of a nuclear Zeeman term of the form:

\[
\sum_{i=1}^{8} g_N^N S_N \cdot I_i
\]

(VI-9)

where \(I_i\) is the nuclear spin of the \(i^{th}\) nearest neighbor and \(g_N\) is the g-value for the fluorine nucleus. The value of the splitting due to the interaction in equation VI-9 can be calculated from NMR data on F\(^{19}\) nuclei. At the field of the transition in Figure VI-12, this interaction would create a splitting of about 5 gauss. The splitting in Figure VI-12 is about 33 gauss and, since an effect would not be expected until these interactions have comparable strengths, it is not surprising that no change is seen in the superhyperfine structure as a function of magnetic field. The temperature dependence of the 35 GHz data is shown in Figure VI-13. As in SrF\(_2\):Cr\(^{2+}\), the change in the
Figure VI-12. Superhyperfine Structure of the $M_S = \pm 2$ Transition of CdF$_2$:Cr$^{2+}$ at 35 GHz.
Figure VI-13. Temperature Dependence of CdF₂:Cr²⁺ at 35 GHz with the Magnetic Field Parallel to the [100] Axis.
intensity of the $M_s = \pm 1$ transition relative to the $M_s = \pm 2$
transition implies that D is negative. An accurate measurement of the
magnitude of D was not possible because the signal to noise was not
great enough at 1.3K to resolve the $M_s = \pm 1$ transition. Hence, only
an upper limit to the ratio of the intensity of the $M_s = \pm 1$ transition to
the $M_s = \pm 2$ transition could be obtained at that temperature.
This upper limit can be used to determine a lower limit to the value of $|D|$.
The data indicate that the magnitude of D must be greater than 1.95 cm$^{-1}$.
Fortunately, the observation of the high field $M_s = \pm 1$ line with
$H \parallel [100]$ and $H \parallel [011]$ allowed D as well as E to be
determined very easily as discussed in the next section.

The frequency dependence of the CdF$_2$:Cr$^{2+}$ data can
be used to determine the value of $\Delta_2$ in the same manner as
explained in the previous section. The results of the
analysis of the data in Table VI-4 is found in Table VI-3.
These results are important as a check on the method of
the measurement for systematic error. After including the
corrections for misalignment as explained in the previous
sections, the value measured here agrees very well with
the published results discussed in the conclusion of the
chapter. This value of $\Delta_2$ is used in the analysis dis-
cussed in the next section.
Table VI-4. Data for Analysis of CdF₂:Cr²⁺

<table>
<thead>
<tr>
<th>Transition Measured</th>
<th>Temperature</th>
<th>Orientation of Measurement</th>
<th>Misalignment</th>
<th>Magnetic Field (Gauss)</th>
<th>Frequency (Gigahertz)</th>
<th>Effective g-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.2K</td>
<td>H</td>
<td></td>
<td>[100]</td>
<td>2.0°</td>
<td>1195.5</td>
</tr>
<tr>
<td></td>
<td>4.2K</td>
<td>H</td>
<td></td>
<td>[100]</td>
<td>2.0°</td>
<td>3942</td>
</tr>
<tr>
<td></td>
<td>4.2K</td>
<td>H</td>
<td></td>
<td>[011]</td>
<td>&lt;0.5°</td>
<td>7553.0</td>
</tr>
<tr>
<td></td>
<td>1.3K</td>
<td>H</td>
<td></td>
<td>[100]</td>
<td>3.5°</td>
<td>4529.2</td>
</tr>
<tr>
<td></td>
<td>4.2K</td>
<td>H</td>
<td></td>
<td>[011]</td>
<td>&lt;0.2°</td>
<td>6398.0</td>
</tr>
</tbody>
</table>
2) Isofrequency Plots and Final Analysis

The major difference between the analysis of the CdF$_2$:Cr$^{2+}$ data and the analysis of the SrF$_2$:Cr$^{2+}$ data arose from the lack of a good measurement of $|D|$ in CdF$_2$:Cr$^{2+}$ from the temperature dependence of the data. Fortunately, the observation of the $M_s = \pm 1$ transition of the center whose axis is always perpendicular to the field at both extreme positions, $H||[100]$ and $H||[011]$, allowed the solution of the problem. The isofrequency plot program was run with several different values of $D$ and, then, for several different values of $E_D$ for each $D$. It was determined that the position of the isotropic line was determined by the value of $D$ and that the anisotropic variation of the field of this transition was determined primarily by the value of $E$ (see Figure VI-7). So, the average of the two field values, when $H||[100]$ and $H||[011]$, could be used to determine $D$ and, then, $E$ could be varied to give the proper difference between these two fields. Finally, the value of $D$ and $E_D$ could be "fine tuned" to agree as closely as possible with the measured values. This last step is necessary because a non-zero value of $E$ does cause a slight shift of the average field from the $E = 0$ value. This technique was used with the data in Table VI-4 to give the results in Table VI-3.
C. CaF$_2$:Cr$^{2+}$

1) Description of Data and Initial Measurements

The angular dependence of the effective $g$-value of CaF$_2$:Cr$^{2+}$ as the field is rotated in the (0\bar{1}1) plane is shown in Figure VI-14. Figure VI-15 shows data when $T = 4.2K$ and the magnetic field is along two high symmetry directions in the (0\bar{1}1) plane. The line near 4.5 kilogauss is the least intense of the three observations of the $M_s = \pm 1$ line arising from the center whose $z$-axis is along the [0\bar{1}1] direction; it is at least an order of magnitude less intense than the $M_s = \pm 2$ transition observed near 1.2 kilogauss where the two intensities are comparable in the two systems discussed previously. This line did demonstrate the same qualitative behavior as the field angle was rotated away from the [100] direction, it split, neither line was isotropic, and they broadened as the field was rotated until they were no longer observed.

The superhyperfine structure of the $M_s = \pm 2$ transition when the D.C. and microwave magnetic fields are both parallel to a \langle 110 \rangle axis is shown in Figure VI-16. Even though it is not as well resolved, it has the same features as the previous systems, five lines with relative intensity of 1:4:6:4:1. The splitting is about 15.8 gauss and each superhyperfine line has a peak-to-peak width of about 10 gauss.
Figure VI-14. Angular Dependence of the Effective g-value of CaF$_2$:Cr$^{2+}$ with the Magnetic Field in the (011) Plane

$\nu = 9.237 \text{GHz}$.
Figure VI-15. Representative Data for CaF₂·Cr²⁺ with the Magnetic Field Along Two High Symmetry Axes
Figure VI-16. Superhyperfine Structure of CaF$_2$:Cr$^{2+}$
with the D.C. and Microwave Magnetic Fields Both Along the [011] Axis.
Figure VI-17 shows data at 35 GHz and its temperature dependence. As observed in the other two systems, the $M_S = \pm 1$ line is an excited state and so $D$ is a negative quantity. As with the CdF$_2$:Cr$^{2+}$ data, the $M_S = \pm 1$ signal is never observed when $T = 1.3K$ so only a lower limit for the magnitude of $D$ can be established. The best data give:

$$|D| > 2.0 \text{ cm}^{-1}$$

Table VI-5 gives the results of the measurements on this sample with the NMR Probe. These measurements are the most consistent taken and required the minimum amount of correction for misalignment effects. More measurements were taken because the results disagreed with the values of the parameters which had been published previously. This point will be discussed more in the conclusion of the chapter. The results of the $g$-shift measurements are given in Table VI-3.

2) Isofrequency Plots and Final Analysis

The final analysis of these data is not as conclusive as that for the other two $d^4$ systems. Essentially, this system lacks a good method for determining a value for $D$. The temperature dependence gives a lower limit of 2.0 cm$^{-1}$. Only one extreme of the $\Delta M_S = \pm 1$ line that is isotropic if $E = 0$ is observed so the method used with the CdF$_2$:Cr$^{2+}$ data cannot be used. The values in Table VI-3 were obtained by using the value for $\Delta 2$ obtained from the $g$-shift and
Figure VI-17. Temperature Dependence of CaF$_2$:Cr$^{2+}$ at 35 GHz with the Magnetic Field Along the [011] Axis
Table VI-5

Data for g-Shift Analysis of CaF$_2$·Cr$^{2+}$

| Orientation for Measurement | Temperature | Misalignment | Frequency (Gigahertz) | Measured $g_{||}$ (Effective) |
|-----------------------------|-------------|--------------|-----------------------|-------------------------------|
| H||H$_z$||[011]       | 1.3K        | 0°           | 9.2491                 | 7.8920                       |
|                             | 4.2K        | 0°           | 9.2844                 | 7.8886                       |
| H||[100]                    | 4.2K        | 0°           | 9.2665                 | 7.8872                       |
| H||[100]                    | 1.3K        | 1.4°         | 35.320                 | 7.8085                       |
| H||[100]                    | 4.2K        | 1.5°         | 36.166                 | 7.7927                       |
adjusting D and E to fit the one other reliable datum, the position of the high field $M_s = \pm 1$ line at 9 GHz.
D. Correlation and Discussion of Data

The first question to be addressed in discussing these results is the question of the accuracy of the measurements. The general agreement between the measurements of the previous chapter and the data taken in other labs indicate the reliability of these values. A further check is the measurement on the CdF$_2$:Cr$^{2+}$ system. The values for $g$ and $\Delta_2$ reported in this thesis agree very well with the published results given in Table VI-6. The corresponding values for CaF$_2$:Cr$^{2+}$ do not agree well at all; the values for $g_{\parallel}$ differ by about 1%, a large error for such a measurement, and the values for $\Delta_2$ differ by 30%. Because of this discrepancy, extra care was taken in the measurements of these values. Since the rest of the results indicated that the measurements on this sample could not be inaccurate by this amount, the reason for the differences in the values remains a mystery.

What can be inferred from the results in Table VI-3? The major piece of information is that there is a variation of fifteen to twenty per cent in the value of the axial zero field splitting for the three systems. This fact argues against the explanation that the $\langle 110 \rangle$ distortion is the result of a fortuitous circumstance in which several coupling parameters have values within a narrow range so that the $\langle 110 \rangle$ distortion is stable. The second fact that
Table VI-6

Previous Measurements of $d^4$ Ions
in Alkaline Earth Fluorides

| System   | $g_{||}$ | $\Delta_2$       |
|----------|---------|------------------|
| CaF$_2$:Cr$^{2+}$ | 1.931   | $6.21 \times 10^{-2}\text{ cm}^{-1}$ (1.86 GHz) |
| CdF$_2$:Cr$^{2+}$ | 1.947   | $4.20 \times 10^{-2}\text{ cm}^{-1}$ (1.26 GHz) |
these measurements indicate is that the \langle110\rangle distortion is not purely axial, that it has a definite nonaxial character that is consistent with the orthorhombic symmetry of the \langle110\rangle axes.
VII. Conclusions and Future Studies

The systems studied in this thesis offer information on two of the most interesting problems which need to be solved for an understanding of the behavior of the spectra of orbital triplet states influenced by vibronic coupling. The first problem concerns the results of an orbital triplet state coupled to triply degenerate vibrational modes. If the coupling is strong enough, the (111) distortions observed in the data of Chapter V from the $d^3$ ions, $V^{2+}$ and $Cr^{3+}$, in alkaline earth fluorides are expected. However, the vibronic ground state of such a system is a quartet, composed of a vibronic triplet at the same energy as a vibronic singlet. Tunneling between the (111) distortions should split the singlet from the triplet; it is not clear what changes in the spectra of such a system would be observed as the result of this splitting. Further work on this problem, at this stage, would be theoretical. Questions that need to be answered concern the prediction of the effects of the tunneling splitting, the analysis of the correlation between the zero field splitting of the spin three halves system and the vibronic coupling parameters, explanations for the difference in the superhyperfine structure of $V^{2+}$ and $Cr^{3+}$, and possible explanations for the very unusual variations in the line intensity of the $\text{SrF}_2:V^{2+}$ data as a function
of the temperature and magnetic field orientation. Experimental efforts that might contribute to the solution of these problems take three forms. First, it would be very helpful to be able to study the behavior of the (111) distortions in a system with lower spin, a spin of one-half or even a spin one system. Reports have been made by Zaripov of a (111) distortion in the system of CaF$_2$:Ni$^{2+}$ but these signals have not been observed elsewhere in spite of efforts to do so.\textsuperscript{(64)} Second, it is possible that ENDOR measurements on these systems could elucidate the superhyperfine structure, but no clear ideas for very useful measurements are available. Third, Raman spectroscopy shows some promise as a technique that might be able to measure a tunneling splitting directly, if it existed in any of these systems. This experiment probably has the greatest chance for interesting results since only a limited Raman study\textsuperscript{(66)} has been made on one orbital triplet system that displays a Ham Effect rather than a static distortion.

The second problem this thesis has addressed is the stability problem of (110) distortions which arise from vibronic coupling involving orbital triplets. This distortion should not be observed according to vibronic coupling theories which include only linear and harmonic coupling terms. Even theories which include nonlinear and anharmonic contributions require either very substantial
contributions from the higher order terms or a very delicate balance between the values of several coupling coefficients to allow stable \langle 110 \rangle distortions. The data from \text{Cr}^{2+} in \text{SrF}_2, \text{CdF}_2, and \text{CaF}_2 argue against the possibility of the stabilization of the \langle 110 \rangle distortion resulting from a special set of coupling parameters. If the parameters need such special conditions, they should result in experimentally observed parameters that do not vary by twenty percent; also, the stable distortion would not be observed in three systems which should have noticeable variations in coupling strengths arising from the different hosts. General physical ideas argue against the idea that the nonlinear and anharmonic terms would interact with near equal strength as the linear and harmonic terms.

So, it has been demonstrated that the \langle 110 \rangle distortion is a more general occurrence than would be expected from present theories.

On a different level, the observation and explanation of a second transition in these systems have confirmed the explanation of the \text{d}^4 ion in terms of a more physically meaningful \text{S} = 2 Spin Hamiltonian. There is now a quantitative basis for the nonaxial character of the orthorhombic, \langle 110 \rangle symmetry distortion. It is hoped that this more complete experimental description of an anomalous center will be helpful in developing new theoretical ideas which might explain such a system.
The most promising experimental approach which might contribute to an understanding of these orthorhombic distortions is the use of Raman spectroscopy. Not only might it solve the problem by detailing the nature of the excited vibronic states, but it might also reveal a tunneling splitting which could occur in the ground vibronic sextet that the six equivalent (110) distortions imply.

It is clear that these problems are both very complex and very interesting challenges for future work.
Appendix A

Perturbation Calculation for Orbital Triplet
in Cubic Symmetry

The purpose of this section of the appendix is to
calculate the value of the parameters of the effective
Hamiltonian, equation II-23(a), which describes an orbital
triplet in a cubic crystal field. The calculation will
be made for the ground orbital triplet with the transfor-
mation properties of \( T_1 \) which arises from the splitting
of the \( ^4F \) term of the \( ^3d \) ion in a cubic crystal field (0\(_h\)
symmetry). The other four orbital states form an excited
orbital triplet which transforms like \( T_2 \) and is excited
by the energy 8 Dq, and an orbital singlet which transforms
like \( A_2 \) and is excited by 18 Dq. The calculation will
follow the method discussed for an orbital singlet ground
state in Pake and Estle\(^{45}\) and used for degenerate
ground states elsewhere.\(^{(67)}\)

The Effective Hamiltonian can be written as:

\[
\hat{H}_e = \sum_a \sum_{\alpha} A_{a}^{\alpha} U_{a} T_{\alpha} - \sum_{\alpha, \alpha'} B_{a}^{\alpha \alpha'} U_{a} T_{\alpha} T_{\alpha'} \quad (A.1)
\]

The \( T_{\alpha} \) are spin operators, the \( U_{a} \) are the symmetrized com-
binations of the projection operators within the orbital
triplet manifold that are given in Table II-5 of the text,
and the \( A_{a}^{\alpha} \) and \( B_{a}^{\alpha \alpha'} \) are constants which are defined from
the relations:
\[ \sum_a A_a^\alpha \langle m|U_a|n\rangle = \langle m|F_\alpha|n\rangle \]  
(A.2)

and:
\[ \sum_a B_a^{\alpha\alpha'} \langle m|U_a|n\rangle = \sum_{\lambda>N} \frac{\langle m|F_\alpha|\lambda\rangle\langle \lambda|F_{\alpha'}|n\rangle}{E_{\lambda}-E_0} \]  
(A.3)

The \( F_\alpha \) are the operators which operate on spatial variables only and are obtained from the physical terms which are considered. The states \(|m\rangle\) and \(|n\rangle\) represent the orbital triplet and the states \(|\lambda\rangle\) represents the excited states which are to be included in the calculation, which, in this case, are the \( T_2 \) triplet and \( A_2 \) singlet.

In the present calculation, the effects of the Zeeman interaction and the Spin-Orbit interaction are to be included in the \( F_\alpha \). These terms are:
\[ \mathcal{H}_1 = \beta(L+g_e S) \cdot \vec{H} + \lambda(\vec{L} \cdot \vec{S}) \]
\[ = (\lambda \vec{L} + g_e \vec{S} \cdot \vec{H}) \cdot \vec{S} + \beta \vec{H} \cdot \vec{L} \]  
(A.4)

From the second form, Table A.1 can be written for the \( F_\alpha \) and \( T_\alpha \).

To determine the \( A_a^{\alpha} \), the following process can be used. Write out the expressions for each matrix element of \( F_\alpha \); for example:
\[ \langle x|F_\alpha|x\rangle = A_1^{\alpha} - A_\theta^{\alpha} + \sqrt{3} A_\epsilon^{\alpha} \]
\[ \langle y|F_\alpha|y\rangle = A_1^{\alpha} - A_\theta^{\alpha} - \sqrt{3} A_\epsilon^{\alpha} \]  
(A.5)
\[ \langle z|F_\alpha|z\rangle = A_1^{\alpha} + 2A_\theta^{\alpha} \]
<table>
<thead>
<tr>
<th>α</th>
<th>( F_α )</th>
<th>( T_α )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \beta \overrightarrow{H} \cdot \overrightarrow{L} )</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>( \lambda L_x + g_e \beta H_x )</td>
<td>( S_x )</td>
</tr>
<tr>
<td>3</td>
<td>( \lambda L_y + g_e \beta H_y )</td>
<td>( S_y )</td>
</tr>
<tr>
<td>4</td>
<td>( \lambda L_z + g_e \beta H_z )</td>
<td>( S_z )</td>
</tr>
</tbody>
</table>
This process can be done easily from the matrix forms of the \( U_a \). In the three matrix elements just written, the \( A_1^\alpha \), \( A_\theta^\alpha \), and \( A_\epsilon^\alpha \) constants are the only ones involved because the three operators, \( \mathcal{J}(U_1) \), \( U_\theta \), and \( U_\epsilon \) are the only operators with diagonal elements. Since no other operators have diagonal elements, the expressions for \( A_1^\alpha \), \( A_\theta^\alpha \), and \( A_\epsilon^\alpha \) can be written by inspection:

\[
A_1^\alpha = \frac{1}{3} \left( \langle x | F_\alpha | x \rangle + \langle y | F_\alpha | y \rangle + \langle z | F_\alpha | z \rangle \right)
\]

\[
A_\theta^\alpha = \frac{1}{6} \left( 2 \langle z | F_\alpha | z \rangle - \langle x | F_\alpha | x \rangle - \langle y | F_\alpha | y \rangle \right)
\] \hspace{1cm} (A.6)

\[
A_\epsilon^\alpha = \frac{\sqrt{3}}{6} \left( \langle x | F_\alpha | x \rangle - \langle y | F_\alpha | y \rangle \right)
\]

The rest of the \( A_a^\alpha \) can be expressed in an analogous fashion. Now, the expressions for \( A_a^\alpha \) can be determined for each value of \( \alpha \) and substituted into equation A.1 for the first order Effective Hamiltonian terms.

A key step in the calculation is the evaluation of the matrix elements of the components of the orbital angular momentum, \( L_x \), \( L_y \), and \( L_z \). The critical step is to determine the transformation properties of the \( ^4T_1 \), \( ^4T_2 \), and \( ^4A_2 \) states which originate from the \( ^4F \) term when a cubic crystal field is applied. The angular dependence of the \( ^4F \) states can be expressed by the spherical harmonics with \( \lambda = 3 \). Watanabe has listed the linear combinations of these states which transform like \( ^4T_1 \), \( ^4T_2 \), and \( ^4A_2 \) in cubic symmetry and these are reproduced in Table A.2.
### Table A.2

Basis Functions of $^4F$ Term in cubic symmetry (65)

<table>
<thead>
<tr>
<th>Irreducible Representation</th>
<th>Basis Functions Expressed in Spherical Harmonics ($Y_{LM}^\prime$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$ $</td>
<td>\alpha\rangle$</td>
</tr>
<tr>
<td>$T_2$ $</td>
<td>\xi\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>\eta\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>\zeta\rangle$</td>
</tr>
<tr>
<td>$T_1$ $</td>
<td>\chi\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>\gamma\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>\delta\rangle$</td>
</tr>
</tbody>
</table>
The orbital angular momentum operators, \( L_z, L_+, \) and \( L_- \) can be easily applied to these expressions to derive the entries of the nonzero matrix elements in Table A.3. Since \( \langle m | L \uparrow | m \rangle = 0 \) (the angular momentum is quenched by the crystal field), all \( A^a_\alpha \) for which \( F^\alpha \) contains a component of \( \vec{L} \) are zero. So, \( A^1_1 = A^0_0 = A^c_\varepsilon = 0 \) for \( \varepsilon = 1, 2, 3, 4 \) and \( A^2_1, A^3_1, \) and \( A^4_1 \) give a spin Zeeman term. The nonzero off-diagonal matrix elements within the \( T_1 \) ground state given in Table A.3 will produce the rest of the terms in the total first order contribution to the Effective Hamiltonian:

\[
\kappa^{(1)}_{\text{eff}} = \mathbf{g}_e^\beta \mathbf{H} \cdot \mathbf{S} \mathbf{J} + \frac{3}{2} \lambda \mathbf{S} \cdot \mathbf{U} + \frac{3}{2} \beta \mathbf{H} \cdot \mathbf{U} \quad \text{(A.7)}
\]

The dot products with \( \mathbf{U} \) are a short notation relating the components of \( \mathbf{S} \) and \( \mathbf{H} \) to \( U_x, U_y, \) and \( U_z. \)

The second order contributions are just as straightforward to compute even though slightly more laborious. First, it should be noted that there are no matrix elements between the \( ^4T_1 \) ground states and the \( ^4A_2 \) excited state. Therefore, only the \( ^4T_2 \) term will be included, and the energy difference, \( 8 \text{ Dq} \) will be expressed as \( \Delta. \) The expressions for \( B^\alpha a \) are found by replacing the \( F^\alpha \) in the expressions for \( A^\alpha a \) (for example, in equation A.6) by the expression:

\[
\sum_{\Delta > N} \frac{F^\alpha \uparrow | \Delta \rangle \langle \Delta | F^\alpha \uparrow}{E^\Delta - E_0} \quad \text{(A.8)}
\]
Table A.3
Nonzero Matrix Elements of $\mathbf{L}$ Between
the Ground $T_1$ State and Itself
and the Excited $T_2$ States

<table>
<thead>
<tr>
<th>$\mathbf{L}_x$</th>
<th>$\mathbf{L}_y$</th>
<th>$\mathbf{L}_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle z</td>
<td>\mathbf{L}_x</td>
<td>y \rangle = -\frac{3}{2} i$</td>
</tr>
<tr>
<td>$\langle y</td>
<td>\mathbf{L}_x</td>
<td>z \rangle = \frac{3}{2} i$</td>
</tr>
<tr>
<td>$\langle \zeta</td>
<td>\mathbf{L}_x</td>
<td>\eta \rangle = -i \frac{\sqrt{15}}{2}$</td>
</tr>
<tr>
<td>$\langle \eta</td>
<td>\mathbf{L}_x</td>
<td>\zeta \rangle = -i \frac{\sqrt{15}}{2}$</td>
</tr>
<tr>
<td>$\langle \xi</td>
<td>\mathbf{L}_x</td>
<td>\eta \rangle = i \frac{\sqrt{15}}{2}$</td>
</tr>
<tr>
<td>$\langle \eta</td>
<td>\mathbf{L}_x</td>
<td>\zeta \rangle = i \frac{\sqrt{15}}{2}$</td>
</tr>
</tbody>
</table>
Most of the $B_{a}^{a'}$ will be zero. Only representative nonzero values will be given here. In general, $B_{a}^{a'}$ will contain terms proportional to $\lambda^{2}$, $\lambda\bar{s}H$, and $\bar{s}^{2}H^{2}$. The terms proportional to $\bar{s}^{2}H^{2}$ will be very small compared to $\lambda^{2}$ and $\lambda\bar{s}H$ and will be neglected here.

For $a = 1$, the nonzero values of $B_{1}^{a}{}^{a'}$ are:

$$B_{1}^{12} = B_{1}^{21} = \frac{5}{2\Delta} \beta \lambda H_{x}$$
$$B_{1}^{13} = B_{1}^{31} = \frac{5}{2\Delta} \beta \lambda H_{y}$$
$$B_{1}^{14} = B_{1}^{41} = \frac{5}{2\Delta} \beta \lambda H_{z}$$
$$B_{1}^{22} = B_{1}^{33} = B_{1}^{44} = \frac{5\lambda^{2}}{2\Delta}$$

and the resulting second order contribution to the Effective Hamiltonian is:

$$\left[ -\frac{5\lambda}{\Delta} \bar{H} \cdot \bar{s} - \frac{5\lambda^{2}}{2\Delta} \bar{s} \cdot \bar{s} \right]$$

For $a = \theta$, the nonzero values are:

$$B_{\theta}^{12} = B_{\theta}^{21} = \frac{5}{8\Delta} \beta \lambda H_{x}$$
$$B_{\theta}^{13} = B_{\theta}^{31} = \frac{5}{8\Delta} \beta \lambda H_{y}$$
$$B_{\theta}^{14} = B_{\theta}^{41} = -\frac{5}{4\Delta} \beta \lambda H_{z}$$
$$B_{\theta}^{22} = B_{\theta}^{33} = \frac{5\lambda^{2}}{8\Delta}$$
$$B_{\theta}^{44} = -\frac{5\lambda^{2}}{8\Delta} 2$$

so the second order contribution is:
\[-u \left[ \sum_{\alpha} \frac{5\lambda}{8\Delta} \left( 2H_zS_z - H_xS_x + H_yS_y \right) \right. \\
\left. \frac{5\lambda^2}{8\Delta} \left( 2S_z^2 - S_x^2 - S_y^2 \right) \right] \] (A.12)

Similarly, for \( B_x^{\alpha x'} \), the nonzero values are:

\[
B_x^{13} = -B_x^{31} = -i \frac{15}{8\Delta} \beta \lambda H_z \\
B_x^{14} = -B_x^{41} = -i \frac{15}{8\Delta} \beta \lambda H_y \\
B_x^{34} = -B_x^{43} = i \frac{15\lambda^2}{8\Delta} \] (A.13)

but, the second order contributions form the term:

\[
\frac{15\lambda^2}{8\Delta} \mathcal{S} \cdot \mathcal{U} \] (A.14)

since the sum of the terms \( B_x^{13}H_zS_y + B_x^{31}H_zS_y \) is zero

(the commutation relations are applied to the other terms).

Finally, for \( B_\xi^{\alpha x'} \), the nonzero values are:

\[
B_\xi^{34} = B_\xi^{43} = \frac{15\lambda^2}{8\Delta} \\
B_\xi^{13} = B_\xi^{31} = \frac{15}{8\Delta} \lambda \beta H_z \\
B_\xi^{14} = B_\xi^{41} = \frac{15}{8\Delta} \lambda \beta H_y \] (A.15)

so the second order contribution is:

\[-u \left[ \sum_{\xi} \frac{15}{4\Delta} \lambda \beta (H_zS_y + H_yS_z) + \frac{15\lambda^2}{8\Delta} (S_zS_y + S_xS_z) \right] \] (A.16)

In conclusion, this calculation provides values for the coefficients of the electronic Hamiltonian in equation
II-23(a) of the text. Equation II-23(a) was derived completely from symmetry considerations. Comparison of that equation with the terms derived in this calculation gives the expressions:

\[ f_1 = g_0 \frac{3}{\Delta} \frac{\lambda}{3} (H \cdot S) - \frac{5}{\Delta} \frac{\lambda^2}{2} \frac{\mathbf{S} \cdot \mathbf{S}}{2} \]

\[ f_\theta = \frac{5}{4\Delta} \frac{\lambda}{8} (2H_z S_z - H_x S_x - H_y S_y) + \frac{5\lambda^2}{8\Delta} (2S_z^2 - S_x^2 - S_y^2) \]

\[ f_z = \frac{5}{4\Delta} \frac{\lambda}{8} \sqrt{3} (S_x S_z - S_y S_y) + \frac{5\lambda^2}{8\Delta} \sqrt{3} (S_x^2 - S_y^2) \]

\[ f_x = \left( \frac{3}{2} \lambda + \frac{15\lambda^2}{8\Delta} \right) S_x U_x + \frac{3}{2} \frac{\lambda}{8} H_x U_x \]

\[ f_y = \left( \frac{3}{2} \lambda + \frac{15\lambda^2}{8\Delta} \right) S_y U_y + \frac{3}{2} \frac{\lambda}{8} H_y U_y \quad (A.17) \]

\[ f_z = \left( \frac{3}{2} \lambda + \frac{15\lambda^2}{8\Delta} \right) S_z U_z + \frac{3}{2} \frac{\lambda}{8} H_z U_z \]

\[ f_\phi = -\frac{15}{4\Delta} \frac{\lambda}{8} (H_z S_y + H_y S_z) - \frac{15\lambda^2}{8\Delta} (S_y S_z + S_z S_y) \]

\[ f_r = -\frac{15}{4\Delta} \frac{\lambda}{8} (H_z S_x + H_x S_z) - \frac{15\lambda^2}{8\Delta} (S_z S_x + S_x S_z) \]

\[ f_\sigma = -\frac{15}{4\Delta} \frac{\lambda}{8} (H_x S_y + H_y S_x) - \frac{15\lambda^2}{8\Delta} (S_x S_y + S_y S_x) \]
Appendix B

Perturbation Calculation for \(\{111\}\) Jahn-Teller Split Orbital Triplet

The problem worked in this section of the appendix is to describe the effects of the two excited adiabatic potential energy surfaces on the EPR of the ground vibronic state with a perturbation calculation similar to the one in Appendix A. The states will be taken as electronic states made up of linear combinations of the electronic triplet, \(|x\rangle, |y\rangle, \text{and } |z\rangle\). The ground state, at energy \(-E_J^T\), is:

\[
|g\rangle = \frac{1}{\sqrt{3}} \left( |x\rangle + |y\rangle + |z\rangle \right) \quad (B.1)
\]

The excited states, both at energy \(\frac{1}{2} E_J^T\), are:

\[
|ex\rangle = \frac{1}{\sqrt{6}} \left( 2 |z\rangle - |x\rangle - |y\rangle \right) \\
|ey\rangle = \frac{1}{\sqrt{2}} \left( |x\rangle - |y\rangle \right) \quad (B.2)
\]

The state, \(|g\rangle\), transforms like \(\Gamma_1^+\) in the \(D_{3d}\) symmetry of the distorted configuration and the states \(|ex\rangle\) and \(|ey\rangle\) transform like the partners of \(\Gamma_3^+\) in \(D_{3d}\). While the \(D_{3d}\) symmetry of the distortion has been used to write the electronic states, the calculation will be done in the Cartesian coordinate system of the cubic axes and the result transformed to the coordinates of the distortion.
Consider the Hamiltonian given by the Jahn-Teller splitting, the Zeeman interaction, and the Spin-Orbit interaction:

\[ \mathcal{H} = \mathcal{H}_{JT} + \mathcal{K}_\perp \]

\[ \mathcal{H}_{JT} = \begin{pmatrix} -E_{JT} & 0 & 0 \\ 0 & +\frac{1}{2} E_{JT} & 0 \\ 0 & 0 & +\frac{1}{2} E_{JT} \end{pmatrix} \]  \hspace{1cm} (B.3)

\[ \mathcal{K}_\perp = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \times (\lambda \vec{L} + g_e \vec{S}) \cdot \vec{S} + \vec{\lambda} \cdot \vec{L} \]

The object is to write an effective Hamiltonian of the form:

\[ \mathcal{H}_e = \sum \sum A_a^{\alpha} U_a \Phi_\alpha - \sum B_a^{\alpha\alpha'} U_a \Phi_\alpha \Phi_\alpha' \]  \hspace{1cm} (B.4)

The \( T_\alpha \) are the spin operators, \( U_a \) are the effective orbital operators, and the constants \( A_a^{\alpha} \) and \( B_a^{\alpha\alpha'} \) are defined by:

\[ \langle m | F_\alpha | n \rangle = \sum A_a^{\alpha} \langle m | U_a | n \rangle \]  \hspace{1cm} (B.5)

and

\[ \sum_{\ell > N} \frac{\langle m | F_\alpha | \ell \rangle \langle \ell | F_\alpha' | n \rangle}{E_{\ell} - E_0} = \sum B_a^{\alpha\alpha'} \langle m | U_a | n \rangle \]  \hspace{1cm} (B.6)

where \( F_\alpha \) are the "real" orbital operators and the summation for \( \ell > N \) means that \( | \ell \rangle \) is an excited electronic state.
(|ex⟩ and |ey⟩) lying at an energy $E_{\omega} - E_0 + \frac{3}{2} E_{JT}$ higher than the ground state. For the Hamiltonian in equation B.3, the "real" orbital operators and spin operators are given in Table A.1. The ground state is the singlet, |g⟩, and therefore a has only one value for this problem and the subscript will be dropped from $A_a^\alpha$ and $B_a^{\alpha\beta}$. The constants, $A^\alpha$, will be given by:

$$A^\alpha = \langle g | F^\alpha | g \rangle$$

$$= \frac{1}{3} \left( \langle x | F^\alpha | x \rangle + \langle y | F^\alpha | y \rangle + \langle z | F^\alpha | z \rangle \right)$$

$$+ \frac{1}{3} \left( \langle x | F^\alpha | y \rangle + \langle y | F^\alpha | x \rangle \right)$$

$$+ \langle y | F^\alpha | z \rangle + \langle z | F^\alpha | y \rangle$$

$$+ \langle z | F^\alpha | x \rangle + \langle x | F^\alpha | z \rangle \right)$$

(B.7)

The matrix elements in this equation can be found using Table A.3 and the results are:

$$A^1 = 0$$

$$A^2 = \frac{1}{3} \left( g_e 2H_x + g_e 2H_x + g_e 2H_x \right) = g_e 2H_x$$

(B.8)

$$A^3 = g_e 2H_y$$

$$A^4 = g_e 2H_z$$

so the first order result demonstrates the quenching of the orbital angular momentum:

$$\chi^{(1)}_e = g_e \vec{\vec{S}} \cdot \vec{\pi}$$

(B.9)
The second order terms can be obtained from the matrix elements in Table B.1. The $B^{11}$ term will be dropped because it is quadratic in the magnetic field and will be too small to be observed. The other terms will be:

\[
B^{12} = B^{21} = \frac{\lambda S}{2E_{JT}} (2H_x - H_y - H_z)
\]

\[
B^{13} = B^{31} = \frac{\lambda S}{2E_{JT}} (2H_y - H_x - H_z)
\]

\[
B^{14} = B^{41} = \frac{\lambda S}{2E_{JT}} (2H_z - H_x - H_y)
\]

\[
B^{22} = B^{33} = B^{44} = \frac{\lambda^2}{E_{JT}}
\]

\[
B^{23} = B^{24} = B^{34} = B^{32} = B^{42} = B^{43} = -\frac{\lambda^2}{2E_{JT}}
\]

Substituting these values into equation B.4 gives the Effective Hamiltonian:

\[
\kappa_e = g_e S \cdot \vec{H} - \frac{3\lambda S}{E_{JT}} \left\{ \frac{1}{3} (2H_x - H_y - H_z) S_x + \frac{1}{3} (2H_y - H_x - H_z) S_y \right. \\
+ \left. \frac{1}{3} (2H_z - H_x - H_y) S_z \right\} \\
- \frac{\lambda^2}{E_{JT}} (S_x^2 + S_y^2 + S_z^2) \\
+ \frac{\lambda^2}{2E_{JT}} (S_x S_y + S_y S_x + S_x S_z + S_z S_x + S_y S_z + S_z S_y)
\]

(B.11)

The final step is to rotate the coordinate system to a system with the z-axis along a \langle111\rangle direction. First, some algebra reveals that:
Table B.1

Matrix Elements of $\mathbf{L}$ between $|g\rangle$ and $|ex\rangle, |ey\rangle$

|       | $|g\rangle$ | $|ex\rangle$ | $|ey\rangle$ |
|-------|-------------|---------------|---------------|
| $\langle g | L_x \rangle$ | 0            | $\frac{3}{2 \sqrt{2}}$ i | $\frac{3}{2 \sqrt{6}}$ i |
| $\langle g | L_y \rangle$ | 0            | $-\frac{3}{2 \sqrt{2}}$ i | $\frac{3}{2 \sqrt{6}}$ i |
| $\langle g | L_z \rangle$ | 0            | 0             | $-\frac{3}{\sqrt{6}}$ i |
\[
\frac{1}{3} \left[ (2H_x - H_y - H_z)S_x + (2H_y - H_x - H_z)S_y + (2H_z - H_x - H_y)S_z \right]
\]
\[= \vec{H} \cdot \vec{S} - \frac{1}{3} (H_x + H_y + H_z) (S_x + S_y + S_z) \tag{B.12}
\]

Now, define the new coordinate system so that the z-axis is along the [111] direction by making the substitution:

\[
\hat{x}' = \frac{1}{\sqrt{6}} (2\hat{z} - \hat{x} - \hat{y})
\]
\[
\hat{y}' = \frac{1}{\sqrt{2}} (\hat{x} - \hat{y}) \tag{B.13}
\]
\[
\hat{z}' = \frac{1}{\sqrt{3}} (\hat{x} + \hat{y} + \hat{z})
\]

so that the last term above becomes \((\vec{H}' \cdot \vec{S}' - H'_z S'_z)\). The last term of equation B.11 contains a sum of cross terms like \(S_i S_j\) which, when the change of coordinates is made, becomes:

\[
2S'_z^2 - S'_x^2 - S'_y^2 \tag{B.14}
\]

The result in the new coordinate system is (dropping the primes):

\[
\tilde{\mathcal{H}}_e = g_e B S \cdot \vec{S} + \frac{3\lambda^3}{E_{JT}} (H_z S_z - \vec{H} \cdot \vec{S})
\]
\[- \frac{\lambda_2}{E_{JT}} \vec{S} \cdot \vec{S} \tag{B.15}
\]
\[+ \frac{\lambda_2}{2E_{JT}} (3S_z^2 - \vec{S} \cdot \vec{S})
\]

The terms proportional to \(\vec{S} \cdot \vec{S} = S(S+1)\) simply shift the zero of energy in the Spin Hamiltonian and can be included
or dropped when convenient. Rewriting this result for comparison to the Spin Hamiltonian in equation IV-1 gives:

\[ K_s = g_e B H_z S_z + \left( g_e - \frac{3\lambda}{E_{JT}} \right) B (H_x S_x + H_y S_y) \]

\[ + \frac{3\lambda^2}{2E_{JT}} (S_z^2 - \frac{1}{3} \vec{S} \cdot \vec{S}) \]  

and the comparison reveals:

\[ g_{||} = g_e \]

\[ g_\perp = g_e - \frac{3\lambda}{E_{JT}} \]

\[ D = \frac{3\lambda^2}{2E_{JT}} \]  

(B.17)
Appendix C

Fortran Program for Isofrequency

Plots for an S=3/2 Spin Hamiltonian

ISOFREQUENCY PLOT PROGRAM, S=3/2

This is the main control program, primarily responsible for
organization of input data and its use in controlling the search
routine. The first data card should be done in I4 format and
contains the number of equivalent centers to be considered. Then,
the data describing the equivalent centers; first, a numerical
index followed by the direction cosines of the X, Y, Z axes,
respectively, of that center's coordinate system in terms of the
coordinates of the problem.

Next, in I4 format, the number of times the program will be
run with different data. Finally, the rest of the data is input
using the namelist feature. The input card has the format:
SPACE$PARAM3(SPACE)'DATA-NAME'='VALUE', ....$END . On the
first card all parameters must be specified; after that, only
the parameters which should change need to be specified.

The input parameters are: IFLAG, the flag for transition
probabilities, 1 if they are wanted, 0 if they are not;
TEMP, the temperature in degrees Kelvin; DIN, the zero field
parameter, in inverse centimeters; HIN, the microwave frequency,
in hertz; MA, the maximum magnetic field, in gauss;
FS, the magnetic field step, in gauss; GPA, the value of
G parallel; GPD, the value of G perpendicular;
GAMMA is the misalignment angle measured when H is along (100) and
DELTA is the misalignment angle measured when H is along (011).
Both are input and output in degrees.

The comma must be directly after the data value (no space) for
correct input.

The IMSL library function, EIGCH, is used to perform the
diagonalization; it requires the input of the matrix, A, in
Hermitian storage mode, i.e. the lower half of the matrix stored
rowwise, or one row after another. The parameter, IJOB, permits
computation of the eigenvector as well as the eigenvalues.

The subroutine, AMATRIX, sets up the input matrix for EIGCH.
N is the number of the dimensions of the matrix throughout the
problem.

BODY OF THE SOURCE PROGRAM FOR ISOFREQUENCY PLOTS

INITIALIZATION

REAL*8 WK(32), TEMP, DIN, HIN, ACENT(6,10), COR(9),
PI, HPLANK, BETA, CLITE, DLA, XX, YY, HN, GPA, GPD, CENTER(6,10)
REAL*8 B GAMMA, B DELTA, GAMMA, DELTA
INTEGER N,N2,IFLAG,NCENT,NDATA,INCREM,DR,MA,FS
COMPLEX*16 A(16),Z(4,4)
COMMON DLA,XX,YY,GPA,GPD,HIN,N,N2,MA,FS,II,DR,IFLAG,JJ,TEMP,CENTER
NAMELIST /PARAM3/IFLAG,TEMP,DIN,HIN,MA,FS,GPA,GPD,BGAMMA,BDELT
DATA  HPLANK,CLITE/ 6.626196D-27, 2.997928D10/
N=4
N2=N*(N+1)/2
PI=3.14159265358979323846
BGAMMA=0.00000
BDELT=0.00000
C HERE STARTS THE INPUT OF THE DATA WHICH REMAINS FOR THE ENTIRE RUN
READ(5,1) NCENT
DO 10 I=1,NCENT
READ(5,2) (ACENT(I,J),J=1,10)
10 CENTER(I,1)= ACENT(I,1)
READ(5,1) NDATA
C NOW, START THE LOOP FOR THE INPUT AND SOLUTION OF EACH 'DATA SET'
DO 20 INCREM=1,NDATA
READ(5,PARAM3)
WRITE(6,7) DIN,HIN,MA,FS,GPA,GPD,TEMP,BGAMMA,BDELT
C CONVERT TO ENERGIES IN UNITS OF THE AXIAL ZERO FIELD ENERGY.
DLA=DIN*HPLANK*CLITE
HN=HIN*HPLANK/DLA
C SET UP THE MISALIGNMENT ROTATION MATRIX.
GAMMA=PI*BGAMMA/1.8D2
DELT=PI*BDELT/1.8D2
COR(1)=DCOS(GAMMA)
COR(9)=DCOS(DELT)
COR(2)=DSIN(GAMMA)*(1.0D0+COR(9))/2.0D0
COR(3)=DSIN(GAMMA)*DSIN(DELT)/2.0D0
COR(4)=-1.0D0*COR(2)
COR(5)=COR(1)*COR(9)
COR(6)=DSIN(DELT)*(1.0D0+COR(1))/2.0D0
COR(7)=COR(3)
COR(8)=-1.0D0*COR(6)
C NOW, BEGIN THE LOOP OVER THE EQUIVALENT CENTERS.
DO 30 II=1,NCENT
C CORRECT THE CENTERS FOR MISALIGNMENT.
CENTER(II,2)=COR(1)*ACENT(II,2)+COR(2)*ACENT(II,3)+
  2 COR(3)*ACENT(II,4)
CENTER(II,3)=COR(4)*ACENT(II,2)+COR(5)*ACENT(II,3)+
  3 COR(6)*ACENT(II,4)
CENTER(II,4)=COR(7)*ACENT(II,2)+COR(8)*ACENT(II,3)+
  4 COR(9)*ACENT(II,4)
CENTER(II,5)=COR(1)*ACENT(II,5)+COR(2)*ACENT(II,6)+
  5 COR(3)*ACENT(II,7)
CENTER(II,6)=COR(4)*ACENT(II,5)+COR(5)*ACENT(II,6)+
  6 COR(6)*ACENT(II,7)
CENTER(II,7)=COR(7)*ACENT(II,5)+COR(8)*ACENT(II,6)+
  7 COR(9)*ACENT(II,7)
CENTER(II,8)=COR(1)*ACENT(II,8)+COR(2)*ACENT(II,9)+
  8 COR(3)*ACENT(II,10)
CENTER(I,8)=COR(4)*ACENT(I,8)+COR(5)*ACENT(I,9)+
9   COR(6)*ACENT(I,10)
CENTER(I,10)=COR(7)*ACENT(I,8)+COR(8)*ACENT(I,9)+
1   COR(9)*ACENT(I,10)
LA=CENTER(I,1)
WRITE(6,6)
WRITE(6,4) LA
WRITE(6,6)
C NOW, BEGIN THE LOOP FOR THE ANGLES, THETA, MEASURED FROM THE (100)
C AXIS IN THE CRYSTAL.
DO 40 DR=1,91,10
C THE SUBROUTINE, SEARCH, SUBTRACTS ONE FROM THE VALUE OF DR TO GET
C "THETA" WHICH IS USED IN CALCULATION AND OUTPUT.
C SEARCH FINDS ALL RESONANCES AT ANGLE THETA AND OUTPUTS THE DATA.
CALL SEARCH
40 CONTINUE
DR=56
CALL SEARCH
30 CONTINUE
20 CONTINUE
WRITE(6,99999)
STOP
99999 FORMAT (12H END OF RUN!)
1 FORMAT (I4)
2 FORMAT (4F20.17)
4 FORMAT (17HCENTER INDEX IS,I4)
6 FORMAT (1HO)
7 FORMAT (34H THE AXIAL ZERO FIELD SPLITTING IS,7X,F10.4,
1   21H INVERSE CENTIMETERS/
2   27H THE MICROWAVE FREQUENCY IS,14X,-9PF10.6,11H GIGAHERTZ/
3   30H THE MAXIMUM MAGNETIC FIELD IS,11X,I10,7H GAUSS/
4   18H THE FIELD STEP IS,23X,I10,7H GAUSS/
5   14H G PARALLEL IS,0PF10.6/19H G PERPENDICULAR IS,0PF10.6/
6   19H THE TEMPERATURE IS,F8.4/
7   44H MISALIGNMENT ANGLES, GAMMA AND DELTA, ARE: ,F10.3,
8   5H AND ,F10.3,8H DEGREES/I10)
END
SUBROUTINE SEARCH

REAL*8 PI, TH, SI, CO, PHI, DLA, XX, YY, HN, GPA, GPD, HM, HL, HR, SLOPE, DIFF,
1     RESINT, CENTER(6, 10)
2     D(4), DL(4), AS(4), E0(4), WK(32)
REAL*8 TEMP, KT, FRI, TF, DG(4)
1     , E01(4), DB(4), SL(4), DT(4), HB, HT
COMPLEX*16 A(10), Z(4, 4)
INTEGER DR, MA, FS, X, Y, DRI
COMMON DLA, XX, YY, GPA, GPD, HN, N, N2, MA, FS, II, DR, IFLAG, JJ, TEMP, CENTER
IZ=N
IJOB=0
PI=DARCOS(-1.0000)

C COMPUTE ANGLES APPROPRIATE TO SPIN HAMILTONIAN FROM CENTER DATA
C AND THETA.
1000 TH=(DR-1.)*PI/1.8D02
   DR1=DR-1
   SI=DSIN(TH)
   CO=DCOS(TH)
   TH=DARCOS(CENTER(II, 8)*SI+CENTER(II, 10)*CO)
   PHI=DATAN2((CENTER(II, 5)*SI+CENTER(II, 7)*CO),(CENTER(II, 2)*SI
1   +CENTER(II, 4)*CO))

C BEGIN THE LOOP OVER THE FIELD VALUES.
HL=0.0D00
K=MA+1
DO 50 NHM=1, K, FS
   HM=(NHM-1)
   A MATRIX SETS UP THE MATRIX AND EIGCH DIAGONALIZES IT.
   CALL AMATRIX(HM, TH, PHI, A)
   CALL EIGCH(A, N, IJOB, D, Z, IZ, WK, IER)
C THE FOLLOWING SECTION PERFORMS A LINEAR FIT TO SEARCH FOR RESONANCE.
   IF (HM.EQ. HL) GO TO 190
   AS IS THE AVERAGE SLOPE OF EACH ENERGY LEVEL OVER THE INTERVAL.
   DO 80 X=1, N
80   AS(X)=(D(X)-DL(X))/(HM-HL)
   EQ IS THE ENERGY EXTRAPOLATED TO H=0.
   DO 90 X=1, N
90   EQ(X)=DL(X)-AS(X)*HL
C PREPARE FOR THE NEXT HIGHER FIELD RANGE (PART ONE).
190  DO 160 X=1, N
160  DL(X)=D(X)
   IF (HM.LT.HL) GO TO 70
C SET UP A LOOP OVER ALL PAIRS OF ENERGY LEVELS.
   K3=N-1
   DO 100 X=1, K3
      K1=X+1
      DO 100 Y=K1, N
         CALL LINFIT(HM, HL, HR, N, EQ, AS, X, Y, HN, DRI)
140  IF (HR.EQ.0.0) GO TO 100
   HB=HR-2.5D01
   HT=HR-2.5D01
CALL AMATRIX(HB,TH PHI,A)
CALL EIGCH(A,N,IJOB,DB,Z,IZ,WK,IER)
CALL AMATRIX(HT,TH PHI,A)
CALL EIGCH(A,N,IJOB,DT,Z,IZ,WK,IER)
DO 801 I=1,N
801 SL(I)=(DT(I)-DB(I))/(HT-HB)
DO 901 I=1,N
901 EO1(I)=DB(I)-SL(I)*HB
CALL LINFIT(HT,HB,HR,N,EO1,SL,X,Y,HN,DR1)
RESINT=0.0
IF (IFLAG.EQ.0) GO TO 150
C THIS SECTION DOES THE INTENSITY CALCULATION. IT IS SKIPPED
C IF IFLAG IS ZERO.
DIFF=0.0
TF=0.0
FRI=0.0
CALL AMATRIX(HR,TH PHI,A)
IJOB=2
CALL EIGCH(A,N,IJOB,D,Z,IZ,WK,IER)
IJOB=0
DIFF=DABS(D(Y)-D(X))-HN
CALL INTENS(CENTER,Z,II,RESINT,X,Y)
DO 10 I=1,N
10 DO(I)=(D(I)-D(I))
KT=-TEMP*(1.38062259D-16)/DLA
DO 20 I=1,N
20 TF=TF+DEXP(DO(I)/KT)
TF=DABS(DEXP(DO(Y)/KT)-DEXP(DO(X)/KT))/TF
FRI=RESINT*TF
C THE ARRIVAL POINT IF IFLAG IS ZERO. CALL THE OUTPUT ROUTINE.
150 CALL OUTPUT(DR1,HR,X,Y,RESINT,DIFF,WK(I),TF,FRI)
100 CONTINUE
C PREPARE FOR NEXT (HIGHER) FIELD RANGE (PART TWO).
70 HL=HM
50 CONTINUE
RETURN
END
SUBROUTINE LINFIT(HM,HL,HR,N,E0,AS,X,Y,HN,DRI)
C THIS SUBROUTINE DOES THE ACTUAL LINEAR FIT TO THE ENERGY LEVELS
C AND CHECKS IF THERE IS A RESONANCE BETWEEN THE LOW FIELD, HL,
C AND THE HIGH FIELD, HM. ANY RESONANCE THAT IS FOUND IS RETURNED
C IN HR.
C THE OCCURRENCE OF TWO PARALLEL ENERGY LEVELS CAUSES AN APPROPRIATE
C MESSAGE TO BE PRINTED AND THE SUBROUTINE TO EXIT.
C
INITIALIZATION
C
REAL*8 AS(4), SLOPE, E0(4), HN, HM, HL, HR
INTEGER NUMB, X, Y, N, DRI
SLOPE = AS(Y) - AS(X)
NUMB = 0
IF (SLOPE.EQ.0.0) GO TO 110
GO TO 120
110 IF (DABS(DABS(E0(X) - E0(Y)) - HN).LT.1.0D-06) GO TO 130
C PUNT: I DO NOT KNOW WHAT TO DO.
WRITE (6,5) DRI, X, Y, HL, HM
HR = 0.0
RETURN
C COMPUTE THE POSITION OF RESONANCE.
120 HR = (HN - E0(Y) - E0(X))/SLOPE
C CHECK IF RESONANCE IS IN THE RANGE OF THE FIT (BETWEEN HL AND HM).
IF((HL.LE.HR).AND.(HR.LT.HM)) RETURN
HR = 0.
IF (NUMB.EQ.1) RETURN
HN = -HN
NUMB = 1
GO TO 120
130 HR = (HL + HM)/2.
RETURN
5 FORMAT (35H THE TOTAL SLOPE WAS ZERO FOR ANGLE, I3,
1 16H, BETWEEN LEVELS, I2,4H AND, I2,21H, FOR HL AND HM EQUAL,
2 F8.2,5H AND ,F8.2)
END
SUBROUTINE INTENSE(CENTER,Z,II,RESINT,X,Y)
C     THIS SUBROUTINE CALCULATES THE MATRIX ELEMENT BETWEEN THE TWO
C     LEVELS, X AND Y, AT THE FIELD OF RESONANCE, \( H_R \). IT USES THE
C     OPERATOR MATRIX, \( M \), TO INCLUDE THE GEOMETRIC EFFECTS WHICH ARE
C     PRESENT SINCE THE MICROWAVE MAGNETIC FIELD IS NOT PERPENDICULAR TO
C     THE Z-AXIS OF THE PARTICULAR CENTER.
C     THIS IS THE 4 X 4 VERSION APPROPRIATE TO A SPIN OF THREE HALVES
C
C     INITIALIZATION
C
COMPLEX*16 Z(4,4),M(4,4),CNORM
INTEGER X,Y
REAL*8 CENTER(6,10),RESINT,NORM,A,ZE,ONE,TWO,THRE
DATA ZE,ONE,TWO,THRE/0.000,1.000,2.000,3.000/
N=4
C     FIRST, NORMALIZE THE EIGENFUNCTIONS.
DO 50 I=1,N
      NORM=ZE
      DO 20 J=1,N
          NORM=NORM+DREAL(Z(J,I)*DCONJG(Z(J,I)))
      A=DSQRT(NORM)
      CNORM=DCMPLX(A,ZE)
      DO 10 J=1,N
          Z(J,I)=Z(J,I)/CNORM
      10 CONTINUE
C     NOW, SET UP THE OPERATOR MATRIX, \( M \).
DO 30 I=1,N
      DO 20 J=1,N
          M(I,J)=DCMPLX(ZE,ZE)
          M(1,1)=DCMPLX(THRE/TWO*CENTER(II,9),ZE)
          M(2,2)=DCMPLX(CENTER(II,9)/TWO,ZE)
          M(3,3)=-1.0*M(2,2)
          M(4,4)=-1.0*M(1,1)
          M(2,3)=DCMPLX(CENTER(II,3),-1.0*CENTE.(II,6))
          M(1,2)=M(2,3)*DSQRT(THRE)/TWO
          M(3,4)=M(1,2)
          M(3,2)=DCONJG(M(2,3))
          M(2,1)=DCONJG(M(1,2))
          M(4,3)=M(2,1)
C     NOW, FORM \( \langle X | H_I \cdot S | Y \rangle \)
      CNORM=DCMPLX(ZE,ZE)
      DO 40 I=1,N
      DO 40 I=1,N
          RESINT=RESINT+M(I,J)*Z(J,Y)*DCONJG(Z(I,X))
      40 CONTINUE
RETURN
END
SUBROUTINE AMATRIX(H,TH,PHI,M)
C
   THIS SUBROUTINE SETS UP THE 4 BY 4 MATRIX FOR S = 3/2 IN
C   HERMITIAN STORAGE MODE FOR PROPER INPUT TO THE IMSL LIBRARY
C   ROUTINE, EIGCH. THE AXIAL ZERO FIELD PARAMETER IS D. THE
C   MAGNETIC FIELD IS H AND THE ANGLES OF THE FIELD WITH RESPECT TO
C   THE PARTICULAR CENTER ARE TH AND PHI (SPHERICAL COORDINATES).
C   THE TWO G VALUES ARE GPA AND GPD AND THE RESULT IS THE VECTOR, M.
C
COMPLEX*16 M(10)
REAL*8 BETA,H,D,E,A,TH,PHI,GPA,GPD,HPDX,HPDY,HPA,
1   ZE,ONE,TWO,THRE
COMMON D,E,A,GPA,GPD,HN,N
DATA ZE,ONE,TWO,THRE/0.0000,1.0000,2.0000,3.0000/
BETA=9.274096D-21/D
HPA=GPA*BETA*H*DCOS(TH)
HPDX=GPD*BETA*H*DSIN(TH)*DCOS(PHI)
HPDY=GPD*BETA*H*DSIN(TH)*DSIN(PHI)
M(1)=DCMPLX(DSIGN(ONE,D)+THRE/TWO*HPA,ZE)
M(5)=DCMPLX(HPDX,HPDY)
M(2)=DCMPLX(DSQR(TWO,ZE)*M(5)
M(3)=DCMPLX(-1.0*DSIGN(ONE,D)+HPA/TWO,ZE)
M(4)=DCMPLX(ZE,ZE)
M(6)=DCMPLX(-1.0*DSIGN(ONE,D)-HPA/TWO,ZE)
M(7)=M(4)
M(8)=M(4)
M(9)=M(2)
M(10)=DCMPLX(DSIGN(ONE,D)-HPA*THRE/TWO,ZE)
RETURN
END

SUBROUTINE OUTPUT(NTH,H,I,J,RI,D,P,TF,FRI)
C
   THE DEFINITION OF PARAMETERS SHOULD BE OBVIOUS FROM THE FORMAT
C   STATEMENTS.
REAL*8 H,RI,D,P,TF,FRI
WRITE (6,1) NTH,I,J,H
IF (RI.EQ.0) RETURN
WRITE (6,2) RI,D,P,TF,FRI
RETURN
1 FORMAT (9H THETA IS ,2X,I2,3X,24HRESONANCE BETWEEN LEVELS,5X,I1,
1   5H AND ,I1,10X,3H AT,20X,-3PF10.6,1X,9HKILOGAUSS)
2 FORMAT (16X,40HTHE INTENSITY MATRIX ELEMENT Squared IS ,1PD11.4/
1   16X,21HPopulation factor IS ,D12.5,H AND ,
2   25HTHAT TIMES INTENSITY IS ,D12.5/THO)
END
Appendix D

Fortran Program for Isofrequency

Plots of an S=2 Spin Hamiltonian

ISOFREQUENCY PLOT PROGRAM


THE INPUT CARD HAS THE FORMAT:

(SPACE) $PARAM(SPACE) "DATA-NAME" = VALUE, ... $END


THE COMMA MUST BE DIRECTLY AFTER THE DATA VALUE (NO SPACE) FOR CORRECT INPUT.


THE SUBROUTINE, AMATRIX, SETS UP THE INPUT MATRIX FOR EIGCH. N IS THE NUMBER OF DIMENSIONS OF THE MATRIX THROUGHOUT THE PROBLEM.

BODY OF THE SOURCE PROGRAM FOR 5x5 ISOFREQUENCY PLOTS

INITIALIZATION
REAL*8 WK(45), TEMP, DIN, HIN, ACENT(6,10), COR(9),
        PI, HPLANK, BETA, CLITE, DLA, XX, YY, HN, GPA, GPD,
        CENTER(6,10), BGAMMA, BDELT A, GAMMA, DELTA
INTEGER N, N2, IFLAG, NCENT, NDATA, INCREM, DR, MA, FS
COMPLEX*16 A(15), Z(5,5)
COMMON DLA, XX, YY, GPA, GPD, HN, N, N2, MA, FS, II, DR, IFLAG,
        JJ, TEMP, CENTER
NAMELIST /PARAM/ IFLAG, TEMP, DIN, XX, YY, HIN, MA, FS, GPA, GPD
1 , BGAMMA, BDELT A
DATA HPLANK, CLITE / 6.626196D-27, 2.997928D10/
N=5
N2=N*(N+1)/2
PI=DARCOS(-1.0D00)
BGAMMA=0.0D00
BDELT A=0.0D00

C HERE STARTS THE INPUT OF THE DATA WHICH REMAINS FOR
C THE ENTIRE RUN.
READ(5,1) NCENT
DO 10 I=1, NCENT
READ(5,2) (ACENT(I,J), J=1, 10)
10 CENTER(I,1)=ACENT(I,1)
READ(5,1) NDATA

C NOW, START THE LOOP FOR THE INPUT AND SOLUTION OF EACH
C DATA SET.
DO 20 INCREM=1, NDATA
READ(5, PARAM)
WRITE(6,7) DIN, YY, XX, HIN, MA, FS, GPA, GPD, TEMP, BGAMMA,
        BDELT A

C CONVERT TO ENERGIES IN UNITS OF THE AXIAL ZERO FIELD
C ENERGY.
DLA=DIN*HPLANK*CLITE
HN=HN*HPLANK/DLA

C SET UP THE MISALIGNMENT ROTATION MATRIX.
GAMMA=PI*BDELT A/1.8D02
DELTA=PI*BGAMMA/1.8D02
COR(1)=DCOS(GAMMA)
COR(9)=DCOS(DELT A)
COR(2)=DSIN(GAMMA)*(1.0D0+COR(9))/2.0D0
COR(3)=DSIN(GAMMA)*DSIN(DELT A)/2.0D0
COR(4)=-1.0D0*C OR(2)
COR(5)=COR(1)*COR(9)
COR(6)=DSIN(DELT A)*(1.0D0+COR(1))/2.0D0
COR(7)=COR(3)
COR(8)=-1.0D0*C OR(6)

C NOW, BEGIN THE LOOP OVER THE EQUIVALENT CENTERS.
DO 30 II=1, NCENT

C CORRECT THE CENTERS FOR MISALIGNMENT.
CENTER(II,2)=COR(1)*ACENT(II,2)+COR(2)*ACENT(II,3)+
        COR(3)*ACENT(II,4)
CENTER(II,3)=COR(4)*ACENT(II,2)+COR(5)*ACENT(II,3)+
        COR(6)*ACENT(II,4)
CENTER(II,4)=COR(7)*ACENT(II,2)+COR(8)*ACENT(II,3)+
        COR(9)*ACENT(II,4)

30 CONTINUE
3 COR(9)*ACENT(I1, 4)
4 CENTER(I1, 5)=COR(1)*ACENT(I1, 5)+COR(2)*ACENT(I1, 6)
5 COR(3)*ACENT(I1, 7)
6 CENTER(I1, 6)=COR(4)*ACENT(I1, 5)+COR(5)*ACENT(I1, 6)+
7 COR(6)*ACENT(I1, 7)
8 CENTER(I1, 7)=COR(7)*ACENT(I1, 5)+COR(8)*ACENT(I1, 6)+
9 COR(9)*ACENT(I1, 7)

10 CENTER(I1, 8)=COR(1)*ACENT(I1, 8)+COR(2)*ACENT(I1, 9)+
11 COR(3)*ACENT(I1, 10)
12 CENTER(I1, 9)=COR(4)*ACENT(I1, 8)+COR(5)*ACENT(I1, 9)+
13 COR(6)*ACENT(I1, 10)
14 CENTER(I1, 10)=COR(7)*ACENT(I1, 8)+COR(8)*ACENT(I1, 9)+
15 COR(9)*ACENT(I1, 10)

16 \text{LA}=\text{CENTER(I1,1)}
17 \text{WRITE}(6,6)
18 \text{WRITE}(6,4)
19 \text{WRITE}(6,6)

\text{C}\quad \text{BEGIN THE LOOP FOR THE ANGLES, THETA, MEASURED FROM}
\text{C}\quad \text{THE \{100\} AXIS IN THE CRYSTAL.}
\text{C}
\text{DO 40 DR=1,91,10}
\text{CALL SEARCH}

\text{C}\quad \text{THE SUBROUTINE SEARCH SUBTRACTS ONE FROM THE VALUE OF}
\text{C}\quad \text{DR TO OBTAIN THETA, WHICH IS USED IN CALCULATION AND}
\text{C}\quad \text{OUTPUT. SEARCH FINDS ALL RESONANCES AT ANGLE, THETA,}
\text{C}\quad \text{AND OUTPUTS THE DATA.}
\text{C}
40 \text{CONTINUE}
30 \text{CONTINUE}
20 \text{CONTINUE}

\text{WRITE (6,99999)}
\text{STOP}

99999 \text{FORMAT(' END OF RUN! ')}
1 \text{FORMAT(I4)}
2 \text{FORMAT(4F20.17)}
4 \text{FORMAT(17H1CENTER INDEX IS ,I4)}
6 \text{FORMAT(1H0)}
7 \text{] FORMAT(34H1THE AXIAL ZERO FIELD SPLITTING IS,7X,F10.4,}
1 \quad 21H INVERSE CENTIMETERS/25H THE VALUE OF E OVER D}
2 \quad IS,16X,F10.4/}
3 \quad 25H THE VALUE OF A OVER D IS,16X,F10.4/}
4 \quad 27H THE MICROWAVE FREQUENCY IS,14X,-9PF10.6,}
5 \quad 11H GIGAHERTZ/}
6 \quad 30H THE MAXIMUM MAGNETIC FIELD IS,11X,I10,7H GAUSS/}
7 \quad 18H THE FIELD STEP IS,23X,I10,7H GAUSS/}
8 \quad 14H G PARALLEL IS,F10.6/19H G PERPENDICULAR IS,}
9 \quad F10.6/19H THE TEMPERATURE IS, F8.4/}
1 \quad 44H MISALIGNMENT ANGLES, GAMMA AND DELTA, ARE: ,}
2 \quad F10.3,5H AND ,F10.3,8H DEGREES/1H0)
\text{END}
SUBROUTINE SEARCH

C INITIALIZATION
1 REAL*8 PI, TH, SI, CO, PHI, DLA, XX, YY, HN, GPA, GPD, HM, HL, HR,
   SLOPE, DIFF, RESINT, CENTER(6, 10), TEMP, KT, FRI, TF
2 REAL*8 D(5), DL(5), AS(5), E0(5), WK(45), D0(5), E01(5),
   DB(5), SL(5), DT(5), HB, HT
3 COMPLEX*16 A(15), Z(5, 5)
4 INTEGER DR, MA, FS, X, Y, DRL
5 COMMON DLA, XX, YY, GPA, GPD, HN, N, N2, MA, FS, II, DR, IFLAG,
   JJ, TEMP, CENTER
IZ=N
IJOB=0
PI=DARCOS(-1.0D0)

C COMPUTE THE ANGLES APPROPRIATE TO THE SPIN HAMILTONIAN
C FROM CENTER DATA AND THETA.
1000 TH=(DR-1.)*PI/1.8D02
DRL=DR-1
SI=D.Sin(TH)
CO=DCos(TH)
TH=DARCOS(CENTER(II, 8)*SI+CENTER(II, 10)*CO)
PHI=DATAN2((CENTER(II, 5)*SI+CENTER(II, 7)*CO),
2 (CENTER(II, 2)*SI+CENTER(II, 4)*CO))

C BEGIN THE LOOP OVER THE FIELD VALUES.
HL=0.0D00
K=MA+1
DO 50 NHM=1,K,FS
HM=(NHM-1)

C AMATRIX SETS UP THE MATRIX AND EIGCH DIAGONALIZES IT.
CALL AMATRIX(HM, TH, PHI, A)
CALL EIGCH(A, N, IJOB, D, Z, IZ, WK, IER)

C THE FOLLOWING SECTION PERFORMS A LINEAR FIT TO SEARCH
C FOR RESONANCE.
IF (HM.EQ.HL) GO TO 190

C AS IS THE AVERAGE SLOPE OF EACH ENERGY LEVEL OVER THE
C INTERVAL
DO 80 X=1,N
80 AS(X)=(D(X)-DL(X))/(HM-HL)
C E0 (THAT IS ZERO) IS THE ENERGY EXTRAPOLATED TO H=0.
DO 90 X=1,N
90 E0(X)=DL(X)-AS(X)*HL
C PREPARE FOR THE NEXT (HIGHER) FIELD RANGE (PART ONE).
190 DO 160 X=1,N
160 DL(X)=D(X)
IF (HM.LE.HL) GO TO 70
C SET UP A LOOP OVER ALL PAIRS OF ENERGY LEVELS.
K3=N-1
DO 100 X=1,K3
K1=X+1
DO 100 Y=K1,N
CALL LINFIT(HM, HL, HR, N, E0, AS, X, Y, HN, DRL)
140 IF (HR.EQ.0.0) GO TO 100
C NOW, THE LINEAR FIT IS REPEATED OVER A REDUCED
C RANGE IN ORDER TO FINE TUNE THE EXACT VALUES FOR
C THE RESONANCE ONCE IT HAS BEEN FOUND.
HB=HR-2.5D01
HT=HR+2.5D01
CALL AMATRX(HB,TH,PHI,A)
CALL EIGCH(A,N,IJOB,DB,Z,IZ,WK,IER)
CALL AMATRX(HT,TH,PHI,A)
CALL EIGCH(A,N,IJOB,DT,Z,IZ,WK,IER)
DO 81 I=1,N
81  SL(I)=(DT(I)-DB(I))/(HT-HB)
   DO 91 I=1,N
91  E0(I)=DB(I)-SL(I)*HB
   CALL LINFIT(HT,HB,HR,N,E01,SL,X,Y,HN,DR1)
   RESINT=0.0
   IF (IFLAG.EQ.0) GO TO 150
C THIS SECTION DOES THE INTENSITY CALCULATION. IT IS
C SKIPPED IF IFLAG IS ZERO.
   DIFF=0.0
   TF=0.0
   FRI=0.0D00
   CALL AMATRX(HR,TH,PHI,A)
   IJOB=2
   CALL EIGCH(A,N,IJOB,D,Z,IZ,WK,IER)
   IJOB=0
   DIFF=DABS(D(Y)-D(X))-HN
   CALL INTENS(CENTER,Z,II,RESINT,X,Y)
   DO 10 I=1,N
10  D0(I)=(D(I)-D(1))
   KT=-TEMP*(1.3806D-16)/DABS(DLA)
   DO 20 I=1,N
20  TF=TF+DEXP(D0(I)/KT)
   TF=DABS(DEXP(D0(Y)/KT)-DEXP(D0(X)/KT))/TF
   FRI=RESINT*TF
C THE ARRIVAL POINT IF IFLAG IS ZERO. CALL THE OUTPUT
C ROUTINE.
150  CALL OUTPUT(DR1,HR,X,Y,RESINT,DIFF,WK(1),TF,FRI,IFLAG)
100  CONTINUE
C PREPARE FOR THE NEXT HIGHER FIELD RANGE (PART TWO).
70  HL=HM
50  CONTINUE
RETURN
END
SUBROUTINE LINFIT(HM,HL,HR,N,E0,AS,X,Y,HN,DR1)
REAL*8 AS(5),SLOPE, E0(5),HN,HM,HL,HR
INTEGER NUMB,X,Y,N,DR1
SLOPE=AS(Y)-AS(X)
NUMB=0
IF (SLOPE.EQ.0.0) GO TO 110
GO TO 120
110 IF (DABS(DABS(E0(X)-E0(Y))-HN).LT.1.D-06) GO TO 130
C PUNT; I DO NOT KNOW WHAT TO DO.
WRITE (6,5) DR1,X,Y,HL,HM
HR=0.0
RETURN
C COMPUTE THE POSITION OF RESONANCE. THEN, CHECK IF IT
C IS IN THE RANGE OF THE LINEAR FIT (BETWEEN HL AND HM).
120 HR=(HN-E0(Y)+E0(X))/SLOPE
IF ((HL.LE.HR).AND.(HR.LE.HM)) RETURN
HR=0.0
IF (NUMB.EQ.1) RETURN
HN=-HN
NUMB=1
GO TO 120
130 HR=(HL+HM)/2.
RETURN
5 FORMAT(35H THE TOTAL SLOPE WAS ZERO FOR ANGLE,I3,
1 16H BETWEEN LEVELS,I2,4H AND, I2,
2 21H FOR HL AND HM EQUAL,F8.2,5H AND ,F8.2)
END

SUBROUTINE OUTPUT(NTH,H,I,J,RI,D,P,TF,FRI,FL)
C THE DEFINITION OF THE PARAMETERS SHOULD BE OBVIOUS
C FROM THE FORMAT STATEMENTS.
REAL*8 H,RI,D,P,TF,FRI
INTEGER FL
WRITE (6,1) NTH,I,J,H
IF (FL.EQ.0) RETURN
WRITE (6,2) RI,D,P,TF,FRI
RETURN
1 FORMAT(9H THETA IS,2X,I2,3X,24H RESONANCE BETWEEN LEVELS
1, 5X,I1,5H AND ,I1,10X,3H AT,20X,-3PF10.6,1X,
2 9H KILOGAUSS)
2 FORMAT(16X,40H THE INTENSITY MATRIX ELEMENT SQUARED IS ,
1 1PD11.4/16X,15H HNU-(EF-EI) IS ,D11.4,5X,
2 29H THE PERFORMANCE INDEX IS ,D10.3/
3 16X,21H POPULATION FACTOR IS ,D12.5,5H AND,
4 25HTHAT TIMES INTENSITY IS ,D12.5/H0)
END
SUBROUTINE INTENS(CENTER,Z,II,RESINT,X,Y)
C THIS SUBROUTINE CALCULATES THE MATRIX ELEMENT
C BETWEEN TWO LEVELS AT THE FIELD OF RESONANCE, HR.
C IT USES THE OPERATOR MATRIX, M, TO INCLUDE THE
C GEOMETRIC EFFECTS WHICH ARE PRESENT SINCE THE MICROWAVE
C MAGNETIC FIELD IS NOT PERPENDICULAR TO THE Z-AXIS
C OF THE PARTICULAR CENTER.
C THIS IS THE 5x5 VERSION APPROPRIATE FOR A SPIN OF
C TWO.
C
C INITIALIZATION
C
COMPLEX*16 Z(5,5),M(5,5),CNORM
INTEGER X,Y
REAL*8 CENTER(6,10),RESINT,NORM,A,ZE,ONE,TWO,THRE
DATA ZE,ONE,TWO,THRE/0.0D0,1.0D0,2.0D0,3.0D0/
N=5
C FIRST, NORMALIZE THE EIGENFUNCTIONS
DO 50 I=1,N
NORM=0.0D0
DO 20 J=1,N
20 NORM=NORM+DREAL(Z(J,I)*DCONJG(Z(J,I)))
A=DSQRT(NORM)
CNORM=DCMPLX(A,ZE)
DO 10 J=1,N
10 Z(J,I)=Z(J,I)/CNORM
50 CONTINUE
C NOW, SET UP THE OPERATOR MATRIX, M.
DO 30 I=1,N
DO 30 J=1,N
30 M(I,J)=DCMPLX(ZE,ZE)
M(1,1)=DCMPLX(TWO*CENTER(II,9),ZE)
M(2,2)=DCMPLX(CENTER(II,9),ZE)
M(4,4)=-1.*M(2,2)
M(5,5)=-1.*M(1,1)
M(1,2)=DCMPLX(CENTER(II,3),CENTER(II,6))
M(2,3)=DSQRT(THRE/TWO)*M(1,2)
M(3,4)=M(2,3)
M(2,1)=DCONJG(M(1,2))
M(3,2)=DCONJG(M(2,3))
M(4,3)=DCONJG(M(3,4))
C NOW, FORM \( X! Hl \cdot S \cdot Y \)
CNORM=DCMPLX(ZE,ZE)
DO 40 I=1,N
40 CNORM=CNORM+M(I,J)*Z(J,Y)*DCONJG(Z(I,X))
RESINT=DREAL(CNORM*DCONJG(CNORM))
RETURN
END
SUBROUTINE AMATRX(H, TH, PHI, M)
C     THIS SUBROUTINE SETS UP THE 5 BY 5 MATRIX FOR S
C     EQUAL TO TWO IN HERMITIAN STORAGE MODE FOR PROPER
C     INPUT TO THE IMSL LIBRARY ROUTINE, EIGCH.  THE ZERO
C     FIELD PARAMETERS ARE D, E, AND A.  THE MAGNETIC FIELD
C     IS H AND THE ANGLES OF THE FIELD WITH RESPECT TO THE
C     PARTICULAR CENTER ARE TH AND PHI (SPHERICAL
C     COORDINATES).  THE TWO G VALUES ARE GPA AND GPD AND
C     THE RESULT IS THE VECTOR M.
COMPLEX*16 M(15)
REAL*8  BETA, H, D, E, A, TH, PHI, GPA, GPD, HPDX, HPDY, HPA,
1       ZE, ONE, TWO, THRE
COMMON  D, A, E, GPA, GPD, HN, N
DATA    ZE, ONE, TWO, THRE/1.0D0, 2.0D0, 3.0D0/
BETA=9.274906E-21/D
HPA=GPA*BETA*H*DCOS(TH)
HPDX=GPD*BETA*H*DSIN(TH)*DCOS(PHI)
HPDY=GPD*BETA*H*DSIN(TH)*DSIN(PHI)
M(1)=DCMPLX(TWO*HPA+DSIGN(TWO,D),ZE)
M(2)=DCMPLX(HPDX,HPDY)
M(3)=DCMPLX(HPA-DSIGN(ONE,D),ZE)
M(4)=DCMPLX(TWO*DSQRT(THRE)*E,ZE)
M(5)=DSQRT(THRE/TWO)*M(2)
M(6)=DCMPLX(-DSIGN(TWO,D),ZE)
M(7)=DCMPLX(ZE,ZE)
M(8)=DCMPLX(THRE*E,ZE)
M(9)=M(5)
M(10)=DCMPLX(-(HPA+DSIGN(ONE,D)),ZE)
M(11)=DCMPLX(A/TWO,ZE)
M(12)=M(7)
M(13)=M(4)
M(14)=M(2)
M(15)=DCMPLX(DSIGN(TWO,D)-TWO*HPA,ZE)
RETURN
END
References


56. Ventron Corporation, Magnion Division, 144 Middlesex Turnpike, Burlington, Mass.

57. Andonian Associates, 26 Thayer Road, Waltham, Mass.


59. IMSL, 7500 Bellaire Boulevard, Houston, Texas 77036.


