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ELECTRON PARAMAGNETIC RESONANCE OF
GADOLINIUM (III) IN CADMIUM
SULFIDE SINGLE CRYSTALS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
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School of The Ohio State University

By

Richard Rayner Schehl, B.S.

* * * * *

The Ohio State University
1969

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CHAPTER I

INTRODUCTION

The various forms of spectroscopy are based on the observation of transitions between energy levels of molecules, atoms, and nuclei. Numerous regions of the spectrum have been exploited for analytical purposes, and in each of them the interactions that occur in the emission or absorption of radiation of specific frequencies are in some manner characteristic of the matter involved.

Paramagnetic resonance is the phenomenon of inducing transitions among the energy levels of collections of electrons in a magnetic field. Paramagnetism is observed in systems of electrons which exhibit a resultant angular momentum such as (a) ions of the transition elements with partially filled inner shells; (b) atoms or molecules having an odd number of electrons; (c) conduction electrons in metals and semiconductors; and (d) compounds whose normal bonds have been modified or broken by irradiation or dislocation. The keen interest shown to paramagnetic resonance lies in the information that can be gleaned from it concerning interactions involving the individual paramagnetic ions and their neighbors in the 'crystalline' environment.

The first experimental observations of laboratory-induced transitions among electronic Zeeman levels were those of Zavoisky¹ in Russia reported in 1945 using 25-meter wavelength radiation. Subsequently Cumberow and Halliday² in the United States published a resonance of Mn^{++} in $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ at a frequency of 2930 MHz. Bagguley and Griffiths³ performed experiments at the Clarendon Laboratory on Cr^{3+} resonance in a chrome alum crystal at 3.18 cm wavelength in 1947 and there followed at the Clarendon Laboratory a fruitful period of research in which much of our present day understanding was established. The development of electron paramagnetic resonance is chronicled up to 1955 in Reports on Progress in Physics^{4, 5}. Moreover, several books, such as Low⁶, Pake⁷, Assenheim⁸, Townes and

¹E. Zavoisky, J. Phys. USSR, 9, 211 (1945)

²R. L. Cumberow and D. Halliday, Phys. Rev. 70, 433 (1946)

³D. M. S. Bagguley and J. H. E. Griffiths, Nature, 160, 532 (1947)

⁴B. Bleaney and K. W. H. Stevens, Repts. Progr. In Phys., 16, 108 (1953)

⁵K. D. Bowers and J. Owen, Repts. Progr. In Phys., 18, 304 (1955)

⁶W. Low, Paramagnetic Resonance in Solids, Academic Press, New York, (1960)

⁷G. E. Pake, Paramagnetic Resonance, W. A. Benjamin, Inc., New York, (1962)

⁸H. M. Assenheim, Introduction to Electron Spin Resonance, Hilger and Watts Ltd., London, (1966)

Schawlow⁹, and McMillan¹⁰ have recently appeared on this subject.

There has been considerable interest in the study of rare earth ions in semiconducting II-VI crystals throughout the past decade. In particular the S-state ions have been investigated in some detail in CdSe, CdS, and CdTe. Gd^{3+} was observed in CdTe and CdSe by Title¹¹ in 1965. Title¹² examined Eu^{++} in CdTe and Eu^{++} was further investigated in CdS by Dorain¹³ and CdSe by Title¹². Ludwig and Ham¹⁴ have reported observations of Gd^{3+} and Eu^{++} in CdS but their study consisted only of the effect of static electric fields on the crystalline field splitting.

Much work also has been done with the non S-state ions such as Nd^{3+} , Dy^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} . Nd^{3+} was studied in CdS by Morigaki¹⁵. In addition, spin resonance

⁹C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, (1955)

¹⁰J. A. McMillan, Electron Paramagnetism, Reinhold, New York, (1963)

¹¹R. S. Title, Phys. Rev. 138, A631 (1965)

¹²R. S. Title, Phys. Rev. 133, A198 (1964)

¹³P. R. Dorain, Phys. Rev. 120, 1190 (1960)

¹⁴G. W. Ludwig and F. S. Ham, Paramagnetic Resonance, ed. W. Low (Academic Press, New York, 1963) pp.620-627

¹⁵K. Morigaki, J. Phys. Soc. Japan, 18, 1636 (1963)

studies by Watts and Holton^{16, 17, 18} have been performed on Dy^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} in the wurtzite structure of CdS and CdSe and zinc-blend structure of ZnSe, ZnTe, and CdTe.

Until recently, spectroscopy of rare earths in crystals was of interest to only a few specialists. However, Physicists and chemists have learned that a great deal of information about the fundamental structure of the solid state may be gleaned from the behavior of rare earth probes in crystalline lattices¹⁹. The more favorable conditions for the study of rare earths, created by their greater availability (with the exception of promethium, an artificial element and highly radioactive), were probably the principal reasons for the increased activity in this field. Another stimulus came from the invention of the laser in 1960, which created a practical interest in properties of the rare earth doped crystals for their potential use in lasers.

¹⁶R. K. Watts and W. C. Holton, Phys. Rev., 173, 417 (1968)

¹⁷R. K. Watts and W. C. Holton, Phys. Rev. Letters, 24A, 365 (1967)

¹⁸R. K. Watts, Solid State Communications, 4, 549 (1966)

¹⁹G. H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals, J. Wiley & Sons, New York, (1968)

The present work is the first step in a detailed study of the rare earths in cadmium sulfide crystals. These crystals were prepared by Professor William Anderson and Dexter Girton of the Electrical Engineering Department at the Ohio State University. A brief analysis of the sample preparation technique will be given in CHAPTER III.

Luminescence spectra, under the direction of Professor Anderson, have been accumulated on the rare earths in CdS and it seems to indicate that the sites responsible for the optical spectra may not be the sites responsible for the EPR spectra. That is, the luminescence spectra appear to be consistent with the transitions of the rare earth ion associated with a near neighbor defect or a substitutional site while the EPR spectra, appearing in the literature to date, display the symmetry of the cation site.

The present work is limited to the electron paramagnetic resonance study of triply ionized gadolinium in a cadmium sulfide host at 2°K, 77°K, and 300°K at various crystal orientations. The principal objective of the dissertation is the experimental determination of the parameters found in the spin Hamiltonian.

CHAPTER II

THEORY

1. The electron paramagnetic spectrum

The application of a magnetic field $\underline{B}$ to an isolated electron produces an interaction energy of amount $-\underline{\mu} \cdot \underline{B}$. $\underline{\mu}$ is the magnetic moment of a free electron and may be related to the electron spin angular momentum $\underline{S}$ by $\underline{\mu} = -g\beta \underline{S}$, where g is the spectroscopic splitting factor and β is the Bohr magneton. This interaction is described by the very simple Hamiltonian $H = g\beta \underline{B} \cdot \underline{S}$.

The eigenvalues of the Schrodinger equation, $H\psi = g\beta \underline{B} \cdot \underline{S}\psi = E\psi$, are $E = g\beta BM_s$, where the M_s are the magnetic quantum numbers $\pm\frac{1}{2}$. Thus, for a free electron, there are two Zeeman levels as illustrated below.

Figure 1. Energy level diagram of a free electron in a Magnetic field.

If the one electron system is irradiated with photons whose frequency satisfies the relation $h\nu = E_{+\frac{1}{2}} - E_{-\frac{1}{2}}$, then transitions are induced between these energy levels.

In any physical situation, paramagnetic ions contain many such electrons and the relative population⁹ of the energy levels clearly depends on the temperature, T . If the electrons are in thermal equilibrium with the lattice²⁰ the population ratio $N_{+\frac{1}{2}}/N_{-\frac{1}{2}}$ is given by Maxwell-Boltzmann's statistics as

$$N_{+\frac{1}{2}}/N_{-\frac{1}{2}} = \exp(-(E_{+\frac{1}{2}} - E_{-\frac{1}{2}})/kT)$$

if $E_{+\frac{1}{2}} - E_{-\frac{1}{2}} \ll kT$, where $N_{\pm\frac{1}{2}}$ are the number of electrons in the states $M_s = \pm\frac{1}{2}$ respectively, k is Boltzmann's constant, and T is the absolute temperature.

Electrons promoted from $E_{-\frac{1}{2}}$ to $E_{+\frac{1}{2}}$ relax by their interaction with the lattice (spin-lattice relaxation) through which they return to the lower level by a radiationless process. Thus, a steady absorption of photons from the incident rf field may take place. At the same time, a finite spin-lattice relaxation time, which increases with decreasing temperature, limits the power fed into the sample; otherwise, saturation⁶ would occur. In other words, if the power fed to the sample is such that the rate at

²⁰C. P. Slichter, Principles of Magnetic Resonance, New York, (1963)

which they can return to the lower level by the spin-lattice mechanism and both levels are soon equally populated. Accordingly, the net absorption of rf power approaches zero.

Perhaps a more lucid approach to the understanding of the relaxation processes may be made through the phenomenological equations of Bloch²¹. Bloch introduced a set of equations to typify nuclei, however, the physical considerations underlying the equations apply to both nuclei and electrons.

If the magnetization $\underline{M}$ is defined as

$$\underline{M} = \sum_{\text{unit vol.}} \underline{\mu}_i$$

the equations of Bloch in the laboratory reference frame are:

$$dM_x/dt = \gamma (\underline{B} \times \underline{M})_x - M_x/T_2 \quad (2-2)$$

$$dM_y/dt = \gamma (\underline{B} \times \underline{M})_y - M_y/T_2 \quad (2-3)$$

$$dM_z/dt = \gamma (\underline{B} \times \underline{M})_z + (M_0 - M_z)/T_1 \quad (2-4)$$

where γ is the 'gyromagnetic' ratio and M_0 is the value of the magnetization in thermal equilibrium. T_1 is known as the spin-lattice relaxation time and is a measure of the characteristic time required for the z component of $\underline{M}$ to reach the equilibrium value. T_2 is called the spin-spin relaxation time and is the characteristic time for

²¹F. Bloch, Phys. Rev. 70, 460 (1946)

the decay of the transverse components of the magnetization. The transverse rate of decay may differ from the longitudinal. In contrast to the longitudinal decay, the transverse decay conserves energy in the static field.

Bloch's equations provide a convenient, classical approach to paramagnetism, although their utility is limited. In the case at hand, of course, one is not dealing with isolated electrons, or even free radicals^{22, 7}, but with paramagnetic ions under the influence of a crystalline electric field. In order to understand more fully the processes involved, it is necessary to examine the system from a quantum mechanical viewpoint. The Hamiltonian describing such a system may be written in the form

$$H = T + V_C + V_Z + V_{SO} + V_{SS} + V_{SI} + V_X \quad (2-5)$$

where

$$T = \sum_k (p_k^2 / 2m_e)$$

is the kinetic energy of the electrons. p_k is the momentum of the k^{th} electron and m_e is the electronic mass.

The coulomb term, V_C , can be defined by

$$V_C = -\sum_k Ze^2/r_k + \sum_{ij} e^2/r_{ij} \quad (2-6)$$

The first term in (2-6) is the coulomb attraction between the nucleus with charge $+Ze$ and the atomic electrons,

²²J. A. Lyons and W. F. Watson, J. Polymer Sci., 18, 141 (1955)

where the summation index, k , runs over all electrons. The second term is the coulombic repulsion between all pairs of electrons (i, j) .

The third term V_Z , the Zeeman energy, can be written, for the moment, as

$$V_Z = \beta(\underline{L} + g_e \underline{S}) \cdot \underline{B} \quad (2-7)$$

where $\underline{L} = \sum_i \underline{l}_i$, with $\underline{l}_i$ the orbital angular momentum of the i^{th} electron, and $\underline{S} = \sum_i \underline{s}_i$, with $\underline{s}_i$ the spin angular momentum of the i^{th} electron. g_e is the spectroscopic splitting factor for a free electron.

V_{SO} is the potential energy due to the spin-orbit coupling, and is written

$$V_{SO} = \sum_{i,j} \lambda_{ij} \underline{l}_i \cdot \underline{s}_j \quad (2-8)$$

where i and j range over all electrons. If one assumes Russell-Saunders coupling, then as in (2-7)

$$\sum_i \underline{l}_i = \underline{L} \text{ and } \sum_i \underline{s}_i = \underline{S}$$

The vectors $\underline{L}$ and $\underline{S}$ couple to give the total angular momentum

$$\underline{J} = \underline{L} + \underline{S}$$

and (2-8) then takes the form

$$V_{SO} = \Lambda \underline{L} \cdot \underline{S}$$

where Λ is the spin-orbit coupling constant.

The fifth term in (2-5) represents the magnetic dipole-dipole interaction between the electrons and is written as

$$V_{SS} = \sum_{jk} (1/r_{jk}^3) (\underline{s}_j \cdot \underline{s}_k - 3 \underline{s}_j \cdot \underline{r}_{jk} \underline{r}_{jk} \cdot \underline{s}_k / r_{jk}^2). \quad (2-9)$$

Once again, the sum extends over all pairs of electrons. Equation (2-9) may be obtained by substituting the spin vectors $\underline{S}_j$ and $\underline{S}_k$ into the familiar expression for the interaction between a collection of magnetic moments.

The term V_{SI} is the magnetic interaction between unpaired electrons and the nuclear magnetic moments of the same atom. This interaction is usually referred to as the hyperfine interaction. There are two terms included in V_{SI} ; an isotropic Fermi contact interaction that depends on the electron density at the nucleus, and an anisotropic portion similar to (2-9), but between electrons and nuclei. The Fermi term depends on the s-admixture of the electronic state and is proportional to

$$g_e g_n \beta_e \beta_n (8\pi/3) \delta(\underline{r}_k) \underline{S}_k \cdot \underline{I}_j \quad (2-10)$$

where g_n and β_n are the nuclear g-factor and magneton, $\underline{I}_j$ is the nuclear spin vector operator, $\underline{r}_k$ is the position vector of the k^{th} electron relative to the j^{th} nucleus, and $\delta(\underline{r}_k)$ is the Dirac function.

Finally, the last term, V_X , represents the interaction of the paramagnetic ion with the crystal field due to its environment. V_X may be written as

$$V_X = -\sum_k e_k \phi(\underline{r}_k) \quad (2-11)$$

where the summation is extended over all electrons. In the ensuing discussion it will be found that for this work the crystal field interaction is the most important

contribution to the Hamiltonian in that it yields information concerning the surroundings of the paramagnetic ions.

In the iron group, the relative order of magnitude of these terms⁸ for a typical paramagnetic ion in units of cm^{-1} is: $V_C=10^5$, $V_Z=10^0$, $V_{SO}=10^2$, $V_{SS}=10^0$, $V_{SI}=10^{-2}$, and $V_X=10^3$. For the rare earth group these terms are usually approximately as follows: $V_C=10^5$, $V_Z=10^0$, $V_{SO}=10^3$, $V_{SS}=10^0$, $V_{SI}=10^{-2}$, and $V_X=10^2$.

The energy levels, which are studied via microwave transitions, depend in a complicated manner upon the particular paramagnetic ion involved, the spin-orbit coupling, the strength and symmetry of the crystalline electric field, the hyperfine interaction, and other possible interactions. In this case the terms T and V_C may be omitted as they ordinarily remain constant. The Hamiltonian as stated in (2-5) is obviously very complicated and its use in explaining the experimental spectrum is quite limited. However, Pryce²³ and Abragam and Pryce²⁴ have developed a useful method for carrying out perturbation calculations on the energy levels and have applied this especially to the iron group. Elliott and Stevens²⁵ have derived a

²³H. M. L. Pryce, Proc. Phys. Soc. A63, 25 (1950)

²⁴A. Abragam and H. M. L. Pryce, Proc. Roy. Soc. A205, 135 (1951)

²⁵R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. A218, 553 (1953)

similar method for the rare earth group. Before giving the formal derivation of the spin Hamiltonian, it would be illuminating to indicate the physical reasoning behind it.

The various orbital levels of a paramagnetic ion in a crystalline field environment are split by the crystal field. Additional splitting may be induced by the spin-orbit interaction. If the Hamiltonian were diagonalized, taking into account the terms V_X and V_{SO} , the energy levels would be a mixture of the various orbital and spin functions of the free ion. This procedure is very complicated though it has been used for various ions of the iron group by Van Vleck²⁶, Schlapp and Penney²⁷, Seigert²⁸, Polder²⁹, and others.

In the phenomenon of paramagnetic resonance, transitions between the lowest energy levels are observed due to the fact that higher levels are not significantly populated. Accordingly, the levels between which transitions occur may be treated as isolated levels and it is possible to neglect higher lying levels, even though their effect on

²⁶J. H. Van Vleck, Phys. Rev. 41, 208 (1932)

²⁷R. Schlapp and W. G. Penney, Phys. Rev. 42, 666 (1932)

²⁸A. Seigert, Physica 4, 138 (1937)

²⁹D. Polder, Physica 9, 709 (1942)

the ground states may be considerable. A state of quantum number J , in the case of a free ion, splits into $2J+1$ levels in an external magnetic field, hence, if transitions between $2S'+1$ levels are observed experimentally, one may define S' as the effective spin of the system. The $2S'+1$ levels may be treated as if they originated from a fictitious state S' for which the magnetic dipole has $2S'+1$ possible orientations. The effective magnetic moment of this dipole is not given by the Lande g factor, or spectroscopic splitting factor, but by a g factor which may differ considerably from that of a free electron.

Griffith³⁰, Pake⁷, and Assenheim⁸ present treatments of the spin Hamiltonian in brief form and the following discussion is designed to give a cursory outline of the development of the spin Hamiltonian, pertinent to the work in this dissertation, and will follow, in essence, the presentation of Low⁶. Terms that might ordinarily be quite essential in the Hamiltonian in order to describe the experimental observations, such as a term describing the electrostatic interaction with the quadrupole moment of the nucleus and the direct interaction of the nucleus with the external field $\underline{B}$, $-g_n \beta_n \underline{B} \cdot \underline{I}$, are not included in the discussion as they do not contribute significantly in this problem.

³⁰J. S. Griffith, The Theory of Transition Metal Ions, Cambridge University Press (1961)

It is first necessary to transform the various terms in the Hamiltonian (2-5) into the appropriate angular momentum operators $\underline{L}$, $\underline{S}$, and $\underline{J}$ with the restriction that $\underline{L}$ and $\underline{S}$ are considered constant within the manifold $\underline{J}$.

The constituent terms then transform as follows:

$$V_{SO} \rightarrow \lambda \underline{L} \cdot \underline{S}$$

$$V_{SS} \rightarrow \rho ((\underline{L} \cdot \underline{S})^2 + \frac{1}{2}(\underline{L} \cdot \underline{S}) - (1/3)L(L+1)S(S+1))$$

$$\rightarrow \rho (\frac{1}{2}(L_i L_j + L_j L_i) S_i S_j - (1/3)L(L+1)S(S+1))$$

where ρ is a proportionality constant, and i, j are x, y, z .

$$\begin{aligned} V_{SI} \rightarrow & (2\gamma\beta/r^3)((\underline{L} \cdot \underline{I}) + \xi L(L+1)(\underline{S} \cdot \underline{I}) \\ & - (3/2)\xi(\underline{L} \cdot \underline{S})(\underline{L} \cdot \underline{I}) - (3/2)\xi(\underline{L} \cdot \underline{I})(\underline{L} \cdot \underline{S}) \\ & - (2\gamma\beta\kappa/r^3)\delta(\underline{r})(\underline{S} \cdot \underline{I})) \end{aligned}$$

where, again, ξ is a constant and dependent upon L, S , and L . Moreover,

$$V_Z = \beta \underline{B} \cdot (\underline{L} + 2\underline{S})$$

where g_e has been set equal to two. As afore mentioned, T and V_C are taken to be constant and accordingly omitted. Discussion of the term V_X , the effect of the crystalline electric field will be taken up in a later section as it warrants a more thorough development.

Letting $P=2\gamma\beta/r^3$ and collecting all of the above perturbations the Hamiltonian reduces to⁶

$$\begin{aligned} H = & (\lambda - \frac{1}{2}\rho)(\underline{L} \cdot \underline{S}) - \rho(\underline{L} \cdot \underline{S})^2 + \beta \underline{B} \cdot (\underline{L} + 2\underline{S}) + P((\underline{L} \cdot \underline{I}) + \\ & (\xi L(L+1) - \kappa)(\underline{S} \cdot \underline{I}) - (3/2)\xi(\underline{L} \cdot \underline{S})(\underline{L} \cdot \underline{I}) - (3/2)\xi(\underline{L} \cdot \underline{I})(\underline{L} \cdot \underline{S})) \end{aligned}$$

First order perturbation theory is applied to this Hamiltonian under the assumption that there exists a nondegenerate ground state. The first order perturbation, given by the diagonal elements, gives only energy values in operators which do not contain $\underline{L}$ since $\langle 0 | \underline{L} | 0 \rangle = 0$. This is known as 'quenching' of the orbital angular momentum and occurs if the ground state is nondegenerate. Thus, terms like $2\beta \underline{B} \cdot \underline{S}$, $-P(\kappa \delta_{ij} + 3\zeta l_{ij}) S_i I_j$, and $\rho l_{ij} S_i S_j$, where $l_{ij} = \langle 0 | L_i L_j + L_j L_i | 0 \rangle$, are obtained.

The second order calculation necessitates the use of

$$\sum_{n \neq 0} \frac{\langle 0 | H' | n \rangle \langle n | H' | 0 \rangle}{E_n - E_0}$$

where n refers to the orbital levels 1, 2, 3, ...n.

By defining the tensor

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}$$

and neglecting terms in ρ^2 and P^2 which are usually very small, the spin Hamiltonian takes the form

$$H_S = 2\beta(\delta_{ij} - \Lambda_{ij}) B_i S_j + (-\lambda^2 \Lambda_{ij} - l_{ij}) S_i S_j - P(\kappa \delta_{ij} + 3\zeta l_{ij} + 2\lambda \Lambda_{ij}) S_i I_j$$

This Hamiltonian may be further simplified, according to Assenheim⁸

$$H_S = \beta \underline{B} \cdot \underline{g} \cdot \underline{S} + \underline{S} \cdot \underline{D} \cdot \underline{S} + A \underline{I} \cdot \underline{S}$$

when it is assumed that the hyperfine interaction is isotropic. $\underline{g}$ and $\underline{D}$ in general are tensors of rank two.

Furthermore, specialization to the case of a crystalline field of axial symmetry and an isotropic Zeeman interaction

simplifies the spin Hamiltonian to the form

$$H_S = g\beta \underline{B} \cdot \underline{S} + D(S_z^2 - (1/3)S(S+1)) + A \underline{I} \cdot \underline{S} \quad (2-12)$$

The problem of representing the crystal field potential, V_X , and of calculating the matrix elements poses no obstacle. The potential in question arises from all the other ions in the vicinity of the paramagnetic ion. The surrounding ions, playing a passive role, are considered to be point charges that do not overlap the paramagnetic ion. Therefore, the electrostatic potential obeys Laplace's equation, $\nabla^2 V_X = 0$, and the solutions are the spherical harmonics. The potential may then be expanded in terms of the harmonics

$$V_X = \sum_n \sum_{m=-n}^n \sum_k A_n^m r^n Y_n^m(\theta_k, \phi_k)$$

where the summation, k , is over all electrons. In the case of the rare earths, where the unfilled shell consists of f electrons, the index n ranges only to six (for the iron group, with $l=2$, n ranges only to four). If the Wigner-Eckart theorem is invoked it is obvious that matrix elements with $n > 2l$ vanish. The wave functions of the electrons can also be expanded in the harmonic functions $\psi_1^i \sim R(r_k) Y_1^i(\theta_k, \phi_k)$. Therefore, all terms with odd n must vanish due to the fact that the product $\psi_1^{i*} \psi_1^i$ is left unchanged by inversion symmetry, whereas the potential changes sign thus causing the matrix element to vanish. The term

$n=0$ in the expansion is a constant and hence shifts all the levels of a given electronic configuration by an equal amount.

The matrix elements of the crystal field potential, expressed in terms of the harmonics, could now be easily calculated with the aid of the Wigner Coefficients, C_{mm}^J . However, it is much more useful to expand the potential in terms of the cartesian coordinates of the electrons of the paramagnetic ion. For C_{3h} symmetry, the potential can be written as³¹

$$\begin{aligned} V_{3h} = & A_2^0(3z^2 - r^2) + A_4^0(35z^4 - 30r^2z^2 + 3r^4) \\ & + A_6^0(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6) \\ & + A_6^6(x^6 - 15x^4y^2 + 15x^2y^4 - y^6) \end{aligned} \quad (2-13)$$

For C_{3v} symmetry the potential of the crystalline electric field is⁶

$$\begin{aligned} V_{3v} = & A_2^0(3z^2 - r^2) + A_4^0(35z^4 - 30r^2z^2 + 3r^4) \\ & + A_4^3(z)(x^3 - 3xy^2) + A_6^0(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6) \\ & + A_6^3(11z^3 - 3zr^2)(x^3 - 3xy^2) \\ & + A_6^6(x^6 - 15x^4y^2 + 15x^2y^4 - y^6) \end{aligned} \quad (2-14)$$

Stevens³¹ and Judd³² have developed a method that utilizes the operator equivalent method which facilitates the calculation of the matrix elements. The method is to replace x , y , and z in the potential functions by J_x , J_y ,

³¹K. W. H. Stevens, Proc. Phys. Soc. A65, 209 (1952)

³²B. Judd, Proc. Roy. Soc. (London) A227, 552 (1955)

and J_z . The latter are angular momentum operators for manifolds of constant J .

Taking proper account of the commutation rules of these operators, the functions in the coordinate representation transform, in the notation used by Baker, Bleaney, and Hayes³³ as indicated in TABLE 1.

TABLE 1
OPERATOR EQUIVALENTS INSIDE A MANIFOLD FOR WHICH S IS
CONSTANT

$\sum (3z^2 - r^2) = \alpha \bar{r}^2 (3S_z^2 - S(S+1))$
$\sum (35z^4 - 30r^2 z^2 + 3r^4) = \beta \bar{r}^4 (35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2)$
$\sum z(x^3 - 3xy^2) = \frac{1}{4} \beta \bar{r}^4 (S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z)$
$\sum (231z^6 - 315r^2 z^4 + 105r^4 z^2 - 5r^6) = \gamma \bar{r}^6 (231S_z^6 - 315S(S+1)S_z^4 + 735S_z^4 + 105S^2(S+1)^2S_z^2 - 525S(S+1)S_z^2 + 294S_z^2 - 5S^3(S+1)^3 + 40S^2(S+1)^2 - 60S(S+1))$
$\sum (11z^3 - 3r^2)(x^3 - 3xy^2) = \frac{1}{4} \gamma \bar{r}^6 ((11S_z^3 - 3S(S+1)S_z - 59S_z) \times (S_+^3 + S_-^3) + (S_+^3 + S_-^3)(11S_z^3 - 3S(S+1)S_z - 59S_z))$
$\sum (x^6 - 15x^4 y^2 + 15x^2 y^4 - y^6) = \frac{1}{2} \gamma \bar{r}^6 (S_+^6 + S_-^6)$

³³J. M. Baker, B. Bleaney, F. R. S. and W. Hayes, Proc. Roy. Soc. (London) A247, 141 (1958)

The spin operators listed in TABLE 1 are generally assigned the notation as given in TABLE 2. It seems that this is now a rather standard notation. Articles appearing in the literature before 1957-1958 used the symbol P_n^m for the operator equivalents. The use of O_n^m avoids the confusion where the symbol P_n^m has been used for these operator equivalents as well as for Legendre polynomials. As the two functions do not have the same angular dependence, the latter functions being axially symmetric and the former not necessarily so, there is no justification for using the same symbol.

TABLE 2
NOTATION USED FOR THE OPERATOR EQUIVALENTS

$$O_2^0 = 3S_z^2 - S(S+1)$$

$$O_4^0 = 35S_z^4 - (30S(S+1) - 25)S_z^2 - 6S(S+1) + 3S^2(S+1)^2$$

$$O_4^3 = \frac{1}{2}(S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z)$$

$$O_6^0 = 231S_z^6 - 105(3S(S+1) - 7)S_z^4 + (105S^2(S+1)^2 - 525S(S+1) + 294)S_z^2 - 5S^3(S+1)^3 + 40S^2(S+1)^2 - 20S(S+1)$$

$$O_6^3 = \frac{1}{4}((11S_z^3 - 3S(S+1)S_z - 59S_z)(S_+^3 + S_-^3) + (S_+^3 + S_-^3)(11S_z^3 - 3S(S+1)S_z - 59S_z))$$

$$O_6^6 = \frac{1}{2}(S_+^6 + S_-^6)$$

Hence, combining the crystalline field given by (2-13) with the other terms of importance in the Hamiltonian, (2-12), it is found that the most general Hamiltonian for C_{3h} symmetry is

$$H = g\beta \underline{B} \cdot \underline{S} + B_2^0 U_2^0 + B_4^0 U_4^0 + B_6^0 U_6^0 + B_6^6 O_6^6 + A \underline{I} \cdot \underline{S} \quad (2-15)$$

Similarly, for C_{3v} symmetry the Hamiltonian may be written, with the aid of (2-12) and (2-14)

$$H = g\beta \underline{B} \cdot \underline{S} + B_2^0 U_2^0 + B_4^0 U_4^0 + B_4^3 O_4^3 + B_6^0 U_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6 + A \underline{I} \cdot \underline{S} \quad (2-16)$$

In order to avoid the use of large numbers, it is customary to redefine the parameters found in the spin Hamiltonian as follows:

$$\begin{aligned} b_2^0 &= 3B_2^0, & b_4^0 &= 60B_4^0, & b_6^0 &= 1260B_6^0, \\ b_4^3 &= 3B_4^3, & b_6^3 &= 36B_6^3, & b_6^6 &= 1260B_6^6 \end{aligned}$$

The electronic configuration of gadolinium in its ground state is $(Xe)4f^7 5d^1 6s^2$. If gadolinium is triply ionized, the valence electrons are the two 6s electrons and the 5d electron. Thus, the electronic configuration of the ion, Gd^{3+} , is $4f^7$ which leaves the 4f shell half filled and, according to Hund's rules³⁴, results in a ground state of $^8S_{7/2}$.

The effective spin to be used in our Hamiltonian is, therefore, 7/2. As the ground state of the para-

³⁴J. H. Van Vleck, Electric and Magnetic Susceptibilities, Oxford University Press, New York, (1932)

magnetic ion under investigation is such that $L=0$ (S-state ion), it is justifiable to use only the Fermi contact term in the hyperfine portion of the Hamiltonian. Moreover, the g tensor in the Zeeman term is isotropic for this type of ground state. The above simplifications were justified by the experimental results.

The hyperfine splitting constant, A , was found to be so small experimentally that the splitting of the fine structure lines was not resolved. Therefore, in the subsequent development of the energy levels, discussion of the hyperfine interaction will be deleted.

Matrix elements for the operator equivalents appearing in the Hamiltonians (2-15) and (2-16) are found in the literature^{23, 24, 25}. With their aid Schroedinger's equation for the Hamiltonian H_{3h} may be written

$$(H_{3h})_{ij}(\psi)_j = (E)_{ij}(\psi)_j$$

which gives rise to a secular determinant characteristic of this Hamiltonian. The magnetic field, $\underline{B}$, is taken to be parallel to the c axis of the crystal.

The Zeeman term in the Hamiltonian (at a frequency of 23 GHz) is much larger than the crystal field energy. Accordingly, the eigenvalues of the Hamiltonian may be calculated utilizing perturbation techniques. The zeroth order Hamiltonian is taken to be $g\beta \underline{B} \cdot \underline{S}$, the Zeeman term, and the crystal field is considered a perturbation.

The equations for the energy levels, to second order perturbation, are listed on TABLE 3 for C_{3h} symmetry and on TABLE 4 for C_{3v} symmetry. From the expressions for the energy levels on TABLE 3 and TABLE 4, the relations for the transition energies may be obtained. It is the usual procedure to maintain a constant rf frequency and vary the magnetic field, B , to sweep through the resonance lines. Therefore, the method is to set the energy difference between two levels equal to $h\nu$ and solve for B . Hence, the appropriate expressions may be developed for the values of magnetic field strength at which transitions will occur for given values of the parameters found in the spin Hamiltonians (TABLES 5 and 6).

It will be noticed that if second order effects arising from terms in b_4^3 , b_6^3 , and b_6^6 are neglected in the expressions for magnetic field strengths, B_M , then the transitions are equally spaced about the $M_S = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. In addition, the second order effects are equal in sign and magnitude for the corresponding symmetrical transitions. Hence, taking the difference between corresponding lines on either side of the $M_S = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition one arrives at three simultaneous equations in b_2^0 , b_4^0 , and b_6^0 .

$$g\beta \Delta B_1 = 12b_2^0 + 40b_4^0 + 12b_6^0$$

TABLE 3

EXPRESSIONS FOR THE ENERGY LEVELS OF A SPIN 7/2 ION IN
 C_{3h} SYMMETRY WITH $\underline{B}$ PARALLEL TO THE C AXIS

$$E_{7/2} = (7/2)g\beta B + 7b_2^0 + 7b_4^0 + b_6^0 + 7(b_6^6)^2/6g\beta B$$

$$E_{5/2} = (5/2)g\beta B + b_2^0 - 13b_4^0 - 5b_6^0 + 7(b_6^6)^2/6g\beta B$$

$$E_{3/2} = (3/2)g\beta B - 3b_2^0 - 3b_4^0 + 9b_6^0$$

$$E_{1/2} = (1/2)g\beta B - 5b_2^0 + 9b_4^0 - 5b_6^0$$

$$E_{-1/2} = (-1/2)g\beta B - 5b_2^0 + 9b_4^0 - 5b_6^0$$

$$E_{-3/2} = (-3/2)g\beta B - 3b_2^0 - 3b_4^0 + 9b_6^0$$

$$E_{-5/2} = (-5/2)g\beta B + b_2^0 - 13b_4^0 - 5b_6^0 + 7(b_6^6)^2/6g\beta B$$

$$E_{-7/2} = (-7/2)g\beta B + 7b_2^0 + 7b_4^0 + b_6^0 + 7(b_6^6)^2/6g\beta B$$

TABLE 4

EXPRESSIONS FOR THE ENERGY LEVELS OF A SPIN 7/2 ION IN
 C_{3v} SYMMETRY WITH $\underline{B}$ PARALLEL TO THE C AXIS

$$E_{7/2} = (7/2)g\beta B + 7b_2^0 + 7b_4^0 + b_6^0 + 140(b_4^3 + b_6^3)^2/3g\beta B \\ + 7(b_6^6)^2/6g\beta B$$

$$E_{5/2} = (5/2)g\beta B + b_2^0 - 13b_4^0 - 5b_6^0 + 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ + 7(b_6^6)^2/6g\beta B$$

$$E_{3/2} = (3/2)g\beta B - 3b_2^0 - 3b_4^0 + 9b_6^0$$

$$E_{1/2} = (1/2)g\beta B - 5b_2^0 + 9b_4^0 - 5b_6^0 + 5(4b_4^3 - 7b_6^3)/3g\beta B \\ - 140(b_4^3 + b_6^3)^2/3g\beta B$$

$$E_{-1/2} = (-1/2)g\beta B - 5b_2^0 + 9b_4^0 - 5b_6^0 + 140(b_4^3 + b_6^3)^2/3g\beta B \\ - 5(4b_4^3 - 7b_6^3)^2/3g\beta B$$

$$E_{-3/2} = (-3/2)g\beta B - 3b_2^0 - 3b_4^0 + 9b_6^0$$

$$E_{-5/2} = (-5/2)g\beta B + b_2^0 - 13b_4^0 - 5b_6^0 - 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ - 7(b_6^6)^2/6g\beta B$$

$$E_{-7/2} = (-7/2)g\beta B + 7b_2^0 + 7b_4^0 + b_6^0 - 140(b_4^3 + b_6^3)^2/3g\beta B \\ - 7(b_6^6)^2/6g\beta B$$

TABLE 5

EXPRESSIONS FOR THE MAGNETIC FIELD AT WHICH TRANSITIONS
OF A GIVEN FREQUENCY WILL OCCUR FOR C_{3h} SYMMETRY AND $\underline{B}$
PARALLEL TO THE C AXIS

$$7/2 \leftrightarrow 5/2$$

$$B_{7/2} = (1/g\beta)(h\nu - 6b_2^0 - 20b_4^0 - 6b_6^0)$$

$$5/2 \leftrightarrow 3/2$$

$$B_{5/2} = (1/g\beta)(h\nu - 4b_2^0 + 10b_6^0 + 14b_6^0 - 7(b_6^0)^2/6g\beta B)$$

$$3/2 \leftrightarrow 1/2$$

$$B_{3/2} = (1/g\beta)(h\nu - 2b_2^0 + 12b_4^0 - 14b_6^0)$$

$$1/2 \leftrightarrow -1/2$$

$$B_{1/2} = (1/g\beta)(h\nu)$$

$$-1/2 \leftrightarrow -3/2$$

$$B_{-1/2} = (1/g\beta)(h\nu + 2b_2^0 - 12b_4^0 + 14b_6^0)$$

$$-3/2 \leftrightarrow -5/2$$

$$B_{-3/2} = (1/g\beta)(h\nu + 4b_2^0 - 10b_4^0 - 14b_6^0 - 7(b_6^0)^2/6g\beta B)$$

$$-5/2 \leftrightarrow -7/2$$

$$B_{-5/2} = (1/g\beta)(h\nu + 6b_2^0 + 20b_6^0 + 6b_6^0)$$

TABLE 6

EXPRESSIONS FOR THE MAGNETIC FIELD AT WHICH TRANSITIONS
AT A GIVEN FREQUENCY WILL OCCUR FOR C_{3v} SYMMETRY AND $\underline{B}$
PARALLEL TO THE C AXIS

$$7/2 \leftrightarrow 5/2$$

$$B_{7/2} = (1/g\beta)(h\nu - 6b_2^0 - 20b_4^0 - 6b_6^0 - 140(b_4^3 + b_6^3)^2/3g\beta B \\ + 5(4b_4^3 - 7b_6^3)^2/3g\beta B)$$

$$5/2 \leftrightarrow 3/2$$

$$B_{5/2} = (1/g\beta)(h\nu - 4b_2^0 + 10b_4^0 + 14b_6^0 - 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ - 7(b_6^6)^2/6g\beta B)$$

$$3/2 \leftrightarrow 1/2$$

$$B_{3/2} = (1/g\beta)(h\nu - 2b_2^0 + 12b_4^0 - 14b_6^0 + 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ - 140(b_4^3 + b_6^3)^2/3g\beta B)$$

$$1/2 \leftrightarrow -1/2$$

$$B_{1/2} = (1/g\beta)(h\nu - 10(4b_4^3 - 7b_6^3)^2/3g\beta B \\ + 280(b_4^3 + b_6^3)^2/3g\beta B)$$

$$-1/2 \leftrightarrow -3/2$$

$$B_{-1/2} = (1/g\beta)(h\nu + 2b_2^0 - 12b_4^0 + 14b_6^0 + 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ - 140(b_4^3 + b_6^3)^2/3g\beta B)$$

$$-3/2 \leftrightarrow -5/2$$

$$B_{-3/2} = (1/g\beta)(h\nu + 4b_2^0 - 10b_4^0 + 14b_6^0 - 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ - 7(b_6^6)^2/6g\beta B)$$

$$-5/2 \leftrightarrow -7/2$$

$$B_{-5/2} = (1/g\beta)(h\nu + 6b_2^0 + 20b_4^0 + 6b_6^0 + 5(4b_4^3 - 7b_6^3)^2/3g\beta B \\ - 140(b_4^3 + b_6^3)^2/3g\beta B)$$

$$\begin{aligned}
g\beta \Delta B_2 &= 8b_2^0 - 20b_4^0 - 28b_6^0 \\
g\beta \Delta B_3 &= 4b_2^0 - 24b_4^0 + 28b_6^0
\end{aligned} \tag{2-17}$$

where

$$\Delta B_1 = B_{7/2} - B_{-5/2}$$

$$\Delta B_2 = B_{5/2} - B_{-3/2}$$

$$\Delta B_3 = B_{3/2} - B_{-1/2}$$

Solving this set of equations with the aid of Cramer's theorem one finds that

$$\begin{aligned}
b_2^0 &= (g\beta/1848)(77\Delta B_1 + 88\Delta B_2 + 55\Delta B_3) \\
b_4^0 &= (g\beta/1848)(21\Delta B_1 - 18\Delta B_2 - 27\Delta B_3) \\
b_6^0 &= (g\beta/1848)(7\Delta B_1 - 28\Delta B_2 + 38\Delta B_3)
\end{aligned} \tag{2-18}$$

In addition, the $M_S = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition yields the relation for g ,

$$g = h\nu / \beta B_{1/2}$$

which allows the calculation of the spectroscopic splitting factor to first order.

The above relations for g , b_2^0 , b_4^0 , and b_6^0 are valid for both C_{3v} and C_{3h} symmetries as the diagonal elements for both Hamiltonians are identical.

As mentioned previously, the energy levels thus far derived are valid only when the external magnetic field is parallel to the c axis of the crystal. The reason for this is that the spin operators contained in the crystal

field operator equivalents are referred to the same reference frame as the spin operator, S_z , appearing in the Zeeman Hamiltonian.

Since the Zeeman energy is much greater than the energy due to the crystalline electric field, the effective spin may be considered to be quantized along the external field, $\underline{B}$. In other words, the eigenfunctions of the total Hamiltonian are 'almost' eigenfunctions of the Zeeman Hamiltonian and M_s is 'approximately' a good quantum number. Therefore, if expressions for the energy levels are desired when $\underline{B}$ makes an oblique angle with respect to the unique crystalline axis, it is convenient to choose a representation where the Zeeman Hamiltonian is still diagonal. The crystalline field must then be referred to this new frame of reference.

Figure 2. Angle θ and p , q , and r in relation to x , y , and z .

Let (xyz) be a reference frame fixed with respect to the crystal such that the z axis coincides with the

c axis and (pqr) be a frame related to (xyz) by an Eulerian transformation $(0, \theta, 0)$ as illustrated in Figure 2. Then S_x , S_y , and S_z may be related to S_p , S_q , and S_r as follows:

$$\begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix} = \begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix} \begin{bmatrix} S_p \\ S_q \\ S_r \end{bmatrix}$$

and

$$\begin{bmatrix} B_p \\ B_q \\ B_r \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ B \end{bmatrix}$$

Hence, the transformation of the spin operators is

$$S_x = S_p \cos\theta - S_r \sin\theta$$

$$S_y = S_q$$

$$S_z = S_r \cos\theta + S_p \sin\theta$$

Experimentally it is found that the term B_2^0 is quite large with respect to the other terms in the crystal field Hamiltonian. Thus, a careful calculation of the off diagonal as well as the diagonal elements of B_2^{00} is required for use in second and third order perturbation corrections to the energy levels.

Therefore, letting

$$S_+ = S_p + iS_q$$

$$S_- = S_p - iS_q$$

it follows that

$$S_p = \frac{1}{2}(S_+ + S_-)$$

and

$$S_z = S_r \cos \theta + \frac{1}{2}(S_+ + S_-) \sin \theta$$

Substituting this expression for S_z into the relation for O_2^0 produces the following:

$$\begin{aligned} O_2^0 \rightarrow & (3/2)S_r^2(3\cos^2\theta - 1) + (3/2)S(S+1)\sin^2\theta \\ & - S(S+1) + (3/4)(S_+^2 + S_-^2)\sin^2\theta \\ & + (3/4)\sin\theta \cos\theta (S_r(S_+ + S_-) + (S_+ + S_-)S_r) \quad (2-19) \end{aligned}$$

The transformation of the other operator equivalents found in the crystal field Hamiltonian could be performed in a similar manner. However, it is more convenient to utilize the fact that the operators, O_j^m , transform like the spherical harmonics, $Y_j^m(\theta, \phi)$. Using the rotation properties of the spherical harmonics³⁵, the transformation relations for the O_j^m operators can be obtained:

$$\begin{aligned} D(\phi, \theta, \alpha) O_j^m &= (-1)^m (E_j^m / E_j^0) d_{0,m}^{(j)}(\theta) \cos m\alpha O_j^0 \\ &+ \sum_{m'=1}^j (E_j^m / E_j^{m'}) ((-1)^{m'} (-1)^m d_{m,m'}^{(j)}(\theta) \cos(m'\alpha + m\phi) \\ &\quad + d_{m',-m}^{(j)}(\theta) \cos(m'\alpha - m\phi)) O_j^{m'} \\ &- (-1)^{m'} ((-1)^m d_{m',m}^{(j)}(\theta) \sin(m'\alpha + m\phi) \\ &\quad + d_{m',-m}^{(j)}(\theta) \sin(m'\alpha - m\phi)) O_j^{m'} \end{aligned}$$

where
$$d_{m',m}^{(j)}(\theta) = \left[\frac{(j+m')!(j-m)!}{(j+m)! (j-m')!} \right]^{\frac{1}{2}} \sum_{\sigma} \begin{pmatrix} j+m \\ j-m'-\sigma \end{pmatrix} \begin{pmatrix} j-m \\ \sigma \end{pmatrix} \cdot (-1)^{j-m'-\sigma} (\cos \frac{\theta}{2})^{2\sigma-m'+m} (\sin \frac{\theta}{2})^{2j-2\sigma-m'+m}$$

³⁵A. R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton, Princeton University Press, (1967)

and E_j^m are constant coefficients. For example, for $j=4$, the E_j^m coefficients are:

$$E_4^0 = 8(\pi)^{1/2}/3; E_4^1 = 4(\pi)^{1/2}/3(5)^{1/2}; E_4^2 = 8(\pi)^{1/2}/3(10)^{1/2};$$

$$E_4^3 = 4(\pi)^{1/2}/3(35)^{1/2}; E_4^4 = 16(\pi)^{1/2}/3(70)^{1/2}$$

When these Eulerian rotations are applied to the operator equivalents, each particular O_j^m becomes a linear combination of the $O_j^{m'}$'s where j remains fixed and m' may take on all possible values. For example, O_4^0 transforms as follows³⁶:

$$D(\theta, \phi) O_4^0 = (1/8)(35\cos^4\theta - 30\cos^2\theta + 3)O_4^0$$

$$+ (5/2)\sin 2\theta(3-7\cos^2\theta)O_4^1 - (5/2)(7\cos\theta$$

$$- 8\cos\theta + 1)O_4^2 - 35\cos\theta\sin^3\theta O_4^3 + (35/8)\sin^4\theta O_4^4$$

Since the contributions to the energy levels due to terms in the crystal field (except for the term $B_2^0 O_2^0$) are small, it is possible to neglect all off diagonal matrix elements. This, of course, limits their perturbation correction to first order. The contribution due to B_6^3 is negligably small and the greatest effect of $B_6^6 O_6^6$ on the value of the magnetic field at which the resonances occur is less than .01%. Therefore both of these terms are neglected at this time.

The spin Hamiltonians of interest as a function of the Eulerian angles θ and ϕ then become

³⁶V. Lupei, A. Lupei, and I. Ursu, Rev. Roum. Phys. Tome 13, 4, 327, Bucarest (1958)

$$\begin{aligned}
H_{3h} = & g\beta BS_r + B_2^0((3/2)S_r^2(3\cos^2\theta-1)+(3/2)S(S+1)\sin^2\theta \\
& -S(S+1)+(3/4)(S_+^2+S_-^2)\sin^2\theta + (3/4)\sin\theta\cos\theta(S_r(S_++S_-) \\
& +(S_++S_-)S_r)) + B_4^0(1/8)(35\cos^4\theta-30\cos^2\theta+3)O_4^0 \\
& + B_6^0(1/16)(231\cos^6\theta-315\cos^4\theta+105\cos^2\theta-5)O_6^0 \quad (2-20)
\end{aligned}$$

and

$$\begin{aligned}
H_{3v} = & g\beta BS_r + B_2^0((3/2)S_r^2(3\cos^2\theta-1)+(3/2)S(S+1)\sin^2\theta \\
& -S(S+1)+(3/4)(S_+^2+S_-^2)\sin^2\theta + (3/4)\sin\theta\cos\theta(S_r(S_++S_-) \\
& +(S_++S_-)S_r)) + B_4^0(1/8)(35\cos^4\theta-30\cos^2\theta+3)O_4^0 \\
& \pm B_4^3(1/8)\sin^3\theta\cos\theta\cos 3\varnothing O_4^0 \\
& + B_6^0(1/16)(231\cos^6\theta-315\cos^4\theta+105\cos^2\theta-5)O_6^0 \quad (2-21)
\end{aligned}$$

where the indeterminant sign arises from the two non-equivalent cation sites. The expressions for the eigenvalues of (2-20) and (2-21) are given in TABLES 7 and 8 respectively (note that θ is the measured angle between the c axis of the crystal and the applied magnetic field and $\varnothing$ is the angle between the crystal $(11\bar{2}0)$ planes and the projection of the applied magnetic field to the x-y plane).

Assuming allowed transitions with $\Delta M_s = \pm 1$ the magnetic fields at which the fine structure lines occur may be calculated as a function of θ and $\varnothing$. These expressions appear on TABLES 9 and 10.

To obtain further information, particularly as to the value of b_6^0 , the spectrum must be observed with the

TABLE 7

EXPRESSIONS FOR THE ENERGY LEVELS OF A SPIN 7/2 ION IN
 C_{3h} SYMMETRY WITH $\underline{B}$ MAKING AN OBLIQUE ANGLE WITH THE
 C AXIS

$$\begin{aligned}
 E_{\pm 7/2} = & \pm (7/2)g\beta B + 7b_2^0 q_1 + 7b_4^0 q_{4t} + b_6^0 q_6 \pm 63(b_2^0)^2 q_2^2 / g\beta B \\
 & \pm 21(b_2^0)^2 q_3^2 / 8g\beta B - 378(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\
 & - 13.1(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 + 126(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
 \\
 E_{\pm 5/2} = & \pm (5/2)g\beta B + b_2^0 q_1 - 13b_4^0 q_{4t} - 5b_6^0 q_6 \mp 15(b_2^0)^2 q_2^2 / g\beta B \\
 & \pm 45(b_2^0)^2 q_3^2 / 8g\beta B + 186(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\
 & - 16.9(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 - 162(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
 \\
 E_{\pm 3/2} = & \pm (3/2)g\beta B - 3b_2^0 q_1 - 3b_4^0 q_{4t} + 9b_6^0 q_6 \mp 33(b_2^0)^2 q_2^2 / g\beta B \\
 & \pm 39(b_2^0)^2 q_3^2 / 8g\beta B + 162(b_2^0)^2 q_1 q_2^2 / (g\beta B)^2 \\
 & + 5/6(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 - 56(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
 \\
 E_{\pm 1/2} = & \pm (1/2)g\beta B - 5b_2^0 q_1 + 9b_4^0 q_{4t} - 5b_6^0 q_6 \mp 15(b_2^0)^2 q_2^2 / g\beta B \\
 & \pm 15(b_2^0)^2 q_3^2 / 8g\beta B + 30(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\
 & + 24.4(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 + 90(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2
 \end{aligned}$$

where $q_1 = P_2^0(\cos\theta)$, $q_{4t} = P_4^0(\cos\theta)$, $q_6 = P_6^0(\cos\theta)$
 $q_2 = \cos\theta \sin\theta$, $q_3 = \sin^2\theta$

EXPRESSIONS FOR THE ENERGY LEVELS OF A SPIN 7/2 ION IN
 C_{3v} SYMMETRY WITH $\underline{B}$ MAKING AN OBLIQUE ANGLE WITH THE
 C AXIS

$$E_{\pm 7/2} = \pm (7/2)g\beta B + 7b_2^0 q_1 + 7b_4^0 q_4 + b_6^0 q_6 \pm 63(b_2^0)^2 q_2^2 / g\beta B \\
\pm 21(b_2^0)^2 q_3^2 / 8g\beta B - 378(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\
- 13.1(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 + 126(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
(\pm)(\pm) 140b_4^3 q_5 / 8$$

$$E_{\pm 5/2} = \pm (5/2)g\beta B + b_2^0 q_1 - 13b_4^0 q_4 - 5b_6^0 q_6 \mp 15(b_2^0)^2 q_2^2 / g\beta B \\
\pm 45(b_2^0)^2 q_3^2 / 8g\beta B + 186(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\
- 16.9(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 - 162(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
(\mp)(\mp) 260b_4^3 q_5 / 8$$

$$E_{\pm 3/2} = \pm (3/2)g\beta B - 3b_2^0 q_1 + 6b_4^0 q_4 + 9b_6^0 q_6 \mp 33(b_2^0)^2 q_2^2 / g\beta B \\
\pm 39(b_2^0)^2 q_3^2 / 8g\beta B + 162(b_2^0)^2 q_1 q_2^2 / (g\beta B)^2 \\
+ 5.6(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 - 56(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
(\mp)(\mp) 60b_4^3 q_5 / 8$$

$$E_{\pm 1/2} = \pm (1/2)g\beta B - 5b_2^0 q_1 + 9b_4^0 q_4 - 5b_6^0 q_6 \mp 15(b_2^0)^2 q_2^2 / g\beta B \\
\pm 15(b_2^0)^2 q_3^2 / 8g\beta B + 30(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\
+ 24.4(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 + 90(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\
(\pm)(\pm) 180b_4^3 q_5 / 8$$

where $q_1 = P_2^0(\cos\theta)$, $q_4 = P_4^0(\cos\theta)$, $q_6 = P_6^0(\cos\theta)$
 $q_2 = \cos\theta \sin\theta$, $q_3 = \sin^2\theta$, $q_5 = \sin^3\theta \cos\theta \cos\phi$

TABLE 9

EXPRESSIONS FOR THE MAGNETIC FIELD AT WHICH TRANSITIONS
AT A GIVEN FREQUENCY WILL OCCUR FOR C_{3h} SYMMETRY AND $\underline{B}$
MAKING AN OBLIQUE ANGLE WITH THE C AXIS

$$\pm 7/2 \leftrightarrow \pm 5/2$$

$$B = (1/g\beta)(h\nu \mp 6b_2^0 q_1 \mp 20b_4^0 q_4 \mp 6b_6^0 q_6 - 78(b_2^0)^2 q_2^2 / g\beta B \\ + 3(b_2^0)^2 q_3^2 / g\beta B \pm 564(b_2^0)^2 q_1 q_2^2 / (g\beta B)^2 \\ \mp 3.8(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 \mp 289(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2)$$

$$\pm 5/2 \leftrightarrow \pm 3/2$$

$$B = (1/g\beta)(h\nu \mp 4b_2^0 q_1 \pm 10b_4^0 q_4 \pm 14b_6^0 q_6 - 18(b_2^0)^2 q_2^2 / g\beta B \\ - 3(b_2^0)^2 q_3^2 / g\beta B \mp 24(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\ \pm 22.5(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 \pm 109(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2)$$

$$\pm 3/2 \leftrightarrow \pm 1/2$$

$$B = (1/g\beta)(h\nu \mp 2b_2^0 q_1 \pm 12b_4^0 q_4 \mp 14b_6^0 q_6 + 18(b_2^0)^2 q_2^2 / g\beta B \\ - 3(b_2^0)^2 q_3^2 / g\beta B \mp 132(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\ \pm 18.8(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 \pm 144(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2)$$

$$+1/2 \leftrightarrow -1/2$$

$$B = (1/g\beta)(h\nu + 30(b_2^0)^2 q_2^2 / g\beta B - 15(b_2^0)^2 q_3^2 / 4g\beta B)$$

where $q_1 = P_2^0(\cos\theta)$, $q_4 = P_4^0(\cos\theta)$, $q_6 = P_6^0(\cos\theta)$
 $q_2 = \cos\theta \sin\theta$, $q_3 = \sin^2\theta$

TABLE 10

EXPRESSIONS FOR THE MAGNETIC FIELD AT WHICH TRANSITIONS
AT A GIVEN FREQUENCY WILL OCCUR FOR C_{3v} SYMMETRY AND B
MAKING AN OBLIQUE ANGLE WITH THE C AXIS

$$\pm 7/2 \leftrightarrow \pm 5/2$$

$$B = (1/g\beta)(h\nu \mp 6b_2^0 q_1 \mp 20b_4^0 q_4 \mp 6b_6^0 q_6 - 78(b_2^0)^2 q_2^2 / g\beta B \\ + 3(b_2^0)^2 q_3^2 / g\beta B \pm 564(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\ \mp 3.8(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 \mp 289(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\ (\mp)(\pm) 400b_4^3 q_5 / 8)$$

$$\pm 5/2 \leftrightarrow \pm 3/2$$

$$B = (1/g\beta)(h\nu \mp 4b_2^0 q_1 \pm 10b_4^0 q_4 \pm 14b_6^0 q_6 - 18(b_2^0)^2 q_2^2 / g\beta B \\ - 3(b_2^0)^2 q_3^2 / g\beta B \mp 24(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\ \pm 22.5(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 \pm 109(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\ (\pm)(\mp) 200b_4^3 q_5 / 8)$$

$$\pm 3/2 \leftrightarrow \pm 1/2$$

$$B = (1/g\beta)(h\nu \mp 2b_2^0 q_1 \pm 12b_4^0 q_4 \mp 14b_6^0 q_6 + 18(b_2^0)^2 q_2^2 / g\beta B \\ - 3(b_2^0)^2 q_3^2 / g\beta B \mp 132(b_2^0)^3 q_1 q_2^2 / (g\beta B)^2 \\ \pm 18.8(b_2^0)^3 q_1 q_3^2 / (g\beta B)^2 \pm 144(b_2^0)^3 q_2^2 q_3 / (g\beta B)^2 \\ (\pm)(\mp) 240b_4^3 q_5 / 8)$$

$$\pm 1/2 \leftrightarrow -1/2$$

$$B = (1/g\beta)(h\nu + 30(b_2^0)^2 q_2^2 / g\beta B - 15(b_2^0)^2 q_3^2 / g\beta B)$$

where $q_1 = P_2^0(\cos\theta)$, $q_4 = P_4^0(\cos\theta)$, $q_6 = P_6^0(\cos\theta)$

$$q_2 = \cos\theta \sin\theta, \quad q_3 = \sin^2\theta, \quad q_5 = \sin^3\theta \cos\theta \cos\phi$$

EXPRESSIONS FOR THE MAGNETIC FIELD AT WHICH TRANSITIONS
AT A GIVEN FREQUENCY WILL OCCUR FOR C_{3v} AND C_{3h} SYMMETRY
AND $\underline{B}$ IN A PLANE PERPENDICULAR TO THE C AXIS

$$7/2 \leftrightarrow 5/2$$

$$B = (1/g\beta)(h\nu + 3b_2^0 - (60/8)b_4^0 - (6/16)(b_6^6 \cos 6\theta - 5b_6^0) \\ + \text{Higher Order Corrections})$$

$$5/2 \leftrightarrow 3/2$$

$$B = (1/g\beta)(h\nu + 2b_2^0 + (30/8)b_4^0 + (14/16)(b_6^6 \cos 6\theta - 5b_6^0) \\ + \text{Higher Order Corrections})$$

$$3/2 \leftrightarrow 1/2$$

$$B = (1/g\beta)(h\nu + b_2^0 + (36/8)b_4^0 - (14/16)(b_6^6 \cos 6\theta - 5b_6^0) \\ + \text{Higher Order Corrections})$$

$$1/2 \leftrightarrow -1/2$$

$$B = (1/g\beta)(h\nu + \text{Higher Order Corrections})$$

$$-1/2 \leftrightarrow -3/2$$

$$B = (1/g\beta)(h\nu - b_2^0 - (36/16)b_4^0 + (14/16)(b_6^6 \cos 6\theta - 5b_6^0) \\ + \text{Higher Order Corrections})$$

$$-3/2 \leftrightarrow -5/2$$

$$B = (1/g\beta)(h\nu - 2b_2^0 - (30/8)b_4^0 - (14/16)(b_6^6 \cos 6\theta - 5b_6^0) \\ + \text{Higher Order Corrections})$$

$$-5/2 \leftrightarrow -7/2$$

$$B = (1/g\beta)(h\nu - 3b_2^0 + (60/8)b_4^0 + (6/16)(b_6^6 \cos 6\theta - 5b_6^0) \\ + \text{Higher Order Corrections})$$

Higher order terms arise from the off diagonal matrix
elements of o_2^0 .

external field normal to the crystal c axis. The Hamiltonians (2-15) and (2-16) then transform into

$$\begin{aligned}
 H_{\perp} = g\beta BS_r + B_2^0((3/2)o_2^2 - (1/2)o_2^0) + B_4^0((35/8)o_4^4 \\
 - (5/2)o_4^2 + (3/8)o_4^0) + B_6^0((231/32)o_6^6 \\
 - (63/16)o_6^4 + (105/32)o_6^2 - (5/16)o_6^0) \\
 + B_6^6((1/16)o_6^0 \cos 6\theta + (15/32)o_6^2 + (1/8)o_6^4 \\
 + (1/32)o_6^6)
 \end{aligned} \quad (2-22)$$

The diagonal terms in (2-22) are

$$\begin{aligned}
 H_{\perp} = g\beta BS_r - (1/2)B_2^0 o_2^0 + (3/8)B_4^0 o_4^0 \\
 + (1/16)(B_6^0 \cos 6\theta - 5B_6^0) o_6^0
 \end{aligned} \quad (2-23)$$

If a rotation about the c axis of the crystal is performed each fine structure resonance line should demonstrate a $\cos 6\theta$ dependence as indicated on TABLE 11.

2. The Crystal of Cadmium Sulfide

The crystal of CdS, known as greenockite, has a structure identical to that of hexagonal ZnS³⁷. This type of structure is commonly called wurtzite and has a space group C_{6v}^4 . The Cd^{++} ion is in a tetrahedral sulfur coordination. Since the tetrahedron has a slight distortion along the c axis of the crystal, the crystalline field at the Cd^{++} site has trigonal symmetry (C_{3v}). The

³⁷R. W. G. Wyckoff, Crystal Structures, Vol. III, Interscience Publishers, Inc., New York, (1960)

Figure 3. The structure of wurtzite, CdS. The dashed lines indicate the unit cell. A and B indicate the two magnetically inequivalent sites.

structure of wurtzite is illustrated in Figure 3. The unit cell is indicated by dashed lines.³⁸

The cadmium sites are all physically equivalent to each other but there are two types of sites which are magnetically inequivalent. Figure 3 illustrates the magnetically inequivalent sites A and B. It may be noticed that the tetrahedron of sulfur ions surrounding site A is rotated by 60° from that surrounding site B. The cubic portion of the crystal field which gives rise to the operator equivalents O_4^3 and O_6^3 in the crystal field Hamiltonian reflects this inequivalence. The cubic crystal field axes are rotated from each other about their (111) direction, which coincides with the c axis, by 60° . This inequivalence appears in paramagnetic resonance only for those ions which substitute for Cd^{++} whose spin $S \geq 2$, as the cubic crystal field does not lift the spin degeneracy when $S < 2$. This condition is satisfied for the Gd^{3+} ion as its spin is $7/2$.

³⁸W. L. Bragg, Atomic Structure of Minerals, Cornell University Press, New York, (1937)

CHAPTER III

EXPERIMENTAL PROCEDURE

1. The spectrometer.

The spectrometer used in this experiment was developed at The Ohio State University over a period of the last three years. A block diagram of the system is illustrated on page 44. Facilities are available to observe transitions between Zeeman levels at microwave frequencies of 8.5 to 12 GHz (X-band) and 23 to 25 GHz (K-band). It is also possible to make experimental observations with the sample at liquid helium temperatures (1.5°K to 4.2°K), liquid nitrogen temperature (77°K), as well as at the ambient room temperature.

The static magnetic field was produced by a 12-inch Harvey-Wells magnet, on loan from the Department of Electrical Engineering, which is powered by a Magnion Model HS-22110 power supply. The magnet is capable of being rotated about an axis perpendicular to the static field. Therefore, in the course of an angular study of the spectrum, the crystal under investigation remains fixed with respect to the laboratory while the external magnetic field is rotated.

The microwave power at 24 GHz was generated with a Varian EM 1188 reflex klystron. The klystron frequency was locked to the resonant frequency of the microwave cavity by means of an automatic frequency control device. The automatic frequency control (A.F.C.) utilizes 10 KHz modulation of the repeller voltage. After amplifying the signal reflected from the microwave cavity and performing a phase detection, the A.F.C. applies the demodulated error signal back to the repeller voltage. Thus, when the klystron frequency drifts, the A.F.C. causes the repeller voltage to change slightly to compensate for the drift.

After being generated by the klystron, the microwave radiation passes through a ferrite isolator, a variable attenuator, and a hybrid tee to the microwave cavity. The cavity, being of the reflection TE 102 type, reflects a portion of the microwave power back through the hybrid tee and a wavemeter to the crystal diode detector. When the external magnetic field is not near the resonant condition for the sample (the microwave frequency is held constant), the amount of power reflected from the cavity is small. However, when resonance conditions are satisfied, microwave energy is absorbed by the sample, which lowers the effective Q of the cavity, and the amount of power reflected is changed. This results in a change in the dc output at the crystal detector. In some instances the

Figure 4. Block diagram of the paramagnetic resonance spectrometer.

change in the crystal detector output may be quite significant. With a sample of ZnS doped with 1.7% Mn, the crystal current was found to decrease by a factor of two in the resonance condition.

The crystal of CdS doped with Gd did not demonstrate such strong resonant phenomenon, however, and in order to improve the signal to noise ratio of the output signal, the external magnetic field was modulated. This modulation was achieved through a pair of Helmholtz coils placed on the magnet pole pieces. A 750 Hz signal generated by the Princeton Applied Research phase detector (P.A.R.) was amplified and applied to the modulation coils. Thus, at the crystal diode detector there appeared a 750 Hz signal whose amplitude was proportional to the slope of the resonance absorption line. The modulation was limited to rather low frequencies due to skin depth effects occurring in the silver coating of the double dewar system and in the walls of the microwave cavity.

This 750 Hz signal is then amplified and demodulated by a phase detector in the P.A.R. The dc signal produced by the P.A.R. phase detector is then applied to a Bausch and Lomb "VOM-5" strip chart recorder which displays the first derivative of the absorption line.

A reflection type, rectangular, microwave cavity operated in the TE 102 mode is used in the experiment.

The resonant frequency of the cavity is about 23.75 GHz. The sample is placed approximately $\frac{1}{4}$ of the distance from the top of the cavity on the 'b' face as illustrated in Figure 5.

Figure 5. Microwave cavity showing the sample position.

In this position, the sample experiences a microwave B field that is always perpendicular to the external magnetic field when the electromagnet is rotated.

The cavity, containing the paramagnetic sample, is placed inside the double dewar system (Figure 6). If the observations are to be made at 77°K, liquid nitrogen is placed in the outer dewar while the inner dewar is evacuated and purged with helium gas in order to eliminate water condensation in the cavity. It was found that a period of about two hours was required for the cavity to reach 77°K after nitrogen had been added to the outer dewar.

Figure 6. Diagram illustrating the double dewar system⁴⁷
used for low temperature measurements.

By adding liquid helium to the inner dewar, the sample was bathed by the liquid and therefore at a temperature of 4.2°K. A Stokes Model 212 H-10 vacuum pump was available for pumping on the liquid helium; thereby, temperatures below the λ point (2.2°K) were obtainable. Above the λ point, liquid helium boils to form bubbles. These bubbles pass through the iris of the cavity in order to escape and, hence, inject considerable noise in the signal detected by the crystal diode. Below the λ point, boiling ceases and a significant improvement of the signal to noise ratio is established.

The magnitude of the external magnetic field was measured with a Rawson Type 820 rotating coil gaussmeter. This gaussmeter was calibrated with a proton NMR magnetometer and to insure that the field measured by the gaussmeter was the same as that at the position of the sample a small amount of polycrystalline diphenyl picryl hydrazyl (DPPH) was placed at the site of the sample. Then using the relation

$$h\nu = g\beta B$$

with

$$h = 6.6256 \times 10^{-27} \text{ erg-sec}$$

$$\beta = 0.92732 \times 10^{-20} \text{ erg/gauss}$$

$$g = 2.0036 \text{ for polycrystalline DPPH}$$

$$\nu = 23.755 \times 10^9 \text{ Hz}$$

it is established that the gaussmeter should read 8491 gauss. The position of the gaussmeter probe was then adjusted until good agreement with the above field was achieved. Utilizing a slow sweep generator, the magnetic field was varied at a rate of about 30 gauss/min. and markers were placed every 25 gauss. By interpolating between these markers, the magnetic field at which the resonance lines occurred could be measured with a high degree of reproducibility.

The angle of rotation of the magnet could be measured on the base of the magnet to the nearest tenth of one degree. In order to correlate the reading on the magnet base with the angle that the c axis of the crystal makes with the static magnetic field, the field was rotated in increments of 0.5° in the neighborhood of maximum splitting of the spectrum. Thus, an absolute minimum (or maximum) was located (Figure 7), and this was assigned to be $\theta = 0$.

Figure 7. Example of data used to orient the crystalline sample.

The angular variation of the spectrum in the plane perpendicular to the c axis of the crystal was observed at X-band frequencies ($\nu = 9200$ MHz). Details of the spectrometer are similar to those of the K-band system described in the preceeding paragraphs. A Varian V-4531 multipurpose cavity was used in this portion on the experiment. The sample was cemented to the end of a quartz rod with the c axis of the crystal parallel to the axis of the rod. The rod was then rigidly attached inside a small glass liquid nitrogen dewar and the entire assembly inserted into the cavity. With a protractor attached to the quartz rod, the relative angular displacement of the dewar-rod-crystal sub-assembly in the cavity could be measured.

2. Sample preparation.

The crystals used in the experiment were prepared by Dexter Gorton³⁹ of the Department of Electrical Engineering, The Ohio State University, under the direction of Professor William Anderson. The CdS crystals were doped with rare earth impurities by diffusion. As it is somewhat difficult to introduce rare earth ions into II-VI crystals, the method of diffusion was investigated by Professor Anderson. Previous attempts to prepare certain samples by vapor growth were unsuccessful.

³⁹D. G. Gorton, Thesis, The Ohio State University,
(Department of Electrical Engineering)

Single crystals 1 X 5 X 5 mm were cut from a boule of CdS in such a manner that the c axis was perpendicular to the 5 X 5 mm faces. The boule was oriented by etching the surface, which produces sharply defined hexagonal etch pits on the CdS surface perpendicular to the c axis of the crystal. Optical reflection from the crystal surface then permits the unique axis to be determined.

The CdS crystal was then placed in a clean quartz tube along with a small amount of rare earth turnings and granular sulfur. The tube was evacuated to about 10^{-5} torr and sealed (Figure 8). The sealed tube containing CdS,

Figure 8. Diagram showing the arrangement of the ampoule contents.

Gd, and S was then heated for three days at 960°C . The granular sulfur provided a sulfur vapor pressure of 33 Atm.

A profile luminescence study performed by Dexter Garton⁴⁰ indicated that the concentration of rare earth

impurities was not constant throughout the sample. Higher concentrations were found near the surface of the crystal.

The orientation was confirmed in this laboratory by reetching the doped sample and observing the back scattering of a laser beam from the crystal surfaces. Additional orientation measurements were made utilizing X-ray diffraction methods.

CHAPTER IV

RESULTS

The crystal used in the rotational study in a plane containing the c axis as well as the rotation with the c axis perpendicular to the external magnetic field was about 1 mm X 2 mm X 2 mm. A larger crystal was available but at K-band frequencies the size of the cavity limited the crystal dimensions to those given above. The filling factor, however, was sufficient to give rise to strong transition signals at liquid nitrogen temperature.

When the external magnetic field was parallel to the (0001) direction the spectrum displayed the greatest splitting. The spectrum ranged from approximately 4000 gauss to 13000 gauss for Gd^{3+} . The spectrum consisted of two sets of seven lines each and a strong line located at approximately 4000 gauss. An angular study in a plane containing $\underline{B}$ and the crystal (0001) direction demonstrated that one set of resonance lines (A) could be described by the Hamiltonian H_{3h} , Equation (2-20), and the other set (B) by the Hamiltonian H_{3v} , Equation (2-21). At this time the origin of the resonance in the neighborhood of 4000 gauss is not determined. Angular variation of this resonance

is illustrated in Figure 13. It was found that the set of lines, A, were narrower and more intense than the set B. As predicted by transition probabilities, the intensities of the resonances decreased as one moves from the central transition, $M_s = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$, to the outermost transitions, $M_s = \pm 7/2 \leftrightarrow \pm 5/2$. As a result, the $M_s = \pm 7/2 \leftrightarrow \pm 5/2$ transitions of set B could not be observed in the region $\theta = 10^\circ$ to $\theta = 60^\circ$. In the neighborhood of $\theta = 50^\circ$, the fourteen lines overlapped and positive identification of individual transitions was impossible.

The general angular dependence of the spectra for both set A and set B appears to be the same. This is due to the fact that in both Hamiltonians, H_{3h} and H_{3v} , the coefficient $b_2^0 = 3B_2^0$ gives rise to the dominant term by two orders of magnitude. Figure 9 illustrates the angular dependence of set A where θ is the angle between B and the crystal c axis. A rotation about the c axis demonstrated no $\cos 6\theta$ dependence as predicted by the theory. Thus, it must be assumed that b_6^6 is negligably small. The spectrum did, however, display a cosine dependence with a period of 180° . It was concluded that this variation of the spectrum was due to misalignment of the crystal c axis parallel to the quartz rod. The amplitude of the $\cos 2\theta$ dependence was approximately 7 gauss. This corresponds to an error of alignment of no more than 6° .

Figure 9. Variation of the Magnetic Field for Resonance Condition of Interstitial Ion (Site A) as Angle of Orientation of the C Axis Changes Relative to $\underline{B}$. (o denotes experimental points)

Figure 10. Variation of the Magnetic Field for Resonance Condition of Substitutional Ion (Site B) as Angle of Orientation of the c Axis Changes Relative to $\underline{B}$. (o denotes experimental points)

Figure 11. Cubic Field Splitting Due to the nonequivalent Cadmium Sites as Angle of Orientation Changes Relative to the External Magnetic Field. (o denotes experimental point)

Figure 12. Variation of the Magnetic Field for Resonance Condition as Angle of Orientation Changes for Rotation About the c axis for the Set of Lines Denoted B. (o denotes experimental points)

Figure 13. Angular Dependence of the Unidentified Resonance.
(o denotes the experimental points)

The θ dependence of the resonance lines corresponding to set B is illustrated on Figures 10 and 11. Each fine structure line was split into a doublet due to the two inequivalent cadmium sites. Figure 10 demonstrates only the 'center of gravity' of each resonance line whereas Figure 11 displays the cubic splitting of the $M_s = 3/2 \leftrightarrow 1/2$ and $M_s = -1/2 \leftrightarrow -3/2$ fine structure lines.

Utilizing equations (2-17);

$$b_2^0 = \frac{g\beta}{1848} (77\Delta B_1 + 88\Delta B_2 + 55\Delta B_3)$$

$$b_4^0 = \frac{g\beta}{1848} (21\Delta B_1 - 18\Delta B_2 - 27\Delta B_3)$$

$$b_6^0 = \frac{g\beta}{1848} (7\Delta B_1 - 28\Delta B_2 + 35\Delta B_3)$$

and

$$g = h\nu / \beta B_{\frac{1}{2} \leftrightarrow -\frac{1}{2}}$$

and using the measured values of the magnetic field strengths at which the resonances occurred along with the microwave frequency, it is possible to determine the parameters associated with the set of lines denoted A:

$$g = 1.987$$

$$b_2^0 = -561.4 \times 10^{-4} \text{ cm}^{-1}$$

$$b_4^0 = -1.89 \times 10^{-4} \text{ cm}^{-1}$$

$$b_6^0 = -0.290 \times 10^{-4} \text{ cm}^{-1}$$

Similarly for the set of lines denoted B:

$$g = 1.987$$

$$b_2^0 = -660.7 \times 10^{-4} \text{ cm}^{-1}$$

$$b_4^0 = -6.73 \times 10^{-4} \text{ cm}^{-1}$$

$$b_6^0 = -0.173 \times 10^{-4} \text{ cm}^{-1}$$

The sign of b_4^0 and b_6^0 is determined by the sign of b_2^0 . However, in order to determine the sign of b_2^0 , the relative intensities of the fine structure lines must be measured at liquid helium temperature. The levels with negative quantum numbers will be more fully occupied at liquid helium temperatures and the transitions involving these levels will be more intense⁴⁰. Numerous attempts were made to take data at liquid helium temperature. However, it was found to be impossible to measure the relative amplitudes of the fine structure lines due to saturation. At power levels as low as 1 mW the resonance lines still exhibited strong evidence of saturation, therefore, it was impossible to determine the absolute sign of b_2^0 . The sign of b_2^0 has been chosen to be negative thereby forcing b_4^0 and b_6^0 to be negative (it was found from the experimental data that b_2^0 , b_4^0 , and b_6^0 must have the same sign). The reason for the choice of sign for b_2^0 is discussed in CHAPTER V.

The value of $|b_4^3|$ was determined by carefully measuring the cubic splitting of the $M_s = 3/2 \leftrightarrow 1/2$ and $M_s = -1/2 \leftrightarrow -3/2$

⁴⁰B. Bleaney, H. E. D. Scovil, and R. S. Trenam, Proc. Roy. Soc., (London) A223, 15 (1954)

transitions of set B (Figure 11). From TABLE 10 the magnitude of this splitting is given by

$$B(\theta, \phi) = (60/g\beta) b_4^3 \sin^3 \theta \cos \theta \cos 3\phi$$

The crystal was rotated about the c axis until the cubic splitting was maximized. That is, the magnetic field was then in the crystal $(11\bar{2}0)$ plane with $\phi=0$. With this condition satisfied, the parameter, $|b_4^3|$, could be calculated from eight sets of data and the relation

$$|b_4^3| = (g\beta B(\theta, 0)/60) \sin^3 \theta \cos \theta$$

The average value of b_4^3 was found to be:

$$|b_4^3| = 2.68 \times 10^{-4} \text{ cm}^{-1}$$

Figure 12 illustrates the ϕ dependence of the $M_s = -1/2 \leftrightarrow -3/2$ fine structure line. With the aid of equations found on TABLE 11 and the amplitude of the $\cos 6\phi$ variation, $|b_6^6|$ may be determined as follows:

$$|b_6^6| = (8g\beta/7) \Delta B_{-1/2 \leftrightarrow -3/2}$$

where $\Delta B_{-1/2 \leftrightarrow -3/2}$ is one half the measured difference between the maximum and minimum values of $B_{-1/2 \leftrightarrow -3/2}$. Again it is noticed that in addition to the $\cos 6\phi$ dependence, there exists a slight $\cos 2\phi$ variation that may be accounted for by misalignment of the crystal. The value of $|b_6^6|$ was determined to be

$$|b_6^6| = 5.56 \times 10^{-4} \text{ cm}^{-1}$$

All of the above parameters were measured at 77°K. The data taken at liquid helium temperature proved to be insufficient to determine the magnitude as well as the sign of the parameters. At room temperature it was found that the resonance lines associated with large quantum numbers (i.e. $\pm 7/2$ and $\pm 5/2$) were too weak to provide an accurate measurement.

The solid lines in Figure 9 and Figure 10 are the calculated positions of the fine structure resonances at a given angle θ , whereas the circles are experimental points. The solid lines were calculated using the equations found in TABLE 9 and TABLE 10. These equations were programmed in Fortran language and an IBM 360 digital computer was used to give magnetic field values of each fine structure line at intervals of 5 degrees. The source program is given in the Appendix.

CHAPTER V

DISCUSSION OF RESULTS

The g value for Gd^{3+} in CdS is less than the free-electron value of 2.0023. It is also slightly less than the values reported for Eu^{++} and Gd^{3+} in other crystals. The departure from the free-electron value has been attributed to a partial breakdown of Russell-Saunders coupling which will cause a small admixture of the first excited state ${}^6P_{7/2}$ into the ground state ${}^8S_{7/2}$. The g value is given by

$$g = (1-\alpha^2)g({}^8S_{7/2}) + \alpha^2g({}^6P_{7/2}) \quad (5-1)$$

where α is the amount of admixed ${}^6P_{7/2}$ state in the ground state and is given by

$$\alpha = (14)^{1/2} \lambda / (E_P - E_S)$$

where λ is the spin orbit coupling and $E_P - E_S$ is the separation of the ${}^6P_{7/2}$ state from the ${}^8S_{7/2}$ state.

TABLE 12 lists for comparison the characteristic parameters for the rare earth S-state ions in CdS and CdSe. The parameters for CdTe are not shown as b_{44}^0 and b_6^0 cannot be directly compared with b_{44} and b_6 of CdTe since b_{44}^0 and b_6^0 may contain contributions from the non cubic parts of the field. The parameters of Eu^{++} in CdS

were determined by the author in this laboratory. It may be noticed that the results concur with those of Dorain's. b_4^3 and b_6^6 could not be measured for Eu^{++} in CdS due to the large hyperfine interaction. A description of how the hyperfine constant, A, may be calculated for the two isotopes of Eu is given in the Appendix.

It is noticed in TABLE 12 that if the sign of b_2^0 for Gd^{3+} in CdS is chosen to be negative then a definite pattern is established. An examination of the results for the wurtzite crystals shows that b_2^0 changes sign from negative to positive in going from CdS to CdSe for both S-state ions. Hutchinson, Judd, and Pope⁴¹ demonstrated that contributions to the parameter b_2^0 may come from terms both linear and quadratic in the crystalline field potential. In addition, the linear term is proportional to $1/R^3$, where R is the separation of the charge on the impurity from that on the neighboring anions, whereas the quadratic term involving chiefly terms of sixth order in the crystalline field potential would be expected to vary as $1/R^4$. A change in sign in b_2^0 in going from CdS to CdSe can come about as a result of nearly equal linear and quadratic contributions which differ in sign.

⁴¹C. A. Hutchinson, Jr., B. R. Judd, and D. F. D. Pope, Proc. Phys. Soc. (London) B70, 514 (1957)

TABLE 12
EXPERIMENTALLY DETERMINED PARAMETERS FOR THE
S-STATE IONS OF THE RARE EARTH GROUP IN CdS and CdSe

	Gd ³⁺ Site B CdS	Eu ⁺⁺ CdS	Eu ⁺⁺ CdS	Gd ³⁺ CdSe	Eu ⁺⁺ CdSe
g	1.987	1.991	1.992	1.985	1.989
A ¹⁵¹	-	-23.05	-23.03	-	-23.19
A ¹⁵³	-	-10.41	-10.32	-	-10.22
b ₂ ⁰	-660.7	-341.7	-342.9	+805.5	+239.7
b ₄ ⁰	-6.73	-11.3	-11.9	+6.91	-2.75
b ₆ ⁰	-0.17	+00.56	+0.97	+0.36	+0.24
b ₄ ³	2.68	-	-	17.5	11.7
b ₆ ⁶	5.56	-	-	-	2.4
Temp.	77°K	300°K	300°K	77°K	77°K
Ref.	this work	this work	13	12	11

All parameters, with the exception of the spectroscopic splitting factor, are $\times 10^{-4} \text{ cm}^{-1}$.

It is interesting that in both CdS and CdSe the splitting of the Gd^{3+} ground state is some two to three times that of Eu^{++} . Possible explanations as to why this is so may be obtained by considering first the splitting in CdSe. If the splitting of Eu^{++} in CdSe¹² is compared with that of Eu^{++} in the isomorphous crystal CdS¹³ then it can be shown¹² that the dominant perturbation in the splitting of Eu^{++} in CdSe is given by

$$b_2^0 \sim -12\zeta^3 A_2^0(\bar{r}^2)/5W_P 2W_D \quad (5-2)$$

where ζ is the spin-orbit coupling constant, $A_2^0(\bar{r}^2)$ is the radial factor in the second-order term of the crystalline field potential, and W_P and W_D are the energies of the $^6P_{7/2}$ and $^6D_{7/2}$ levels relative to the $^8S_{7/2}$ ground state. If (5-2) is the dominant perturbation for Gd^{3+} as well as for Eu^{++} in CdS then it must be decided which parameter in (5-2) is altered sufficiently in going from Eu^{++} to Gd^{3+} to account for the two to three times larger b_2^0 for Gd^{3+} .

The parameter ζ will be considered first. In their summary of data for trivalent rare earths Dieke and Crosswhite give 1581.1 cm^{-1} for the value of ζ for Gd^{3+} .⁴² The value of ζ for Eu^{++} has not as yet been measured.

⁴²G. H. Dieke and H. M. Crosswhite, Appl. Opt. 2, 675 (1963)

However, according to McClure and Kiss⁴³ the value of $\int$ does not change much with the state of ionization since the major contributions to this effect occur near the nucleus. Using the value of $\int$ for Eu^{3+} as given by Dieke⁴¹ then the ratio $\int(\text{Gd}^{3+})/\int(\text{Eu}^{3+})$ is 1.20. This ratio is somewhat less than would be required to quantitatively account for the variation of b_2^0 from Gd^{3+} to Eu^{++} .

The value of $A_2^0(\bar{r}^2)$ will certainly be different for Eu^{++} and Gd^{3+} . The Eu^{++} ion is larger than the Gd^{3+} ion⁴⁴. The electronic charge on the Eu^{++} ion is therefore closer to the charges on the neighboring anions and a larger $A_2^0(\bar{r}^2)$ is therefore expected for the Eu^{++} ion because of its larger ionic size. This effect cannot explain the larger b_2^0 for Gd^{3+} . The value of $A_2^0(\bar{r}^2)$ may, however, be affected by the extra positive charge on the Gd^{3+} ion. The extra positive charge at the Gd^{3+} site may symmetrically pull in the negative charges on the neighboring anions leading to a larger $A_2^0(\bar{r}^2)$ for Gd^{3+} . Such an effect has been observed in the alkaline earth fluorides⁴⁵ but it was quite small.

⁴³D. S. McClure and Z. Kiss, J. Chem. Phys. 39, 3251 (1963)

⁴⁴V. M. Goldschmitt, Trans. Faraday Soc. 25, 253 (1929)

⁴⁵J. Sierro, Phys. Letters 4, 178 (1963)

It may be noticed from TABLE 12 that b_4^0 and b_6^0 are the same order of magnitude but differing in sign for Gd^{3+} in CdS and CdSe. b_4^3 , the measure of the cubic contribution of the crystalline field, is considerably smaller for Gd^{3+} in CdS than it is in CdSe. On the other hand, the value of b_6^6 for Gd^{3+} increased by a factor of two in going from CdSe to CdS.

The discussion thus far of the parameters as well as those listed in TABLE 12 has been confined to the substitutional site. That is, from the angular dependence of the spectrum and the relative magnitude of the spin Hamiltonian parameters it is confirmed that the set of lines denoted B are due to Gd^{3+} ions located substitutionally for Cd^{++} ions.

There is still some question as to the location of the Gd^{3+} ions giving rise to the set of lines A. It is a distinct possibility that set A may be due to a near neighbor defect on one of the sulfur ions forming the tetrahedron about a Gd^{3+} ion substituting for a Cd^{++} ion. However, the spectrum clearly displays the c axis of the crystal as being unique. It is not clear why a charge compensation, vacancy, or any type of defect should occur on a selective sulfur site. If the nearest neighbor defect were distributed equally among the sulfur ions, the spectrum of A would display no axial symmetry.

All material appearing in the literature on the rare earth S-state ions in CdS to date makes no mention of a Gd^{3+} site other than the substitutional site for Cd^{++} . Perhaps then, this phenomenon is associated with the method of sample preparation. In the diffusion process, the rare earth ions, indeed, penetrate the lattice along the crystalline c axis. The lattice vibration at 1000°C , however, would seem to preclude any preferential establishment of a defect.

A more attractive possibility for explaining the spectrum of set A is that of an interstitial site. It has not been established at this time which interstitial site for the Gd^{3+} ion would give the C_{3h} symmetry necessary for explaining the spectrum.

There are four possible sources of error. The frequency of the microwave radiation was measured with a Hewlett-Packard K-band frequency meter and the specifications list a tolerance of 0.11% error. Repeated measurements of the frequency during a given period as well as on different days showed that the variation of frequency was certainly within 0.11%.

The applied magnetic field was measured with a Rawson rotating coil gaussmeter listed at 0.10% accuracy. As the measurement of the parameters is determined by the difference between two absolute magnetic field values

(with the exception of the spectroscopic splitting factor and b_6^0) the error induced by the field measurement is probably reduced. There is also an estimated error of 0.12% introduced as a random error in making field markers on the experimental data. Because a minimum of 5 line readings were used to determine the position of a given line and the errors should be random, this error should introduce no more than $1/(5)^{1/2} \times 0.12\%$, or about 0.05% into the determination of the magnetic field measurement.

Finally, it is assumed that a maximum error of 1° is introduced through misalignment of the crystalline c axis relative to the external magnetic field. In the neighborhood of $\theta=0^\circ$, where the parameters g , b_2^0 , b_4^0 , and b_6^0 are measured, the principal term giving rise to the angular dependence is proportional to $P_2^0(\cos\theta)$. For an error of 1° , $P_2^0(\cos\theta)$ varies by approximately 0.2%.

Combining these errors in a worst possible manner one arrives at a combined possible error of 0.46%.

The experimental data of Figures 9, 10, 11, 12, and 13 fit the computer calculated curves with a root mean square deviation of 21.4 gauss. For a minimum field of 4000 gauss this results in a standard error of 0.54%. This compares quite favorably with the estimated error of 0.46%.

In conclusion, the work described previously has confirmed the existence of a substitutional Gd^{3+} site

in CdS and the applicability of the spin Hamiltonian (2-16) with the following experimentally determined parameters:

$$g = 1.987 \pm .009$$

$$b_2^0 = -660.7 \pm 3.0 \times 10^{-4} \text{ cm}^{-1}$$

$$b_4^0 = -6.73 \pm .03 \times 10^{-4} \text{ cm}^{-1}$$

$$b_6^0 = -0.173 \pm .001 \times 10^{-4} \text{ cm}^{-1}$$

$$|b_4^3| = 2.68 \pm .01 \times 10^{-4} \text{ cm}^{-1}$$

$$|b_6^6| = 5.56 \pm .03 \times 10^{-4} \text{ cm}^{-1}$$

In addition, a Gd^{3+} site which is believed to be interstitial in the CdS lattice was observed and the experimental results were found to be explained by the spin Hamiltonian (2-15). The experimentally determined parameters for this site are as follows:

$$g = 1.987 \pm .009$$

$$b_2^0 = -561.4 \pm 3.0 \times 10^{-4} \text{ cm}^{-1}$$

$$b_4^0 = -1.89 \pm .01 \times 10^{-4} \text{ cm}^{-1}$$

$$b_6^0 = -0.290 \pm .001 \times 10^{-4} \text{ cm}^{-1}$$

APPENDIX

COMPUTOR SOURCE PROGRAM USED TO CALCULATE THE ANGULAR
DEPENDENCE OF AN ION WITH SPIN $7/2$ IN A CRYSTALLINE
FIELD OF C_{3h} SYMMETRY

```

C      CALCULATION OF MAGNETIC FIELD POSITION OF FINE
C      STRUCTURE RESONANCE LINES OF GD IN GDS
C      H=8564
C      U=23.755 GHZ
C      G=1.977
C      B2=-561.4*EXP-4
C      B4=-1.89*EXP-4
C      B6=-0.29*EXP-4
      WRITE (6,5)
5  FORMAT (15X,1HT,18X,3HH1T)
      H1T=0
      T=0
10  H1T=8564+3660*(3*(COS(T)**2)-1)/2+34*(35*(COS(T)
    /**4)-30*(COS(T)**2)+3)/8-3380*(COS(T)**2)*(SIN(T)
    /**2)+130*(SIN(T)**4)-1735*(COS(T)**2)*(SIN(T)**2)
    /(3*(COS(T)**2)-1)/2+11.7*(SIN(T)**4)*(3*(COS(T)
    /**2)-1)/2+890*(COS(T)**2)*(SIN(T)**6)
      WRITE (6,20)T,H1T
20  FORMAT (10X,F10.4,10X, F10.1)
      T=T+.0874
      IF(T .LE. 1.6) GO TO 10
      WRITE (6,15)
15  FORMAT (15X,1HT,18X,3HH2T)
      H2T=0
      T=0
28  H2T=8564+2440*(3*(COS(T)**2)-1)/2-17*(35*(COS(T)
    /**4)-30*(COS(T)**2)+3)/8-782*(COS(T)**2)*(SIN(T)
    /**2)-32*(SIN(T)**4)+74*(COS(T)**2)*(SIN(T)**2)
    /(3*(COS(T)**2)-1)/2-69*(SIN(T)**4)*(3*(COS(T)
    /**2)-1)/2-336*(COS(T)**2)*(SIN(T)**6)

```

```

WRITE (6,30)T,H2T
30  FORMAT (10X,F10.4,10X,F10.1)
    T=T+.0874
    IF(T .LE. 1.6) GO TO 28
    WRITE (6,35)
35  FORMAT (15X,1HT,18X,3HH3T)
    H3T=0
    T=0
38  H3T=8564+1220*(3*(COS(T)**2)-1)/2-20*(35*(COS(T)
    /**4)-30*(COS(T)**2)+3)/8+782*(COS(T)**2)*(SIN(T)
    /**2)-130*(SIN(T)**4)+406*(COS(T)**2)*(SIN(T)**
    /2)*(3*(COS(T)**2)-1)/2-58*(SIN(T)**4)*(3*(COS(T)
    /**2)-1)/2-444*(COS(T)**2)*(SIN(T)**6)
    WRITE (6,40)T,H3T
40  FORMAT (10X,F10.4,10X,F10.1)
    T=T+.0874
    IF(T .LE. 1.6) GO TO 38
    WRITE (6,45)
45  FORMAT (15X,1HT,18X,3HH4T)
    H4T=0
    T=0
48  H4T=8564+1300*(COS(T)**2)*(SIN(T)**2)-163*(SIN(T)
    /**4)
    WRITE (6,50)T,H4T
50  FORMAT (10X,F10.4,10X,F10.1)
    T=T+.0874
    IF(T .LE. 1.6)
    WRITE (6,55)
55  FORMAT (15X,1HT,18X,3HH5T)
    H5T=0
    T=0
58  H5T=H5T=8564-1220*(3*(COS(T)**2)-1)/2+20*(35*(COS(T)

```

```

      /**4)-30*(COS(T)**2)+3)/8+782*(COS(T)**2)*(SIN(T)
      /**2)-130*(SIN(T)**4)-406*(COS(T)**2)*(SIN(T)**
      /2)*(3*(COS(T)**2)-1)/2+58*(SIN(T)**4)*(3*(COS(T)
      /**2)-1)/2+444*(COS(T)**2)*(SIN(T)**6)
      WRITE (6,60)T,H5T
60  FORMAT (10X,F10.4,10X,F10.0)
      T=T+.0874
      IF(T .LE. 1.8) GO TO 58
      WRITE (6,65)
65  FORMAT (15X,1HT,18X,3HH6T)
      H6T=0
      T=0
68  H6T=2440*(3*(COS(T)**2)-1)/2 +8564+17*(35*(COS(T)
      /**4)-30*(COS(T)**2)+3)/8-782*(COS(T)**2)*(SIN(T)
      /**2)-32*(SIN(T)**4)-74*(COS(T)**2)*(SIN(T)**2)
      /*(3*(COS(T)**2)-1)/2+69*(SIN(T)**4)*(3*(COS(T)
      /**2)-1)/2+336*(COS(T)**2)*(SIN(T)**6)
      WRITE (6,70)T,H6T
70  FORMAT (10X,F10.1,10X,F10.1)
      T=T+0874
      IF(T .LE. 1.6) TO GO 68
      WRITE (6,75)
75  FORMAT (15X,1HT,18X,2HH7T)
      H7T=0
      T=0
78  H7T=8564-3660*(3*(COS(T)**2)-1)/2-34*(35*(COS(T)
      /**4)-30*(COS(T)**2)+3)/8-3380*(COS(T)**2)*(SIN(T)
      /**2)+130*(SIN(T)**4)+1735*(COS(T)**2)*(SIN(T)**
      /2)*(3*(COS(T)**2)-1)/2-11.7*(SIN(T)**4)*(3*(COS(T)
      /**2)-1)/2-890*(COS(T)**2)*(SIN(T)**6)
      WRITE (6,80)T,H7T
80  FORMAT (10X,F10.4,10X,F10.1)
      T=T+.0874
      IF(T .LE. 1.6) GO TO 78
      STOP
      END

```

APPENDIX B

HYPERFINE INTERACTION OF Eu^{++} IN CDS

The hyperfine interaction of Eu^{++} in CdS is small in comparison to the Zeeman and crystal field effects. Therefore, the hyperfine Hamiltonian may be treated as a perturbation using only first order techniques. The hyperfine Hamiltonian may be expressed as

$$H_{\text{hyp}} = A \underline{I} \cdot \underline{S}$$

The first order correction to an energy level of a given M_S is then

$$E_{\text{hyp}} = A M_I M_S$$

where M_I may take on the values $+I, +I-1, \dots, 0, \dots, -I$. Thus, each electronic energy level is split into $2I+1$ components. The nuclear spin of Eu^{151} and Eu^{153} is $5/2$, hence

$$E_{M_S, (M_I)} = g \beta B M_S + \text{Terms due to crystalline field}$$

$$+ \begin{cases} M_S (5/2) A \\ M_S (3/2) A \\ M_S (1/2) A \\ M_S (-1/2) A \\ M_S (-3/2) A \\ M_S (-5/2) A \end{cases}$$

Accordingly, each electronic fine structure transition is split into $2I+1$ lines with the following magnetic field positions:

$$B_{M_S, (M_I)} = (1/g\beta)(h\nu + \text{Crystal field terms}$$

$$+ \begin{cases} -5A/2 \\ -3A/2 \\ -1A/2 \\ +1A/2 \\ +3A/2 \\ +5A/2 \end{cases})$$

where it is assumed $\Delta M_S = \pm 1$ and $\Delta M_I = 0$.

If one measures the magnetic field separation between the outermost hyperfine lines for a given fine structure transition, one arrives at the following expression:

$$\Delta B_{M_S} = (1/g\beta) 5A$$

or

$$A = (1/5)g\beta \Delta B_{M_S}$$

There are two isotopes of Eu, both with nuclear spin 5/2. Hence, each fine structure line was split into 12 hyperfine lines. After assigning the appropriate nuclear quantum number to the hyperfine lines it was possible to measure A for both isotopes. See TABLE 12.

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