



Optical coherent transients and hole burning of the $7F_0 - 5D_0$ transition in $\text{Eu}(\text{OH})_3$
by Michael Stephen Otteson

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Physics

Montana State University

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Abstract:

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The qualitative behavior of line narrowing in Doubly-resonant two—photon-absorption induced four—wave mixing is explained in terms of the anomalous dispersion. The implications of this dispersion regarding the measurement of the homogeneous linewidth and hyperfine levels hidden within the inhomogeneous profile are discussed with regard to the particular example of LiTbF_4 .

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of

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Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

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APPROVAL

of a thesis submitted by

Michael Stephen Otteson

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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November 30, 1984

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Michael Stephen Otteson was born on April 3, 1951 in Stoughton, Wisconsin. He is the son of Otto C. and Jean M. Otteson.

Educated in the Wisconsin public school system, he graduated from Deerfield High School in 1969. He attended University of Wisconsin-Oshkosh and graduated with a B.S. degree in physics and applied mathematics in 1973 and the M.S. degree in 1976. He received the M.S. degree in physics from Montana State University in Bozeman, Montana in 1979.

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Abstract

The narrowest inhomogeneous optical linewidth ever seen in a solid has been observed in $\text{Eu}(\text{OH})_3$. This transition is quadratically enhanced in a magnetic field and the results are explained completely in terms of second order perturbation theory and the coupling of crystal field energy levels.

Optical coherent transients are reported here for the first time in this optically pure, stoichiometric material. The optical dephasing time, T_2 , is shown to be greater than 2 microseconds for the ${}^7\text{F}_0 - {}^5\text{D}_0$ zero phonon transition.

Hole burning, attributed to optical pumping of nuclear-quadrupole levels, has been used to measure the quadrupole splittings in the excited, ${}^5\text{D}_0$, state. Due to the small magnetic moment, conventional magnetic resonance techniques have failed to make this measurement in all Europium compounds. The new technique developed and used in these hole burning measurements yields the quadrupole coupling coefficients, $|P| = 11.6$ MHz and $|P| = 4.5$ MHz for the 153 isotope and the 151 isotope, respectively.

The qualitative behavior of line narrowing in Doubly-resonant two-photon-absorption induced four-wave mixing is explained in terms of the anomalous dispersion. The implications of this dispersion regarding the measurement of the homogeneous linewidth and hyperfine levels hidden within the inhomogeneous profile are discussed with regard to the particular example of LiTbF_4 .

Chapter 1

INTRODUCTION

The rare earth ion, Eu^{3+} , exhibits several properties which make it interesting in a spectroscopic as well as a practical sense. The well established ground state¹ which is dominantly a ${}^7\text{F}_0$, $J=0$ state, is a nonmagnetic singlet electronic state. The singlet nature of the electronic state is also an attractive position from which to begin the study of higher order interactions such as the hyperfine structure. Because of the singlet electronic state the perturbations due to the crystal field can be described in a more straightforward manner.

In general, there is practical interest in trivalent rare earth ions for solid state lasers.² The rare earths have narrow emission and absorption linewidths and a quantum efficiency near 1.0 for some transitions. These features, and the fact that they can be easily incorporated into a variety of host lattices, make them very attractive as laser materials. The trivalent europium ion in a Y_2O_3 ³ host lattice has displayed laser action. Absorption line-widths as small as 3.5 GHz have been measured in $\text{EuP}_5\text{O}_{10}$ ⁴ at 1.6 K.

A general discussion of rare earth properties and some of the particular characteristics of the spectra are

presented in Chapter 2. This is followed by a description and explanation of two experimental techniques used in this study of $\text{Eu}(\text{OH})_3$. Optical hole burning is explained in Chapter 3 and the measurement of optical dephasing using the new method of optical phase switching is explicated in chapter 4. Experimental details and the CW dye laser used in this study are described in chapter 5 before the discussion of results in chapter 6.

Initial interest in this work was stimulated by measurements of the optical linewidth of the $^7\text{F}_0 - ^5\text{D}_0$ transition in $\text{Eu}(\text{OH})_3$. The measured value of 167 MHz full width at half maximum, FWHM, is the narrowest inhomogeneous width ever observed in any solid. In chapter 6 the experimental linewidth and shape of the absorption profile are discussed in detail along with the possibility of the first resolved optical isotope shift in a solid.

One of the major contributions of this work, is the added understanding of the dynamic change of the optical characteristics of $\text{Eu}(\text{OH})_3$ and other Eu^{3+} compounds in an external magnetic field. The quadratic change in the oscillator strength and the small Zeeman shift are experimentally measured and explained in terms of second order perturbation theory in the second and third parts of Chapter 6 respectively.

The measurement of an optical dephasing time in $\text{Eu}(\text{OH})_3$

is difficult because of the intrinsically small oscillator strength associated with the ${}^7F_0 \longleftrightarrow {}^5D_0$ transition in this material. The development of optical phase switching as a new technique for measuring coherent transients has renewed the interest in making measurements of this type in many different materials. A description of optical phase switching as an experimental method and the expected results of such a measurement are given in Chapter 4. The particular application of optical phase switching to measure the dephasing time in $\text{Eu}(\text{OH})_3$ and conclusions concerning these measurements are discussed in part four of Chapter 6.

The use of spectral hole burning to measure nuclear hyperfine splittings has only recently been used to complement the results obtained by the use of the more standard nuclear magnetic resonance and nuclear quadrupole resonance techniques. In Chapter 3, an explanation of the hole burning process is presented with a discussion of some of the previous measurements. Measurement of the quadrupole coupling constants for each of the europium isotopes, and the new technique used to make these measurements in $\text{Eu}(\text{OH})_3$ is described in detail in the last section of Chapter 6.

In Chapter 8 a new explanation is given for a particular type of four-wave mixing experiment along with the potential use of this type of experiment in measuring hyperfine splittings and homogeneous linewidths.

Chapter 2

RARE EARTH SPECTRA

Typically the spectrum of rare earth ions in a crystal consists of groups of lines; these groups are separated by approximately 1000 cm^{-1} and the sharp lines within a group are generally spread over an energy range of about 200 cm^{-1} . These groups are then labeled by the symbols of the dominant Russell-Saunders component. In fact, each group of states contains admixtures of states characterized by a set of quantum numbers S , L , J , yet for each group, J remains a relatively good quantum number.

The sharp absorption spectra of rare earth ions in ionic crystals were observed long ago.⁵ In many cases these lines are as narrow as those observed in the spectra of free atoms or free molecules. This means widths of 0.01 Angstrom , or 3 GHz , occur in the spectra of these materials in solids at low temperature. These narrow spectral features exhibited by the rare earths imply that, in principle, it is possible to study optical interactions in a solid with an accuracy obtained with free atoms or ions.

The sharp spectra of the rare earth ions are a result of lanthanide contraction. The energy and spatial extension of the $4f$ eigenfunctions suddenly drops at the start of the

lanthanide series. The imperfect shielding of one 4f-electron by another 4f-electron also contributes to this contraction. As one proceeds through the series with each increase in nuclear charge and electron number, the effective nuclear charge increases, which causes a reduction of the entire 4fⁿ shell.⁶ Because of this contraction the f-shell behaves as an inner shell and it is shielded by the outer 5s²5p⁶ closed shells of the xenon structure. As a consequence the rare earth ions do not interact appreciably with the environment and the 4f electrons have little tendency to participate in chemical bonding.

Free Ion

The electronic configuration of trivalent rare earth ions in a solid consists of the xenon structure of electrons with n electrons in the 4f shell, n=1 for cerium up to n=14 for lutecium. The Hamiltonian that determines the 4f energy levels of an isolated ion can be written as

$$H = (-\hbar^2/2m) \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N Z^* e^2 / r_i + \sum_{i < j} e^2 / r_{ij} + \sum_{i=1}^N \xi(r_i) \vec{s}_i \cdot \vec{l}_i$$

where N is the number of electrons, Z^{*}e the screened charge of the nucleus, and $\xi(r_i)$ the spin-orbit coupling function.

The first two parts of the expression are spherically symmetric and therefore do not remove any of the

degeneracies of the 4f electrons. The last two terms, the mutual coulomb interaction and the spin-orbit interaction respectively, are responsible for the free ion energy level structure of the 4f electrons. Labeling these two terms as H_c for the coulomb interaction, and H_{so} for the spin-orbit interactions, there are two limiting cases to be considered. $H_c \gg H_{so}$ in which Russell-Saunders, or LS coupling applies, or $H_{so} \gg H_c$ in which the j-j coupling scheme can be used. The rare earths fit into neither of these cases, so the total Hamiltonian,

$$H_1 = H_c + H_{so},$$

must be diagonalized to determine the energy levels. This approach is called intermediate coupling and usually starts from a basis set of Russell-Saunders states. The general energy level diagram for trivalent europium, as determined by Dieke and Crosswhite,⁷ is shown in Figure 1.

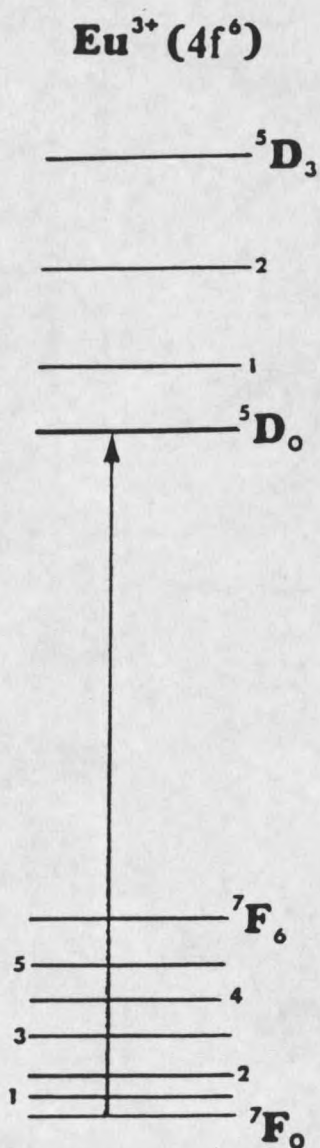


Figure 1: Energy level diagram for the trivalent rare earth ion Europium.

Crystal Field

When the ion is introduced into a crystal the ion experiences an inhomogeneous electric potential produced by the charge distribution in the crystal. Covalency and overlap effects also contribute to the potential. These effects are modeled by a one electron potential called the crystal field which removes some of the remaining degeneracy of the free ion. For rare earth ions, the splittings produced by the crystal field have been shown experimentally to be smaller than the energy separation of the free ion multiplets. So the crystal field splittings are obtained by treating the crystal field potential as a perturbation of the free ion.

The crystal field Hamiltonian is usually written as

$$V = \sum_{k,q,i} B_{kq} V_k^q(x_i, y_i, z_i)$$

where the parameters, B_{kq} , are treated as free parameters in fitting the crystal field energy levels. Before considering symmetry, as many as 27 complex constants would be needed to specify the crystal field potential. With time reversal symmetry this is reduced to 27 independent constants which must be real. The field for C_{3h} symmetry is specified by only four real parameters B_{20} , B_{40} , B_{60} , B_{66} , and the total Hamiltonian for equivalent f electrons can be written in the form⁸

$$H = H_0 + (B_{20}V_2^0 + B_{40}V_4^0 + B_{60}V_6^0 + B_{66}V_6^6)$$

where H_0 is the free ion Hamiltonian⁹ and the V_k^q are polynomials of even degree.¹⁰

Matrix elements of the crystal field operators V_k^q can be calculated using spherical tensor operator methods and the doubly reduced matrix elements tabulated by Nielson and Koster.¹¹ Then the crystal field energies are obtained by using basis states corresponding to the free ion Hamiltonian, H_0 , and diagonalizing the matrix of H on a computer.

Eu³⁺ Ion in Eu(OH)₃

This was done for Eu^{3+} in $\text{Eu}(\text{OH})_3$ by Cone and Faulhaber.¹² The fitted crystal field parameters are given by the following four constants.

$$\begin{aligned} B_{20} &= 211 \pm 11 \text{ cm}^{-1} & B_{40} &= -71 \pm 8 \text{ cm}^{-1} \\ B_{60} &= -54 \pm 3 \text{ cm}^{-1} & B_{66} &= 617 \pm 30 \text{ cm}^{-1} \end{aligned}$$

In the paper by Cone and Faulhaber, absorption transitions between the ground state, $^7F_0$, and $^5D_0$, the lowest excited state in the D manifold were not reported because that transition is forbidden and very weak. But they were able to determine the position of the $^5D_0$ absorption by comparing the fluorescence from the $^5D_0$ state at 4.2K with the absorption from $^7F_1$ to $^5D_0$ at 77K to within an accuracy of about 1 cm^{-1} .

The energy level separations, from the paper by Cone

and Faulhaber¹², which will be necessary in later explanations of the phenomena observed in this crystal are given as follows.

$$\begin{array}{llll}
 {}^7F_0 - {}^7F_2 & \mu = 0 & = & 1151 \text{ cm}^{-1} \\
 {}^5D_0 - {}^5D_1 & \mu = 1 & = & 1753 \text{ cm}^{-1} \\
 {}^5D_0 - {}^5D_1 & \mu = 0 & = & 1771 \text{ cm}^{-1} \\
 {}^5D_0 - {}^5D_2 & \mu = 0 & = & 4230 \text{ cm}^{-1}
 \end{array}$$

The crystal field matrix elements must satisfy the selection rule $J_z - J'_z = q$. This implies a set of crystal quantum numbers μ may be introduced such that $J_z = \mu \pmod{q}$. These crystal quantum numbers are used to label the states given above. Also, complimenting these, are measurements made in this work corresponding to the energy level separations,

$$\begin{array}{llll}
 {}^7F_0 - {}^5D_0 & \mu = 0 & = & 17226.8 \text{ cm}^{-1} \\
 {}^7F_0 - {}^7F_1 & \mu = 1 & = & 339 \text{ cm}^{-1} \\
 {}^7F_0 - {}^7F_1 & \mu = 0 & = & 440.5 \text{ cm}^{-1}
 \end{array}$$

The energy differences, ${}^7F_0 - {}^7F_1$ $\mu = 0, 1$ and ${}^5D_0 - {}^5D_1$ $\mu = 0, 1$, will be used in the second section of chapter 6 to calculate the quadratic increase of the absorption coefficient as a function of the magnetic field. These energy level separations will also be used to calculate the observed Zeeman shift of the ${}^7F_0$ to ${}^5D_0$ transition which similarly varies with the square of the magnetic field strength.

In a calculation of the expected nuclear quadrupole

splittings, it is again necessary to use energy level separations. For this estimate, the difference energies of the ${}^7F_0 - {}^7F_2$ and ${}^5D_0 - {}^5D_2$ states are used in the calculation in Chapter 3. Although this calculation is just an estimate of the quadrupole splittings, it does reinforce the experimental results given in the last section of Chapter 6.

In itself, the existence of a transition between the ${}^7F_0$ ground state and the ${}^5D_0$ excited state is interesting because as pointed out by the Judd-Ofelt theory,¹³ electric dipole transitions between the levels of the $4f^n$ configurations are all forbidden by the parity rule unless the $4f^n$ states have admixtures of opposite parity. The magnetic dipole selection rules are still valid in first order and explains the weak intensity for a $J = 0$ to $J' = 0$ transition. This transition in $\text{Eu}(\text{OH})_3$ is magnetic dipole in character and consistent with the magnetic dipole selection rules given in Table 1 below.

Selection rules are of considerable importance, in all spectroscopic techniques for transitions between two energy levels, and selection rules in crystal spectra are directly connected with the symmetry of the crystal under consideration. The selection rules enable the experimenter to draw conclusions about the nature of the energy levels between which the transition takes place. The mathematical concept which deals with these symmetries is group theory.

Group theory as applied to rare earth crystal spectra was originally developed by Bethe,¹⁴ but now it is readily available in tables for all of the different symmetries.¹⁵ The selection rules for Eu^{3+} , with C_{3h} site symmetry,¹⁶ in $\text{Eu}(\text{OH})_3$ are shown in Table 1.

μ	μ'					
	0	3	-2	2	1	-1
0	m σ	e π	e σ	e σ	m π	m π
3	e π	m σ	m π	m π	e σ	e σ
-2	e σ	m π	m σ	e σ	e π	m π
2	e σ	m π	e σ	m σ	m π	e π
1	m π	e σ	e π	m π	m σ	e σ
-1	m π	e σ	m π	e π	e σ	m σ

Table I. Selection rules and crystal quantum numbers for even-electron ions in C_{3h} symmetry; m, magnetic dipole transition; e, electric dipole transition.

Chapter 3

SPECTRAL HOLE BURNING

A short, general description of hole burning will be given in this chapter with a particular emphasis on saturation holes and long lived holes in rare earth solids. The latter parts of this chapter will focus on an approximate calculation of the parameters one would measure in $\text{Eu}(\text{OH})_3$ using hole burning techniques and a short description of homogeneous line width measurements.

When a spectral line is inhomogeneously broadened, and sufficient electromagnetic power is supplied at a single frequency to cause saturation, only those energy levels at the resonant laser frequency will be saturated. A 'hole' appears in the inhomogeneous line.

On the other hand, in a homogeneously broadened line, all energy levels are affected immediately by the saturating electromagnetic power, the intensity falls throughout the line, and no hole is produced.

The atoms or ions in a liquid or solid interact strongly with one another and with vibrational modes. Thus a saturation hole disappears very quickly because of the relatively rapid relaxation rates frequently encountered in solids. The density which is obtainable in a solid is an

advantage however. Nonlinear effects, such as hole burning, scale linearly with the density which should mean an increase in hole burning efficiency. These same nonlinear interactions scale as the fourth power of the dipole moment which is typically much smaller in many solids than it is in gases. This combination, and the relatively rapid relaxation rates in many solids, limits the use of saturation hole burning in solid materials. It does not limit hole burning in general, however, because a saturation hole is not the only kind of hole that can be burned.

Hole burning in solids is a result of a variety of different mechanisms, depending on the particular solid. A list of some of these mechanisms should include photophysical modification¹⁷, photochemistry¹⁸, metastable population storage¹⁹, two level saturation²⁰, and optical pumping of nuclear hyperfine populations^{21,22}. In solids, one or more of the above may be present but it is the last one which is responsible for long lived holes in rare earth materials.

Hole Burning in Rare Earths

Two level saturation hole burning in rare earth solids requires the use of two lasers. The strong pump laser interacts with the two level system such that the population in the ground and excited states depends on the pump laser intensity as well as the dipole coupling between the levels in the particular system. When a weak probe laser interacts

with the same two level system it will feel the full absorbing power of the inhomogeneous profile unless it is interacting with the ions that are also resonant with the strong pump beam. In that case, the absorption is saturated by the pump beam so the sample appears to be more transparent. A hole is then detected as the probe frequency is scanned through the inhomogeneous absorption profile. Saturated absorption spectroscopy of this type can be used to measure the homogeneous linewidth in rare earth compounds. These measurements and their limitations will be addressed later in this chapter.

In the long lived hole burning process in rare earth solids, population is selectively removed from the ground state level associated with an inhomogeneously broadened transition. This selectivity is in most cases much narrower than the inhomogeneous width of the optical transition, and the ground state hyperfine level population is redistributed as a result of the optical pumping. As these resonant ground state levels are depopulated, the nonresonant level populations are enhanced by the transfer of population between the hyperfine levels during the pumping process. Now transitions from the depleted regions in the spectral line will show holes corresponding to the energy level separations of the excited state hyperfine levels. Simultaneously, antiholes or increased spectral absorption

will appear at energies corresponding to the sum and difference combinations of ground and excited state hyperfine splittings.

By using this method, spectral resolution within the inhomogeneously broadened spectral line is achieved. This is important, because the observed hyperfine splittings are usually much less than the Full Width at Half Maximum, FWHM, of the inhomogeneously broadened line. In other words this is a solid state analogue of Doppler-free spectroscopy in atomic physics.

Hole burning has been of particular interest in Eu^{3+} compounds because as Elliott²³ pointed out there are some major experimental difficulties in doing conventional nuclear magnetic resonance, NMR, and nuclear quadrupole resonance, NQR, experiments on this particular ion. Nuclear resonance is usually observed only in materials which are diamagnetic or very weakly paramagnetic. In paramagnetic ions, the internal field resulting from the electrons creates a field at the nucleus which may be of the order of a million gauss. This is greater than any external field that can be applied in a nuclear resonance experiment and for this reason no direct measurements of nuclear moments by nuclear resonance have been possible in the rare earths, as they do not form diamagnetic compounds.²⁴ Nuclear magnetic moments can be determined from the hyperfine splittings measured in electron paramagnetic resonance

experiments, but moments determined in this way depend on an estimate of the average $\langle r^{-3} \rangle$, where r is the radius of the 4f electron.

Europium does have a non-degenerate electronic ground state which produces no magnetic field at the nucleus, and since conventional NMR and NQR cannot be used because of the limited sensitivity. The development of narrow linewidth, (1MHz), tuneable lasers has provided another means for making these measurements. Ground and excited state hyperfine splittings^{21,25}, Stark effects²⁶, and Zeeman effects²⁷ have all been measured using hole burning techniques. Through the use of hole burning, the hyperfine structure of the $^1D_2 - ^3H_4$ transition in $Pr^{3+}:LaF_3$ ^{21,25}, $Pr^{3+}:LaCl_3$ ²⁸, and $Pr^{3+}:LaBr_3$ ²⁹ have been investigated. Since that time, hole burning and optically detected nuclear quadrupole resonance, ODNQR, techniques have been used to measure the quadrupole splittings in EuP_5O_{10} ³⁰ and $YAlO_3:Eu^{3+}$ ³¹. Since the rare earth optical absorption lines are so narrow due to lanthanide contraction, they are the most attractive candidates to detect the hyperfine structure by the use of direct spectroscopy. Except for two isolated examples this has not been possible. It is possible in Ho^{3+} because of the lucky coincidence of three things, a very small inhomogeneous linewidth, a very large magnetic nuclear moment, and the existence of only one isotope, ^{165}Ho .³² It

has also been observed in 0.01% $\text{CaF}_2:\text{Pr}^{3+}$ which has a large hyperfine splitting constant of 2.7 GHz and a narrow inhomogeneous width of 650 MHz.³³

Recently spectral hole burning has also been used in EuVO_4 ³⁴ to identify the hyperfine splittings of perturbed sites in this material, and it has also shown a usefulness as a very sensitive identification of the particular perturbations of some of the individual sites.

Hole burning measurements of the hyperfine splittings in Pr^{3+} and Eu^{3+} rare earth compounds have complemented the electron paramagnetic resonance measurements obtained in other materials. These experimental measurements have also added a great deal to the understanding of the many contributions which affect the magnitude of the quadrupole tensor in the ground states and the excited states of rare earth materials. In europium compounds this is particularly interesting because of Elliott's prediction²³ that the ground state nuclear quadrupole tensor would be anomalously small.

Nuclear Quadrupole Hamiltonian

The large difference in magnitude of the quadrupole tensor between $^5\text{D}_0$ and $^7\text{F}_0$ states^{30,31} is attributed to the contribution to the electric field gradient of two important mechanisms. Since no first order quadrupole coupling exists for a pure $J = 0$ level, the observed field gradients are due to admixtures of excited states into the $^7\text{F}_0$ and $^5\text{D}_0$ wave

functions and a contribution caused by the crystalline lattice.

The two contributions to the quadrupole splitting, are of opposite sign,^{35,36} and are from the excited states of the $4f^6$ configuration. The contribution for $^5D_0$ which results from the $^5D_2$ level, with an energy denominator of 4230 cm^{-1} in the perturbation expansion, is smaller than the contribution to $^7F_0$ from the $^7F_2$ state which has an energy denominator of 1151 cm^{-1} . So the smaller quadrupole coupling for $^7F_0$ is a result of the lattice contribution which nearly cancels the contribution due to the $^7F_2$ admixture.

To derive an expression for the different contributions to the quadrupole tensor, the quadrupole splittings are first described by the spin Hamiltonian:²⁴

$$H = P[I_z^2 - I(I+1)/3 + \eta(I_x^2 + I_y^2)/3]$$

where each P is proportional to the respective quadrupole moment of each of the two europium isotopes. The asymmetry parameter, $\eta = (V_{xx} - V_{yy})/V_{zz}$, has a value between 0 and 1. For C_{3h} site symmetry, as in $\text{Eu}(\text{OH})_3$, $V_{xx} = V_{yy}$ and $\eta = 0$. The spin Hamiltonian is then

$$H = P[I_z^2 - (1/3)I(I+1)]$$

where

$$P = \sum P_i = P_{4f}^{(1)} + P_{pq} + P_{lat} + P_{4f}^{(2)}.$$

In the above expression, each of the contributions to the total quadrupole coupling constant P will be explained in the order in which they appear. $P_{4f}^{(1)}$ is the first order quadrupole term which is the dominant term observed in nuclear electric quadrupole resonance experiments. P_{pq} is a pseudoquadrupole interaction which is a magnetic effect unrelated to the nuclear quadrupole moment. This term is proportional to the square of $I \cdot J$, so experimentally it cannot be distinguished from the quadrupole effect. Fortunately however this interaction is negligibly small in $\text{Eu}(\text{OH})_3$. P_{lat} is the contribution caused by the crystalline lattice. The external lattice charges tend to induce a polarization of the closed electronic shells which in turn leads to an enhancement of the quadrupole moment. The last term, $P_{4f}^{(2)}$, is a result of the distortion of the electronic charge cloud of the $J=0$ state with admixtures of the $J=2$ states through interactions of the crystal field.

The first order 4f term is given by³⁷

$$P_{4f}^{(1)} = - [3e^2Q/4I(2I - 1)] (1 - R_Q) [3J_z^2 - J(J + 1)] \\ \times \langle r^{-3} \rangle_{4f} \langle J || a || J \rangle .$$

The quantity $\langle J || a || J \rangle$ results from application of the Wigner-Eckart theorem to evaluate the crystal field interaction by an operator equivalent, and $\langle r^{-3} \rangle_{4f}$ is the actual expectation value of r^{-3} for 4f electrons in the ion.

The expectation value of the quadrupole inverse radius cubed, $\langle r^{-3} \rangle_Q$, is given by

$$\langle r^{-3} \rangle_Q = (1 - R_Q) \langle r^{-3} \rangle_{4f},$$

where R_Q is the atomic Sternheimer factor. This first order term, $P_{4f}^{(1)}$, is zero, because there can be no quadrupole splitting for a $J = 0$ level.²⁴

The pseudoquadrupole interaction constant, P_{pq} , has been estimated by several authors to be less than 0.052 MHz^{36,37} which is an entirely negligible contribution compared to the last two terms in the sum.

The quadrupole coupling constant can now be written as the sum of just two terms

$$P = P_{lat} + P_{4f}^{(2)}.$$

The important thing to notice is that these two parts contribute to the nuclear electric quadrupole coupling constant with different signs.

$$P_{lat} = -[3Q(1 - \gamma_\infty) A_2^0] / I(2I - 1)$$

$$P_{4f}^{(2)} = [6e^2QA_2^0 \langle r^2 \rangle_{4f(1-\sigma_2)} \langle r^{-3} \rangle_{4f(1-R_Q)} \times |\langle 20 || \alpha || 00 \rangle|^2] / I(2I-1)(E_{20}-E_{00})$$

Here γ_∞ is the Sternheimer factor for the lattice. In the ground state where the antishielding parameter γ_∞ is large, $\gamma_\infty = -80$,³⁶ the contribution from the lattice nearly cancels the second order contribution from $P_{4f}^{(2)}$. In the excited state $^5D_0$, γ_∞ should be small or even equal to 1,

so that the quadrupole splitting will only be the result of the second order contribution.

Estimate of Quadrupole Splitting in $\text{Eu}(\text{OH})_3$

Using parameters from Cone and Faulhaber¹² and the γ_∞ and σ_2 values for Europium Ethyl Sulfate,³⁷ where measurements of these values have been made, one can calculate an approximate quadrupole coupling constant P for the two isotopes of Eu^{3+} where each of the isotopes have a nuclear spin of $I = 5/2$.

$$(3/5) A_2^0 \langle r^2 \rangle = E_{10} - E_{11} = 101.5 \text{ cm}^{-1}$$

$$A_2^0 \langle r^2 \rangle = 169.2 \text{ cm}^{-1}$$

$$\langle r^{-3} \rangle_{4f} = 7.41 a_0^{-3}$$

$$(1 - \sigma_2) = 0.27$$

$$A_2^0 \langle r^2 \rangle (1 - \sigma_2) = 45.7 \text{ cm}^{-1}$$

$$A_2^0 = 193.4 \text{ cm}^{-1} a_0^{-2}$$

$$(1 - \gamma_\infty) = 81$$

$$E_{20} - E_{00} = 1151 \text{ cm}^{-1}$$

For the ground state $^7F_0$ this gives

$$P_{1at} = -18.6 Q \text{ MHz}$$

$$P_{4f}^{(2)} = 17.3 Q \text{ MHz}$$

with Q, the quadrupole moment, in barns.

$$P = P_{1at} + P_{4f}^{(2)} = -1.3 Q$$

which implies a P of -3.2 MHz for ^{153}Eu and -1.2 MHz for ^{151}Eu .

As a first approximation of the excited state, $^5D_0$,

quadrupole coupling constant one can assume $\gamma_\infty = 1$, so that $P_{lat} = 0$. With the energy difference

$$\begin{aligned} E_{20} - E_{00} &= (21455 - 17225) \text{ cm}^{-1} \\ &= 4230 \text{ cm}^{-1} \end{aligned}$$

and $P = P_{lat} + P_{4f}^{(2)}$

one obtains $P = 0 + 4.71 \text{ Q MHz} = 4.71 \text{ Q MHz}$.

The quadrupole moment for ^{153}Eu is $Q = 2.45$ barns and for ^{151}Eu it is $Q = 0.95$ barns³⁸, so the predicted quadrupole coupling constants are $P = 11.5 \text{ MHz}$ and $P = 4.5 \text{ MHz}$ for the 153 isotope and the 151 isotope respectively.

It should be noted that this is just an approximate calculation because the parameters $\langle r^{+2} \rangle, \langle r^{-3} \rangle_{4f}, (1-\gamma_\infty)$, and $(1 - \sigma_2)$ are by no means the same in the Ethyl Sulfate as they are in $\text{Eu}(\text{OH})_3$. This is especially true for γ_∞ in the excited state because no measurements or estimates exist. The agreement is very good, however, because as we shall see the measured values for these two constants using hole burning techniques are $P = 11.6 \text{ MHz}$ for ^{153}Eu and $P = 4.5 \text{ MHz}$ for ^{151}Eu as discussed in the last section of chapter 6.

Hole Burning Measurement of Dephasing Time

Spectral hole burning can also be used to measure the optical dephasing time or transverse relaxation time T_2 . In this method, the sample is prepared by irradiation at a single frequency, which induces a polarization in the sample with a width H , where $H = 2(\Delta\omega_H + \Delta\omega_I)$. The observed hole

width is then given by a convolution of the homogeneous linewidth, $\Delta\omega_H$, and the instrumental linewidth, $\Delta\omega_I$. For CW dye lasers the instrumental linewidth $\Delta\omega_I$ is the bandwidth of the laser itself, approximately 1 MHz. So for measurements of hole widths greater than 5 or 10 MHz, deconvolution is not necessary, and the instrumental width can be considered negligible. The dephasing time is then given by $T_2 = (\pi\Delta\omega_H)^{-1} = (2/\pi H)$. This is strictly valid in the limit where the laser power goes to zero, but it is often difficult to make measurements which are reliable for the following reasons.

In the low power limit, the hole will still be slightly power broadened and only in the limit of zero power, no light, will the hole display the true homogeneous width. The most important difficulty, however, is the broadening of the hole by time dependent interactions. This is important because spectral diffusion due to radiative and nonradiative transfer will affect the hole depth and width on time scales which may be faster than the time required to measure the width or depth of a hole. One solution involves the use of two lasers, one to burn the hole and the other to monitor or read the spectrum as a function of time. In some cases, this technique has been successful³⁹, but in most cases, it only gives a lower limit on the optical dephasing time T_2 .

In any case, if a hole width, H , can be measured, $T_2 \geq (2/\pi H)$ is always true.

Chapter 4

OPTICAL PHASE SWITCHING

Since the discovery of the photon echo⁴⁰ in ruby, techniques such as free induction decay⁴¹, optical hole burning⁴², laser frequency switching⁴³, and sample frequency switching⁴⁴ have all been used to measure the optical dephasing time in a variety of materials. With some restrictions these methods of transient spectroscopy can all be used to measure the dephasing time in a rarefied gas where the optical dephasing time, T_2 , is simply related to the spontaneous emission time T_1 , $T_2 = 2T_1$. In stoichiometric solids, however, the atoms or ions strongly interact with neighboring atoms or ions and the rest of the environment. This affects the coherence or dephasing time T_2 such that, at low temperatures, it is usually much less than the diagonal lifetime T_1 . So the interest in the optical dephasing time is to better understand the interactions which can lead to a lengthening or shortening of this coherence time. This understanding is an important step in the development of lasers and optical devices in general.

Single Phase Switch

Optical phase switching^{4,5} is a new and powerful approach to coherent transient spectroscopy. By rapidly changing the phase of the laser light passing through an absorbing medium, the phase of the laser polarization is switched relative to the sample polarization which was established in the sample before the phase switch. Once the phase switch has taken place, the sample and the laser are again at the original frequency and as the sample relaxes back into equilibrium, a transient signal is detected.

First consider the laser sample interaction as a preparation stage where the polarization of the sample is driven by the laser. After the phase switch, the small field emitted by the sample propagates collinearly with the laser beam at the same frequency. This results in homodyne mixing of the sample signal with the laser beam which serves as the local oscillator.

Genack et al,^{4,5} in a calculation of the sample response to a sudden phase shift, expressed the laser field whose phase is instantaneously shifted by an amount ϕ at $t=0$ as

$$E(t) = 2E \sin[\omega t + \phi(t)] = -i[E^+ e^{i\omega t} - E^- e^{-i\omega t}]$$

with

$$E^\pm = \begin{cases} E & , t < 0 \\ E e^{\pm i\phi} & , t > 0 \end{cases} \quad 2.1$$

One must then solve the optical Bloch equations for the

sample polarization $P^\pm(t)$ corresponding to $E^\pm(t)$. The Bloch equations can be written as

$$\dot{P}^\pm = (\pm i\Delta - 1/T_2)P^\pm + 2(\mu_{12}^2/\hbar^2)NWE^\pm$$

2.2

$$\dot{NW} = -N(W - W_0)/T_1 - (E^+P^- + E^-P^+)\hbar$$

where a single frequency component, of homogeneous width $1/T_2$, is off resonance from the driving field by an amount Δ as shown in Figure 2. N is the density of molecules, W describes the degree of population inversion, $W = (\rho_{22} - \rho_{11})$. W_0 is the equilibrium value of the inversion with no laser field, and μ_{12} is the dipole matrix element between the ground and excited state.

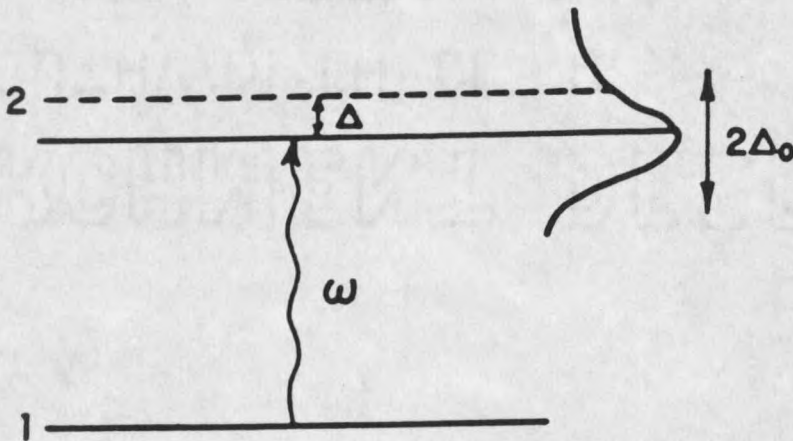


Figure 2: The dashed line is a single frequency component in the inhomogeneous line which is off resonance from the laser field at frequency ω by an amount Δ .

A Laplace transform can be used to solve equation 2.2.^{4,5}

The result is then integrated over the inhomogeneous line profile to obtain the signal $S(t)$,

$$S(t) \begin{cases} 4\pi^{3/2}(\omega n/c)W_0NL\chi^2/[\Delta_0(1+\chi^2T_1T_2)^{1/2}] = S(0) & , t < 0 \\ S(0) + 4\pi^{3/2}(\omega n/c)(W_0/\Delta_0)NL\chi^4T_1T_2\sin^2(\phi/2)g(t) & , t > 0 \end{cases} \quad 2.3$$

$$g(t) = (1/(1-\varepsilon/2))\exp(-2t/T_2) - (\varepsilon/(1-\varepsilon))\exp(-2t/T_2) + (\varepsilon/(1-\varepsilon)(2-\varepsilon))\exp(-t/T_1),$$

for excitation at the center of a Gaussian line when the inhomogeneous width, Δ_0 , is much greater than $1/T_2$. In equation 2.3, $\chi = 2E\mu_{12}/\hbar$ is the Rabi flopping frequency, n is the index of refraction of the sample, and L is the length of the sample. The off-diagonal element of the density matrix divided by the diagonal element is given by the parameter $\varepsilon = (T_2/T_1)$.

The change in signal when the phase switch occurs, $\Delta S = S(0^+) - S(0^-)$, is proportional to the laser intensity squared, χ^4 , so this is a nonlinear effect and the linear effects go to zero as $\Delta_0 \rightarrow \infty$.

The change in the signal after the phase switch can be written as

$$\Delta S = 4\pi^{3/2}(\omega n/c)(W_0/\Delta_0)NL\chi^4T_1T_2\sin^2(\phi/2)g(t). \quad 2.4$$

In general, the decay of the nonlinear signal is

complicated because it depends on both T_1 and T_2 . But in the limit $T_2 \ll T_1$, or $\epsilon \rightarrow 0$, $g(t)$ simplifies to the expression

$$g(t) = \exp(-2t/T_2)$$

and the signal decay is characterized by only one parameter, T_2 . The limit $T_2 \ll T_1$ is very appropriate in many solids at low temperatures and the signal decays at twice the dephasing rate $1/T_2$. The decay at twice the dephasing rate is a result of the two step process in phase switching. For a time when $t < 0$, the laser prepares the ground state and optically excited state in a coherent superposition. During this time a saturation hole with the homogeneous width of the transition, $1/T_2$, is burned into the inhomogeneous profile. The phase shift then occurs at $t=0$, and for times $t > 0$ the laser probes the homogeneous hole burned in the preparation stage. The relaxation rates add together, one from preparation and one from probing, so the signal decays at twice the relaxation rate.⁴⁶

Double Phase Switch

An alternative experimental application of phase switching, known as double phase switching⁴⁷, involves the application of a second phase switch of opposite polarity at a time T after the first phase switch. One can then obtain the dipole dephasing time T_2 , independent of the ratio, $\epsilon = (T_2/T_1)$. The functional dependence of ΔS_2 on the variables T and ϕ is given by⁴⁷

$$\Delta S_2(T, \phi) = \Delta S_1 [[1 - 4 \exp(-2T/T_2) \cos^2(\phi/2)] - 2g(T)(1 - 2\cos^2(\phi/2))],$$

so by setting $\phi = \pi/2$, so that $[1 - 2\cos^2(\phi/2)] = 0$,

one then obtains

$$\Delta S_2(T, \pi/2) = \Delta S_1 [[1 - 2\exp(-2T/T_2)]]. \quad 2.5$$

By considering the second phase switch transient $\Delta S_2(T)$, where T is the time of the second phase shift of $\pi/2$ radians, one can visualize the expected change in the transient signal by regarding two extreme cases. First if $T \gg T_1, T_2$ the first transient response of the sample will have decayed to zero and the second response will be as shown in Figure 3 with $\Delta S_2 = \Delta S_1$. This is because the steady state is approached in a time T which is much greater than T_1 or T_2 . The second limiting case is shown in Figure 4. In this example, the time of the second phase switch T is much less than T_1 or T_2 , $T \ll T_1, T_2$. On that kind of time scale, the nonlinear polarization cannot be much different than it was just before the first phase switch, so $\Delta S_2 \simeq -\Delta S_1$, where ΔS_1 is the change in the nonlinear signal after the first phase switch.

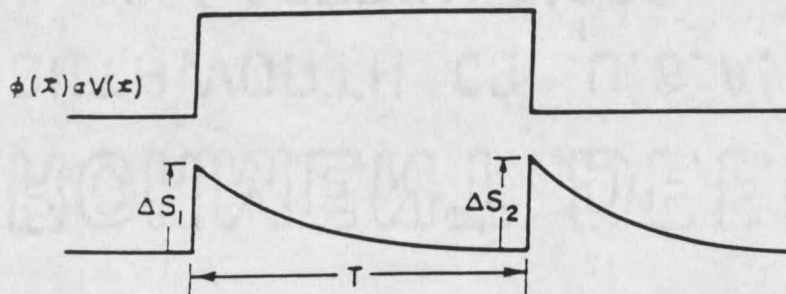


Figure 3: Schematic representation of nonlinear transient absorption. T , the delay between the two phase shifts, is much greater than T_1 or T_2 .

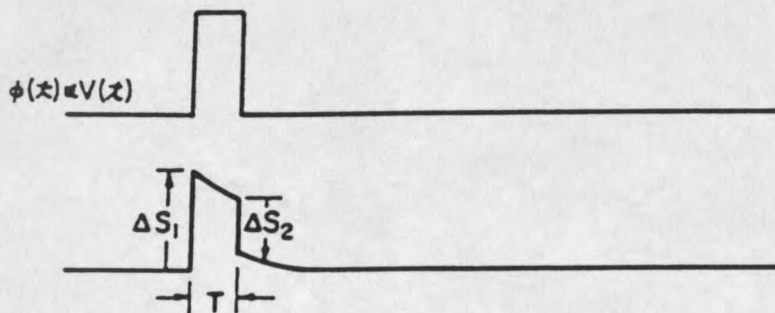


Figure 4: Schematic representation of nonlinear transient absorption. T , the delay between the two phase shifts, is much less than T_1 or T_2 .

From the last two Figures, it is easily seen that the change in the nonlinear signal ΔS_2 changes sign so it must go through zero for some intermediate time $T_0 = T$. By solving equation 2.5 for $T_0 = T$ when $\Delta S_2 = 0$ one obtains an expression which relates the dephasing time to the time at which a second phase shift of $\pi/2$ radians gives no change in the nonlinear signal.

$$T_0 = (T_2/2) \ln(2) \quad 2.6$$

With this method, one can measure the optical dephasing time by varying the time at which a second $\pi/2$ phase switch occurs. The time when the null occurs, $T = T_0$, is then simply related to the dephasing time, with T_2 given by

$$T_2 = (2/\ln(2))T_0(\pi/2).$$

An illustration of this is shown in Figure 5 where the time of the second $\pi/2$ phase switch, T , is increasing from the top of the figure to the bottom of the figure.

The power of the phase switching method lies in its experimental simplicity and applicability in the measurement of fast dephasing times T_2 . The phase is switched by applying a voltage step to an electro-optic modulator in the laser beam. The amount of phase shift is proportional to the amplitude of the voltage step. Typically π radian shifts may be achieved at 70 volts. Since the voltage step is not large, it can be made very fast.

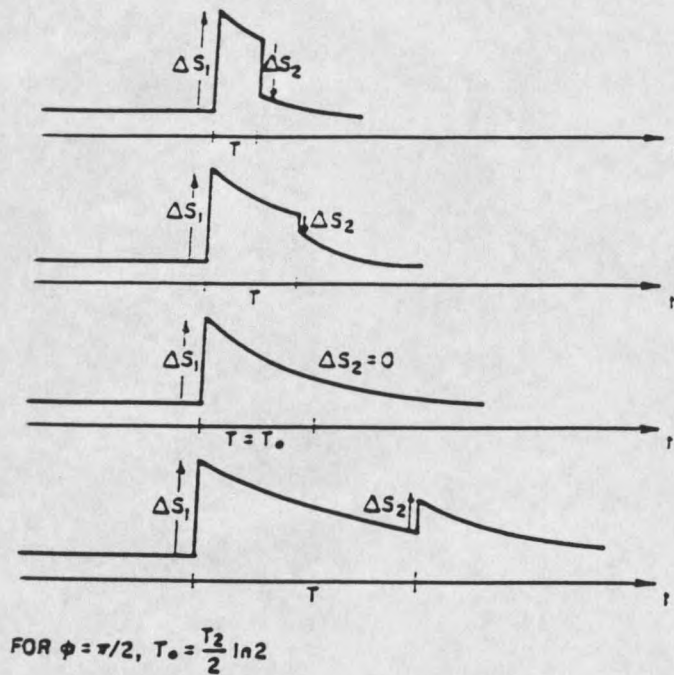
NULL METHOD FOR MEASUREMENT OF T_2 

Figure 5: The transient absorption due to the third order effect is illustrated for increasing delay times between the first and second phase shift. When null occurs in second phase shift $T = (2/\ln 2)T_2$.

A velocity-matched extracavity modulator is used to switch the phase in a time equal to the step rise time which can be as fast as 300 picoseconds depending on the pulser used to generate the voltage step. The light transmitted through the sample is then monitored, and a change in intensity is detected when the phase switch occurs. This is simple in that there is no need to discriminate against the preparation pulses as in the photon echo technique nor is there a need for the larger detection bandwidth of frequency switching transients.

The method of optical phase switching is ideally suited for the measurement of rapid transients, but it is also valid on all longer time scales. The restriction which plays an important role and sets the upper limit, is the laser stability for the duration of the measurement. Most CW dye lasers are actively stabilized to a 1 MHz bandwidth, so the upper limit for a measurement of the dephasing time is approximately 2 microseconds. The reason for this upper limit is that if the laser frequency is changing, during the course of the preparation and probing stages, described earlier, then the decay of the transient signal at twice the dephasing rate is no longer valid. In such a case the result will just display the frequency stability of the laser.

Two other conditions must be met when making measurements with phase switching or double phase switching. One, the expressions for the nonlinear, transient response

require an optically thin sample, $\alpha L \ll 1$, where α is the absorption coefficient and L is the sample length, so that higher order corrections to the nonlinear polarizability can be neglected in the expansion of the nonlinear signal, $\Delta S(t)$. The second condition is that $\chi^2 T_1 T_2 \ll 1$. If this is true, power broadening is negligible, and the transient signal will decay at twice the dipole dephasing rate, but if it is not true the laser will burn a hole in the inhomogeneous profile which is wider than the homogeneous width and this will result in a contribution to the dephasing from different homogeneous packets and a faster apparent dephasing time. If these two conditions, $\alpha L \ll 1$ and $\chi^2 T_1 T_2 \ll 1$, are maintained then phase switched transients can be measured anywhere between 100 picoseconds and 2 microseconds with modern day CW dye lasers.

Chapter 5

SAMPLES AND EXPERIMENTAL APPARATUS

Different samples of $\text{Eu}(\text{OH})_3$ were used in this study to eliminate the possibility of studying a single anomalous crystal. All of the results reported in the following chapters were observed in each of three individual samples. A short description of the samples is followed by a section which details the laser system, the electronics, and the dewars used in this experiment. The last two sections in this chapter respectively describe the particular use of the system in the hole burning and phase switching experiments.

Samples

The $\text{Eu}(\text{OH})_3$ crystals used in the experiments described in the following chapters were grown hydrothermally by S. Mroczkowski with a technique developed by H.E. Meisner.^{48,49} These crystals were obtained from Professor W.P. Wolf of Yale University. The samples are clear, colorless, hexagonal needle shaped crystals with typical dimensions of 2 or 3 millimeters long and a diameter of approximately 0.3 millimeters. The europium ions in these crystals have C_{3h} site symmetry and the threefold c axis corresponds to the needle axis of the crystal.

Laser and general apparatus

A Coherent Radiation 599-21 CW dye laser, mounted on a Newport Research Corporation 4'x10' optical table with pneumatic vibration isolation, was used for all the experiments reported here. This laser consists of a 2 inch solid bar of Invar which serves as the optical bench for the components of the dye laser. The basic configuration is a three-mirror cavity⁵⁰ in which the pump beam is focused on the dye in a direction that is not collinear with the cavity. This laser system has a linewidth of $1/4 \text{ \AA}$ or 20 GHz when used with a three plate birefringent filter. The bandwidth is narrowed by the insertion into the cavity of two etalons and by the electronic control of a Brewster intracavity tipping plate and a piezoelectrically mounted fold mirror. These last two elements control the length of the dye cavity thereby controlling the frequency to within 1 MHz effective linewidth. The laser has a 30 GHz, 1 cm^{-1} , continuous scan range which can be controlled internally, or externally through an input connector to the control box. Rhodamine 6G dye was used in the laser and was water cooled to improve the stability, with typical output powers in the range between 40 and 50 milliwatts at the wavelength of interest.

Wavelength measurements were made with a Spex #14018, 0.85 meter, Czerny-Turner Double Monochromator. This monochromator has two 1800 groove/mm holographic gratings

and it will be referred to as simply the Spex monochromator in the following chapter. Also used in the Zeeman shift measurements was a McPherson Model #218 0.3 meter monochromator with a 1200 groove/mm grating blazed at 5000 Å.

In simple fluorescence excitation experiments, light from the monochromators was detected with a photomultiplier tube and a Keithley 416 picoammeter, the output of which was monitored and stored in a Northern Scientific 575 multi-channel analyzer. The stored data could then be transferred to the CRDS MF-211 (DEC LSI 11) computer for analysis. In the hole burning experiments, the photomultiplier tube output current was monitored directly by the NS-575 where the data was stored and averaged.

In the phase switch experiments the signal was detected with a EG&G FND-100 photodiode. The ${}^7F_0 \longleftrightarrow {}^5D_0$ transition in $\text{Eu}(\text{OH})_3$ was initially identified in the fluorescence excitation mode with the crystal mounted in a three window glass dewar by Pope Scientific. For all the experiments reported here, however, the crystal was mounted in a superconducting solenoid dewar constructed in this lab. The superconducting solenoid was constructed by American Magnetics, with a maximum field rating of 60 kilogauss or 6.0 Tesla.

Hole Burning-Experimental Details

For the hole burning experiments, the burn-read cycle was a computer generated modulated triangular wave so that the laser would repetitively burn and read a hole for signal averaging purposes. The computer was interfaced to a digital-to-analog converter, and this output then scanned the laser. The computer program which controlled the laser is listed in Appendix I. This computer program also controlled the acousto-optic modulator by generating a 1 volt output while the laser was burning, and generating a voltage between 0 and 1 volt while the laser was reading the hole. The amount of light in the read portion of the beam being determined by the equation $I = I_0 \sin^2(\pi V/2)$. A schematic diagram of the experimental arrangement for the hole burning measurements is shown in Figure 6. Also shown at the bottom of Figure 6, is a schematic representation of the modulated triangular wave used to drive the dye laser, and the computer generated burn-read pulses used in controlling the acousto-optic modulator. Because of the long lived holes in $\text{Eu}(\text{OH})_3$, to be discussed in Chapter 6, it was also necessary to erase each hole before making a new measurement. Appendix II is a listing of the computer program which was used to erase a spectral hole.

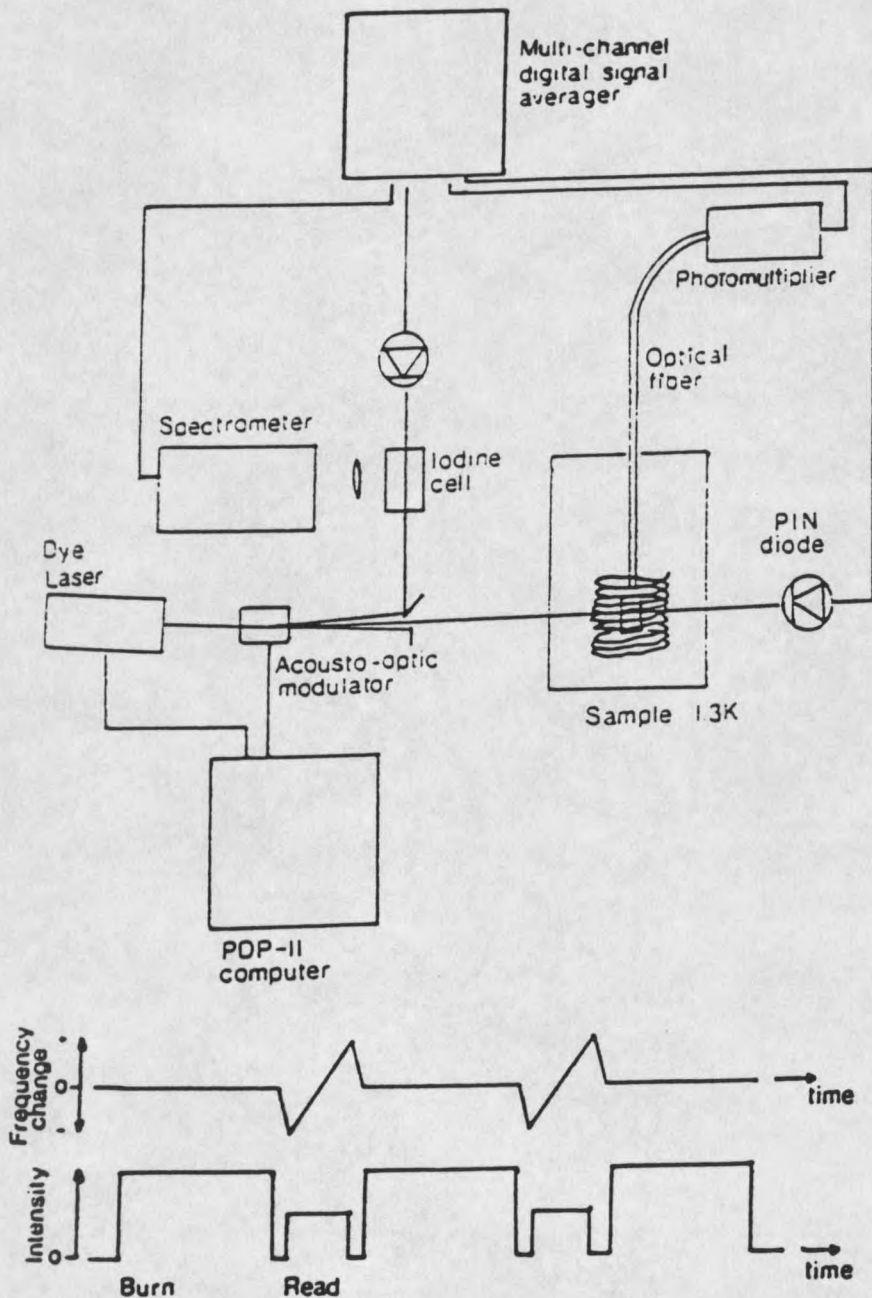


Figure 6: Schematic diagram of hole burning experiment. Computer generated, scan of Dye laser, and Acousto-optic modulator pulses shown at the bottom. The iodine vapor cell used in the Zeeman shift measurements is also shown.

Phase Switching-Experimental Details

A schematic drawing of the optical phase switching experiment is shown in Figure 7. The optical phase switch was accomplished with a Lasermetrics, Inc. Model 3126A phase/frequency modulator. This device consists of a lithium tantalate crystal of dimension 0.5 mm x 0.65 mm x 25 mm. The end faces are polished and antireflection coated. Gold electrodes deposited on the upper and lower faces form a parallel-plate transmission line. The ratio of height to width of the crystal (0.65 mm to 0.50 mm) was chosen so that the crystal appears to be a 50 Ω transmission line, given the microwave dielectric constant of lithium tantalate ($\epsilon=43$).⁵¹ With correct impedance matching, this modulator is a velocity matched device in which the rise time of the dc square wave pulse is as fast as the transit time of light through the crystal. The phase shift generated by this modulator is proportional to the laser wavelength, the length of the crystal, the electro-optic index of the crystal, and inversely proportional to the thickness. Therefore the crystal is chosen to be as thin as possible. The induced phase shift from manufacturer's specifications is $26.2/\lambda$ milliradians/volt which works out to $2.57^\circ/\text{volt}$ at the ${}^7F_0 \longleftrightarrow {}^5D_0$ transition wavelength of 5805 Å. A 10 cm lens was used to focus the laser beam through the LiTaO₃ modulator. It was then recollimated with another 10 cm lens. This resulted in a waist in the modulator of 48

microns, a confocal parameter $b = 2\pi\omega_0^2/\lambda$ of 26 mm, and a beam diameter of 150 microns at the entrance and exit faces of the crystal. As a result of the small aperture, the crystal must be aligned to within an angle of approximately 2 milliradians and positioned to within 100 microns to avoid beam distortion. The alignment of the modulator is probably the most difficult part of doing a phase switched experiment.

To provide the voltage pulse to the electro-optic modulator a Tektronix Model 109 reed relay pulser with 150 picosecond rise time and 700 Hz repetition rate was used in the initial experiments. In later experiments, it was necessary to have longer pulses and control of the pulse repetition rate. A pulser was then designed which could be triggered externally. This pulser would provide pulses of up to 80 volts, using n-channel enhancement-mode VMOS power FETs in a push-pull arrangement, with 10 nanosecond rise and fall times. The pulse length in this pulser could be varied by interchanging digital delay lines in the circuit.

In the phase switching experiments, the laser was scanned between each averaged shot of the phase switched transient. This was done, as in the hole burning experiments, by driving the laser externally with the CRDS MF-211 (DEC LSI 11) computer in the laboratory. The scan was accomplished by generating a triangular wave. The computer program which drives the dye laser during a phase switch

experiment is given in Appendix III. This program is essentially the same as the program for hole burning, Appendix I, except the burn pulse was very short, 2-10 μ sec. Since the rise time of the D/A converter was not fast enough to be used on these time scales, a pulser was constructed from 74121 monostable multivibrators. With this pulser the A/O pulse and the phase switch pulse had fast rise times and could be controlled independently. The light transmitted through the crystal was monitored with an EG+G FND-100 PIN photodiode with 90 volt reverse bias and a rise time of less than 1 nsec. The transient signal, due to the phase switch, was stored and averaged with a Tektronix 7912AD transient digitizer which was interfaced to the computer to transfer the averaged data.

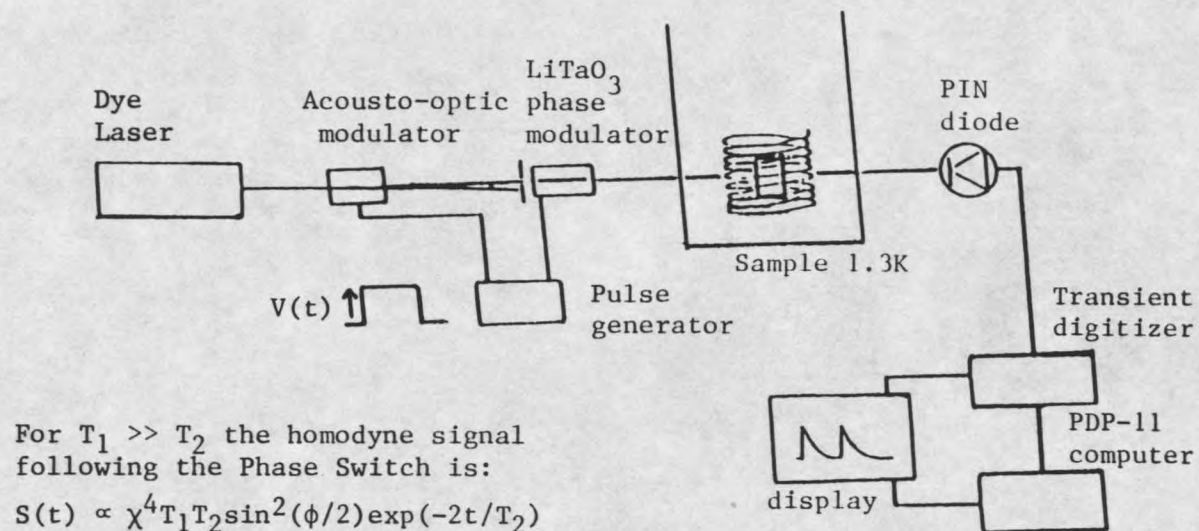


Figure 7: Schematic diagram of Phase Switched transient experiment in $\text{Eu}(\text{OH})_3$

Chapter 6

EXPERIMENTAL RESULTS

Linewidth

The first experiments on $\text{Eu}(\text{OH})_3$ were performed in the fluorescence excitation mode in a glass dewar at 1.3 K. In this mode the laser was scanned through a frequency range containing the absorption transition ${}^7\text{F}_0 \longrightarrow {}^5\text{D}_0$ while the fluorescence was monitored for the transition from ${}^5\text{D}_0$ to ${}^7\text{F}_1$ $\mu=\pm 1$. This identified the transition which showed three fluorescence excitation lines in a 25 GHz frequency range.

It is well known that if local sites are perturbed, due to defects, impurities, or dislocations in the crystal, this can lead to a perturbation of the rare earth site symmetry. When this occurs, more than one transition will appear in the fluorescence excitation spectrum. The fact that there were three lines observed in the spectrum then implied that the europium site symmetry can be perturbed in several different ways, but observations in EuVO_4 ^{3,4} indicate that there are at least 30 different ways to disturb the site symmetry in that case. The small number of extra lines indicates that our crystals were of very high quality. This initial identification of the ${}^7\text{F}_0 \longrightarrow {}^5\text{D}_0$ transition indicated that all three lines were extremely narrow,

ranging between 167 MHz and 670 MHz full width at half maximum, FWHM.

Typical line widths in many rare earth compounds are between 15 GHz and 30 GHz wide. In Eu^{3+} compounds however the ${}^7\text{F}_0 \longleftrightarrow {}^5\text{D}_0$ transition is usually narrower than for other rare earth transitions. Previously, the narrowest known inhomogeneous width for this transition, 3.5 GHz, was measured in the $\text{EuP}_5\text{O}_{10}$ compound.⁵² This narrow inhomogeneous profile can be understood in first order because the ground state electronic level is non-magnetic. Thus the $J=0$ ground state is not magnetically affected by its nearest neighbors or next nearest neighbors as a magnetic ion would be affected. The narrowest of these lines, 167 MHz wide, is exceptionally narrow compared to transitions in other rare earth materials.

To investigate this further, several different crystals were taken to the IBM Research Laboratory for experiments in collaboration with Roger Macfarlane, Bob Shelby, and Gary Bjorklund. Gary Bjorklund has developed a technique called FM spectroscopy⁵³ capable of measuring very weak absorption. In using this technique the laser beam is frequency modulated. The laser beam side band frequencies will normally be of the same intensity, but as the laser scans into an absorption profile, one sideband becomes weaker than the other. Heterodyne detection of the beats between the

modulated and unmodulated portions of the laser beam, allows the detection of very weak absorption lines. This experiment did not show any absorption, which means that the ${}^7F_0 \longrightarrow {}^5D_0$ transition in $\text{Eu}(\text{OH})_3$ absorbs less than one part in one thousand of the light in the laser beam. Although this experiment did not add anything new to the information on this transition in $\text{Eu}(\text{OH})_3$, it did reconfirm the fact that there were three transitions in the neighborhood, and the narrowest of the three was 167 MHz FWHM.

Isotope Shift

By measuring the quadratic dependence of the absorption strength, as discussed in the next section of this chapter, it was possible to determine that the narrowest line, 167 MHz FWHM, was the intrinsic line associated with an unperturbed axial site in the $\text{Eu}(\text{OH})_3$ crystal. This narrow line is most interesting because it shows structure which could be associated with the superposition of two different lines. Since the ${}^7F_0$ ground state and the ${}^5D_0$ excited state are each singlet states, this apparent splitting can be the result of several different perturbations. The first of these to be considered would be perturbed sites or strains in the crystalline lattice. The observed quadratic dependence of the oscillator strength on the magnetic field, as discussed in the following section, makes this an unlikely explanation for the structure however. Another possibility is a nuclear splitting of the electronic ground

state. On the basis of the hole burning measurements in the last section of this chapter this can also be eliminated as the cause of structure in the inhomogeneous profile. Finally, the structure may be associated with an isotope shift of the spectral line. There are two stable europium isotopes, ^{153}Eu and ^{151}Eu , with abundances of 52.18% and 47.82% respectively. Isotope shifts in solid state materials have never been seen in a clearly resolved way because these shifts are small compared with the inhomogeneous linewidth of the optical transitions. Because the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition is so narrow in $\text{Eu}(\text{OH})_3$, it may be the first time in which there is clear evidence of an isotope shift. It may also provide the first clear chance to measure this shift and compare it with the theoretical estimates that exist.⁵⁴

Figure 8, shows the experimental line shape in fluorescence excitation for the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition in $\text{Eu}(\text{OH})_3$. The FWHM of this line is 167 MHz and the best fit for the superposition of the two gaussian peaks is shown in Figure 9. These two gaussian lines each have FWHM of 96 MHz with the low energy peak on the left accounting for 54% of the total area and the high energy peak on the right accounting for 46% of the total area.

Although this is not a perfect match with the isotope abundances, it does provide some motivation for

further experiments to measure this shift and compare the results with current measurements⁵⁵ and theories.⁵⁴

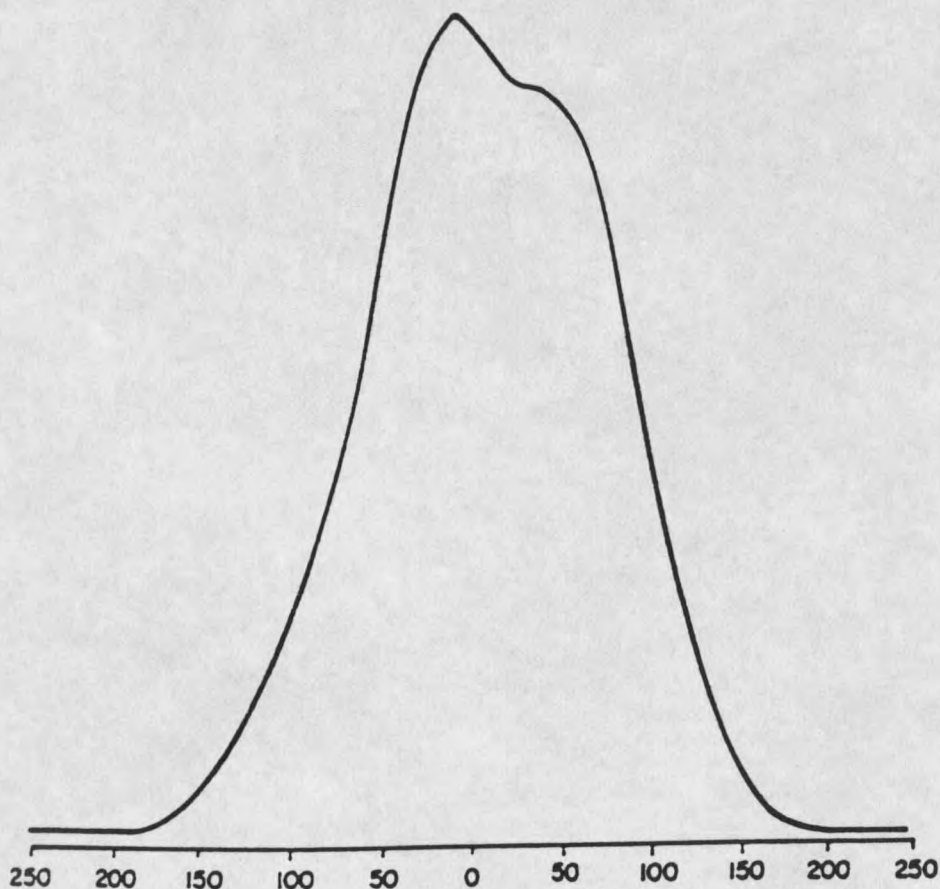


Figure 8: Experimental line shape of the $7F_0 \rightarrow 5D_0$ fluorescence excitation line in $\text{Eu}(\text{OH})_3$.
FWHM = 167 MHz.

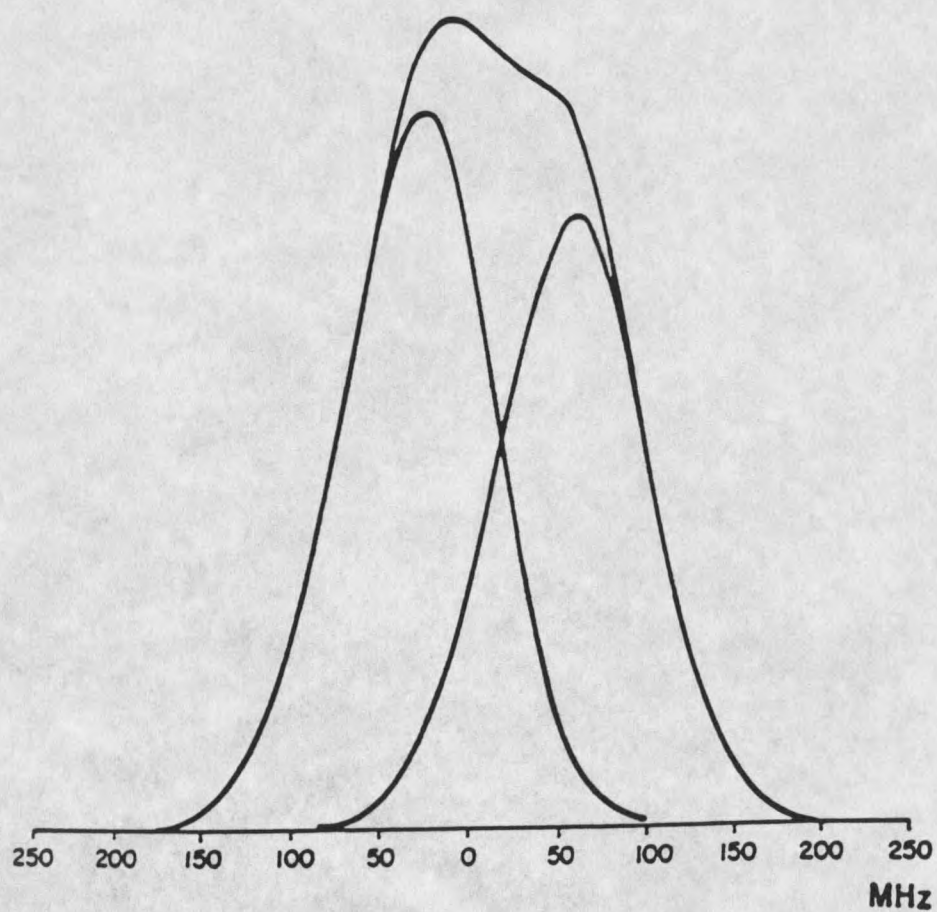


Figure 9:

Best fit superposition of two gaussian peaks. Peak on the left, high energy side, 54% of total area. Peak on the right 46% of total area. Isotope abundances, ^{153}Eu 52.2%, ^{151}Eu 47.8%.

Quadratic Magnetic Field Dependence

Optical transitions in the immediate vicinity of a crystal field transition can be interpreted in terms of defect sites adjacent to the optically active rare earth ion. The defect sites create a local distortion and thereby a different crystal field. This small change in the crystalline field then leads to a change in the energy levels of the perturbed site.

A distortion of the crystalline field due to a defect will affect the symmetry associated with the crystalline potential. For some symmetries,^{5 6} an odd harmonic term can exist in the crystal field expansion. If these terms exist, forced electric dipole optical transitions between the crystal field levels are possible. Experimental measurements have shown that the ${}^7F_0 \longleftrightarrow {}^5D_0$ transition of the Eu^{3+} ion often appears when it is allowed by the site symmetry.^{5 7} The intensity of forced electric dipole transitions are in many cases the same order of magnitude as allowed magnetic dipole transitions. This makes it very difficult to identify the intrinsic crystal field transition in many crystals.

Enhancement

It was realized, with the help of Dr. Cone, that if one of these transitions was the intrinsic transition, an applied magnetic field would enhance the magnetic dipole transition strength through the admixture of the nearby ${}^7F_1$ states into the ${}^7F_0$ ground state (see Figure 1). This admixture of $J=1$ states into the $J=0$ state would then result in an oscillator strength for the ${}^7F_0-{}^5D_0$ transition which should vary as the square of the magnetic field strength.

Experimentally this enhancement was easily identified. One $\text{Eu}(\text{OH})_3$ crystal was mounted in the superconducting magnet dewar with the c-axis of the crystal parallel to the magnetic field axis. The beam was focused to a diameter of 60 microns and was placed in the sample along a line perpendicular to the c-axis of the crystal. By monitoring the fluorescence excitation signal as a function of the magnetic field, it was obvious that there was a very dramatic effect when the magnetic field was changed. With the photomultiplier voltage adjusted for a full scale deflection at zero field, a number 2 neutral density filter was inserted in front of the Spex monochromator in order to keep the signal on scale with a magnetic field of 20 kG. At 50 kilogauss the fluorescence excitation signal had changed by almost three orders of magnitude and a number 3 neutral density filter was used to avoid saturating the photomultiplier tube.

This phenomenal change as a function of magnetic field implied that the ${}^7F_0 \rightarrow {}^5D_0$ absorption could be directly detected. This was easily done by monitoring the laser light transmitted through the crystal with an EG + G FND-100 PIN photodiode. The result, shown in Figure 10, demonstrates the change that occurred. The transition could only be detected in fluorescence excitation at zero magnetic field. There was no detectable absorption at zero field. In a field of 50 kilogauss, however, this 300 micron thick crystal would absorb almost 45% of the laser light.

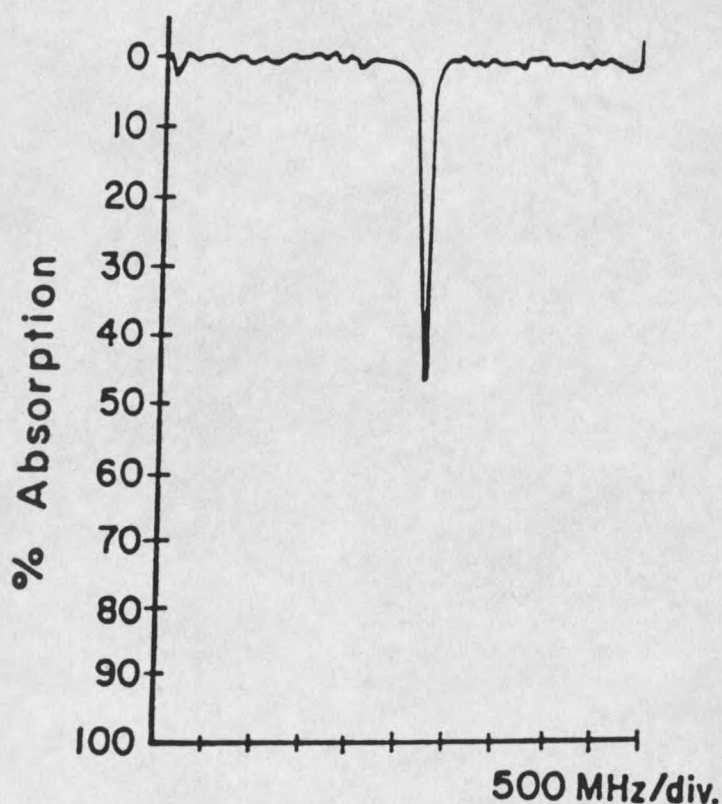


Figure 10: ${}^7F_0 \rightarrow {}^5D_0$ absorption profile of $\text{Eu}(\text{OH})_3$ crystal at 1.3 K in a 50 kgauss magnetic field.

Although this did demonstrate a large physical change, further measurements were made in order to be sure this change was quadratically dependent on the field strength. The absorption profile was recorded as a function of magnetic field strength. The raw data was transformed from transmitted intensity into absorption coefficient, $\alpha(\omega)$, using Beer's law

$$I(\omega) = I_0 e^{-\alpha(\omega)L}$$

which implies

$$\alpha(\omega) = \ln(I_0/I(\omega))/L$$

where $\alpha(\omega)$ is the absorption coefficient in inverse centimeters, I_0 is the laser intensity, $I(\omega)$ is the transmitted laser intensity, and $L = 0.03$ cm, is the crystal thickness. A plot of the result for 5 kG increments from 10 kG to 50 kG is given in Figure 11. Plotting the maximum absorption coefficient as a function of the magnetic field then gives the result shown in Figure 12. This is a log-log plot and the line through the data points has a slope of 2.0. This then establishes the quadratic dependence of the absorption coefficient, or oscillator strength, on the magnetic field strength.

As a further check, this was repeated by measuring the absorption coefficient with the magnetic field perpendicular to the c-axis of the crystal. This also varies as the square of the magnetic field as illustrated in Figure 13 with $\alpha(\omega)$ at each field plotted in Figure 14.

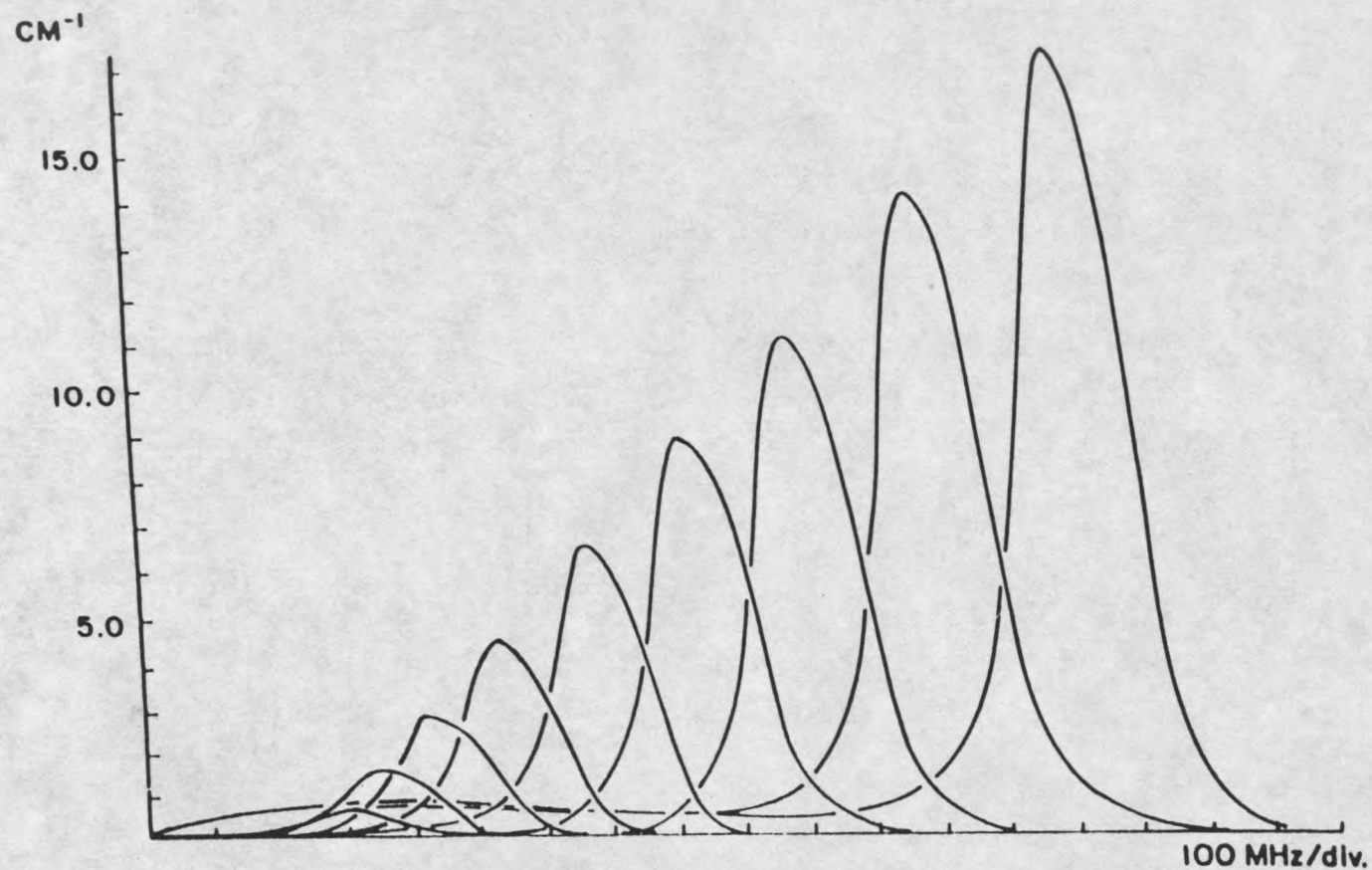


Figure 11: Absorption coefficient, $a(\omega)$, in inverse centimeters. Magnetic field changed in 0.5 Tesla increments between 1.0 T and 5.0 T. Magnetic field parallel to c-axis, $B \parallel c$.

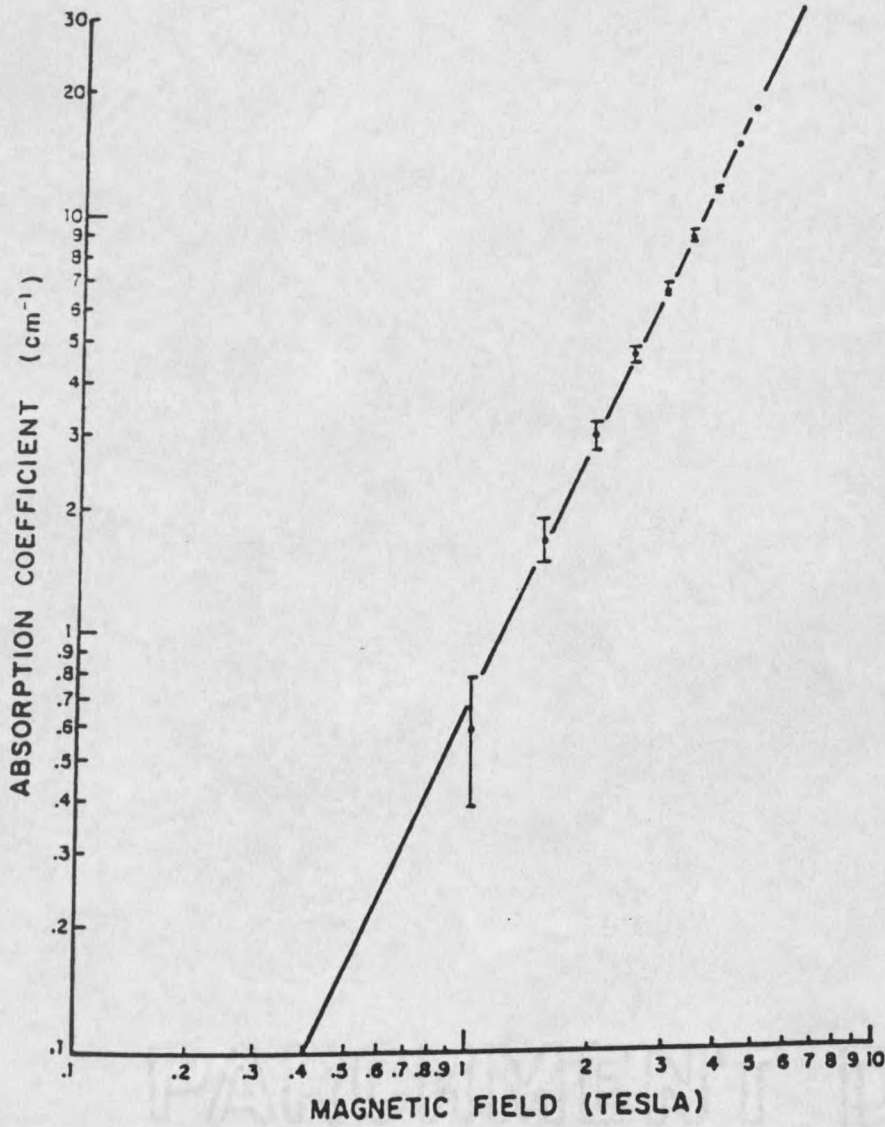


Figure 12: Maximum absorption coefficient, $\alpha(\omega)_{\max}$, with magnetic field parallel to c-axis, $B \parallel c$. Slope= 2.0.

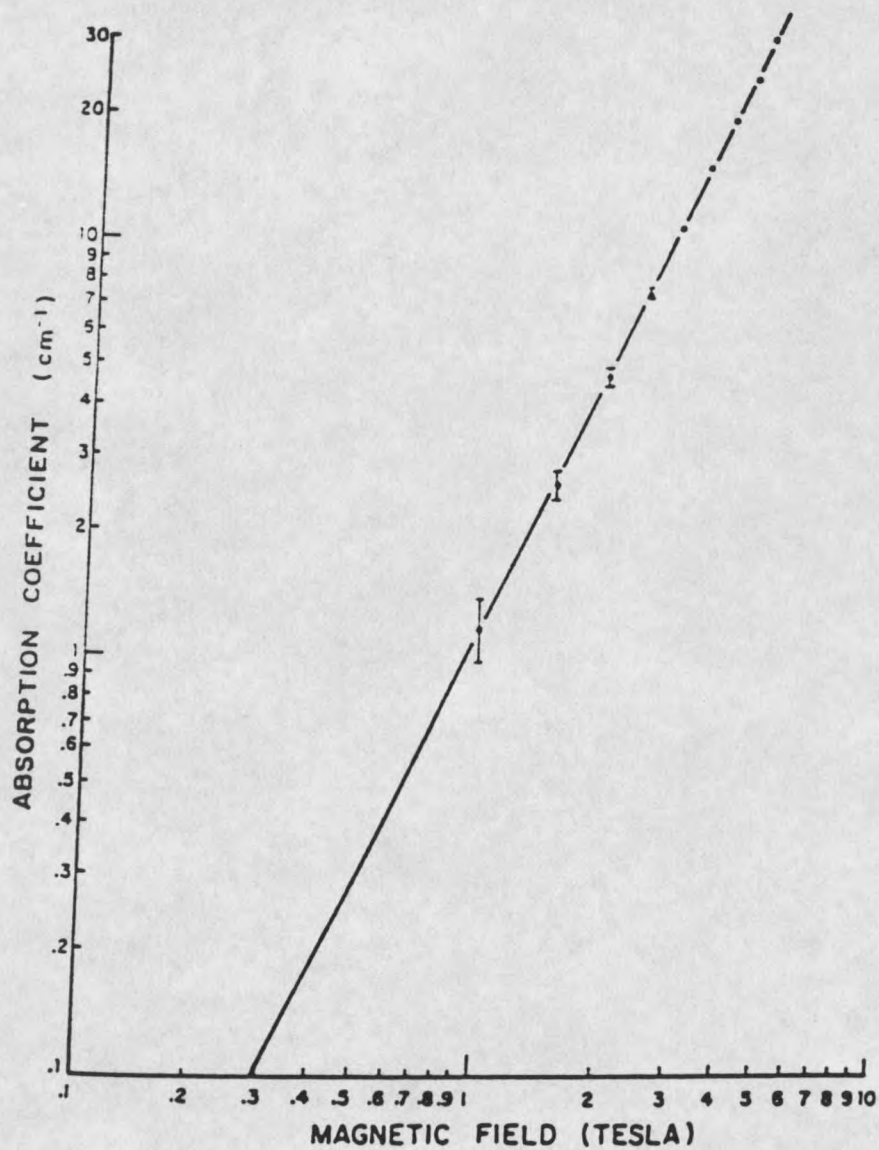


Figure 13: Maximum absorption coefficient, $\alpha(\omega)_{\max}$, with magnetic field perpendicular to c-axis, $B \perp c$. Slope = 2.0.

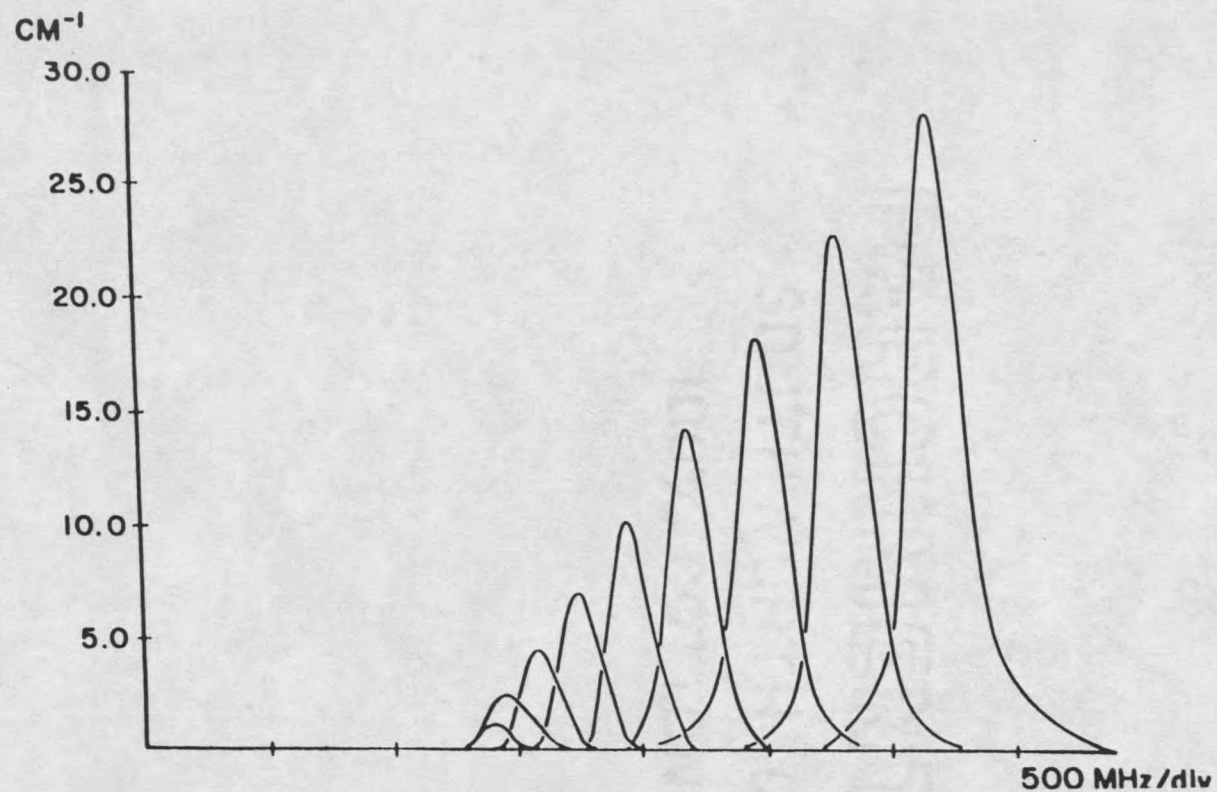


Figure 14: Absorption coefficient, $\alpha(\omega)$, in inverse centimeters. Magnetic field changed in 0.5 Tesla increments between 1.0 T and 5.0 T. Magnetic field perpendicular to c-axis.

Two things should be noted in the last four figures. From Figure 12 and Figure 13 the maximum absorption coefficient at 50 kG is 17.0 cm^{-1} for $B \parallel c$ in Figure 12 and 28.6 cm^{-1} for $B \perp c$ in Figure 13. From perturbation theory, one would expect the change to be proportional to the inverse of the energy difference. Since the ${}^7F_0 \mu=1$ energy level at 339 cm^{-1} is closer to the ground state than the ${}^7F_0 \mu=0$ state at 440.5 cm^{-1} , it makes sense that the absorption coefficient is larger for the admixture with the $\mu=1$ energy level. The other thing to notice is that in Figures 11 and 14, the absorption profile is plotted with frequency on the horizontal axis. This frequency shift as a function of field can be calculated from second order perturbation theory also, and will be discussed in detail in the Zeeman shift section of this chapter.

Oscillator Strength

From the absorption data, the oscillator strength or f number can also be calculated. This calculation is important because this number had been calculated on a computer by Dr. Cone, and a comparison of the two numbers would indicate the accuracy of the interpretation concerning this magnetic field dependent admixture of the $J=1$ crystal field states into the $J=0$ state.

For the computer calculation, the magnetic moment operator in the Russell-Saunders coupling case, was transformed into the intermediate coupling representation

using the free ion wave functions of Carnall and Crosswhite.⁵⁸ This gave the intermediate coupling magnetic moment operator between the $^7F_1$ and $^5D_0$ states. From this the oscillator strength could be calculated using standard techniques⁵⁹

$$f_{MD} = (8\pi^2 mc / 3he^2) k |(-e/2mc) \langle F_{10} | L+2S | D_{00} \rangle|^2 n$$

$$f_{MD} = (4.028 \times 10^{-11}) k n |\langle F_{10} | L+2S | D_{00} \rangle|^2$$

where k is the transition energy in wavenumbers, $k=16785\text{cm}^{-1}$ and n is the index of refraction, $n = 1.5$. The computer result for the transition $^7F_1 \rightarrow ^5D_0$, was

$$|\langle F_{10} | L+2S | D_{00} \rangle|^2 = (0.201)^2$$

This results in an oscillator strength of $f_{MD} = 4.09 \times 10^{-8}$ for the $^5D_0 \rightarrow ^7F_1$ transition and by including the admixture factor of $(0.0032)^2$, the resulting oscillator strength for the $^5D_0 \rightarrow ^7F_0$ transition at 15 kG is

$$f_{MD} = 4.1 \times 10^{-13}$$

The experimental oscillator strength can also be calculated by standard techniques⁶⁰

$$f_{MD} = (2mce_0 / \pi e^2 h) (1/n) (1/N_0) \int \alpha(\omega) d\omega$$

$$f_{MD} = 4.00 \times 10^9 / N_0 \int \alpha(\omega) d\omega$$

From the lattice constants $a = 6.32 \text{ \AA}$ and $c = 3.63 \text{ \AA}$ ⁶¹ the number density of europium ions can be calculated,

$$N_0 = 7.965 \times 10^{21} \text{ ions/cm}^3$$

and the integration of the absorption coefficient over the

experimental profile gives

$$\int \alpha(\omega) d\omega = 0.705 \text{ cm}^{-1} \text{ GHz} .$$

This implies an experimental oscillator strength of

$$f_{\text{MD}} = 3.54 \times 10^{-13} .$$

The computer calculation of the oscillator strength is dependent on the small admixture coefficients of states which result in nonzero matrix elements of the magnetic dipole operator, $L + 2S$. This means the magnitude of the calculated oscillator strength can easily vary by an order of magnitude. Considering this, the agreement between the measured and calculated oscillator strengths is excellent. This agreement, with the quadratic dependence, is another confirmation of this admixture process in $\text{Eu}(\text{OH})_3$.

Electronic Zeeman Shift

As mentioned in the previous chapter, perturbation theory predicts a correction to the ground state wave function and energy. This change appears as a Zeeman shift in the energy which is proportional to the square of the magnetic field strength. Because the inhomogeneous line width is so narrow, the following calculation demonstrates that $\text{Eu}(\text{OH})_3$ presents an ideal opportunity to measure the calculated intermediate coupling matrix element.

From any quantum mechanics text^{6,2} the second order correction to the energy is given by

$$\Delta E = \langle F_{00} | H_1 | F_{00} \rangle + |\langle F_{00} | H_1 | F_{10} \rangle|^2 / (E_{00} - E_{10})$$

where F_{00} and E_{00} are the ground state wave function, $J=0$ and $\mu=0$, and energy, $E_{00}=0$, respectively, and where the wave function of the J, μ crystal field level is denoted by $F_{J\mu}$, and the energy by $E_{J\mu}$. The perturbation H_1 has no diagonal matrix elements, so $\langle F_{00} | H_1 | F_{00} \rangle$ equals zero and the energy shift, or Zeeman shift is then

$$\Delta E = |\langle F_{00} | H_1 | F_{10} \rangle|^2 / (E_{00} - E_{10})$$

where H_1 is the Zeeman term in the Hamiltonian which can be written

$$H_1 = (e/2mc) \vec{B} \cdot (\vec{L} + 2\vec{S}) = \mu_B B (L_z + 2S_z)$$

and $\mu_B = e\hbar/2mc$ is the Bohr magneton. B is the applied

magnetic field, $B = B_z$, and $(L_z + 2S_z)$ is the magnetic moment operator. In LS or Russell-Saunders coupling the matrix element is $\langle F_{00} | L_z + g_s S_z | F_{10} \rangle = 2.00232.^{59}$

The ${}^7F_1$ $\mu=0$ energy level is 440.5 cm^{-1} above the ground state ${}^7F_0$, and the Bohr magneton is $\mu_B = (1/21.42) \text{ cm}^{-1}$ per kilogauss, so the change in energy is

$$\begin{aligned} \Delta E &= -(2\mu_B B)^2 / 440.5 \text{ cm}^{-1} \\ &= -(2/21.42)^2 (\text{cm}^{-1})^2 / (\text{kG})^2 (1/440.5 \text{ cm}^{-1}) B^2 \\ &= -(1.979 \times 10^{-5} \text{ cm}^{-1} / (\text{kG})^2) B^2 \end{aligned}$$

$$\Delta E = -(0.59374 \text{ MHz} / (\text{kG})^2) B^2$$

This implies a total Zeeman shift of only 1484 MHz for a field of 50 kilogauss. This is an extremely small change in energy, and if it were not for the fact that the linewidth for this transition in $\text{Eu}(\text{OH})_3$ is so small, 167 MHz, it would be impossible to measure. This lucky coincidence, narrow linewidth, means that one has an ideal opportunity to check the interpretation and understanding of this admixture process.

Measurements of this Zeeman shift, which will be described in detail presently, gave a total energy shift of $1265 \text{ MHz} \pm 30 \text{ MHz}$. To compare the calculations with this number, the elements for the LS coupling case were transformed into the intermediate coupling representation and this calculation resulted in a new value of the matrix element,

$$\langle F_{00} | (L_z + 2S_z) | F_{10} \rangle = 1.965.$$

One must also realize that an external magnetic field also causes an admixture of $J=1$ states into the $J=0$ excited state, $^5D_0$. A similar calculation for the excited states gives a matrix element,

$$\langle D_{00} | (L_z + 2S_z) | D_{10} \rangle = 1.280,$$

for the excited state admixture. So the energy shift for the excited state is in the same direction but much smaller because the $^5D_1 \mu=0$ excited state is 1771 cm^{-1} higher in energy than the $^5D_0$ excited state.

$$\Delta E = (1.280/21.42)^2 B^2 (30,000 \text{ MHz/cm}^{-1}) / (-1771 \text{ cm}^{-1})$$

$$\Delta E = -151 \text{ MHz at } 50 \text{ kG}$$

Since each of the energy levels is depressed as the magnetic field strength increases, the measured Zeeman shift will be the difference given by

$$\Delta E = (1433 - 151) \text{ MHz} = 1282 \text{ MHz}$$

which compares very well with the measured Zeeman shift of $1265 \text{ MHz} \pm 30 \text{ MHz}$.

Magnetic Field Parallel to c-axis

To measure an energy shift this small, two things are required; one that has already been mentioned, is the very narrow inhomogeneous width of the ${}^7F_0 \longleftrightarrow {}^5D_0$ transition in $\text{Eu}(\text{OH})_3$. The other is an absolute frequency calibration for the laser. This is necessary because the 599-21 CW-dye laser is only stable to within ± 100 MHz/hour and a measurement of the Zeeman shift can only be completed in a one to two hour time period. The time is necessary to change the magnetic field in 5 kilogauss increments, because recording the frequency shift at each field takes about one minute. To avoid frequency drift between scans, the Zeeman shift measurements were made by simultaneously recording the fluorescence excitation signal from the $\text{Eu}(\text{OH})_3$ sample, and the fluorescence excitation signal from a 10 cm. glass cylinder filled with iodine vapor at a pressure of approximately 100 millitorr. The schematic diagram of this experiment was shown in Figure 6, where two different inputs of the multi-channel analyzer recorded the spectrum from the sample and iodine cell simultaneously. An example of this is shown in Figure 15, where the $\text{Eu}(\text{OH})_3$ absorption spectrum at 50 kG is shown in Figure 15(a) and the absorption spectrum of I_2 vapor is shown in Figure 15(b). This gives both a relative and an absolute calibration of the frequency as a function of field. The result shown in Figure 16 is

the Zeeman shift of the ${}^7F_0$ to ${}^5D_0$ absorption at 5 kilogauss increments between 50 kilogauss and 10 kilogauss. This is plotted on a log-log graph, again showing the quadratic dependence on the magnetic field strength. More accurate measurements can be made by monitoring the fluorescence excitation signal because in that case there is adequate sensitivity to record the signal right down to zero magnetic field. The measurement for the fluorescence excitation is shown in Figure 17, from which the Zeeman shift of $1265 \text{ MHz} \pm 30 \text{ MHz}$ was quoted, for the magnetic field parallel to the c-axis of the crystal.

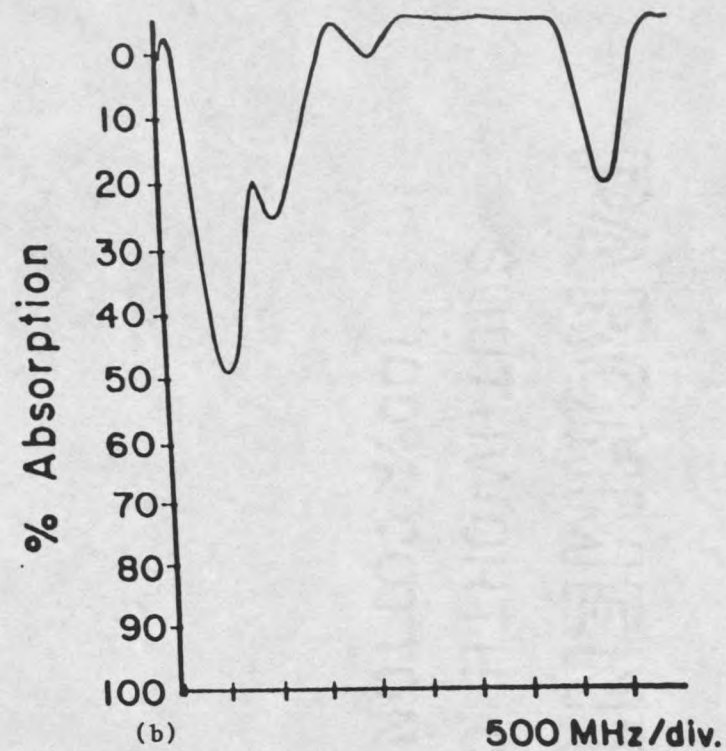
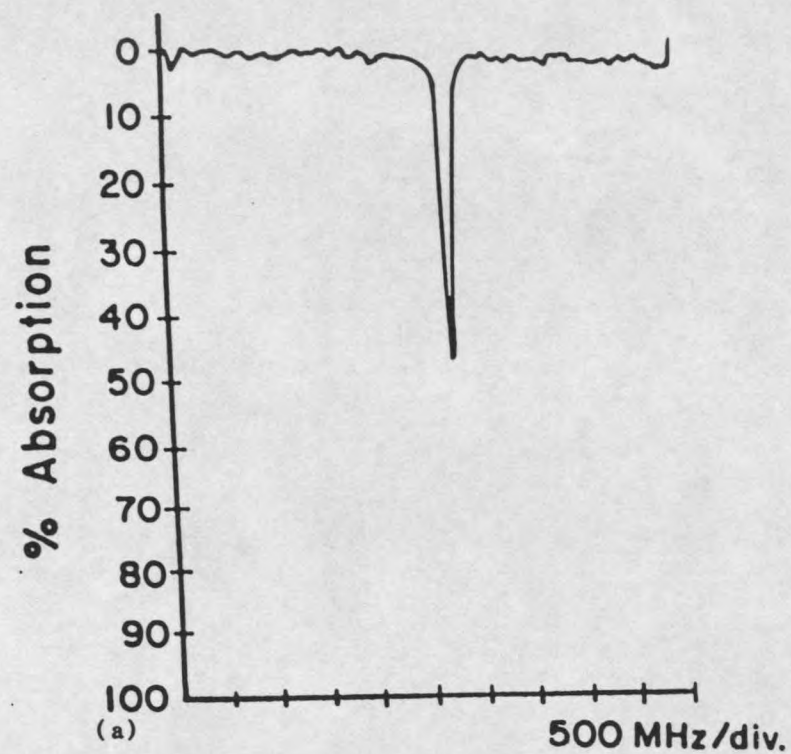


Figure 15: Simultaneous absorption spectra of $\text{Eu}(\text{OH})_3$ and I_2 vapor.
 (a) Absorption spectrum of $7F_0 \rightarrow 5D_0$ transition in $\text{Eu}(\text{OH})_3$ in a magnetic field of 50 kG.
 (b) Absorption spectrum of I_2 vapor

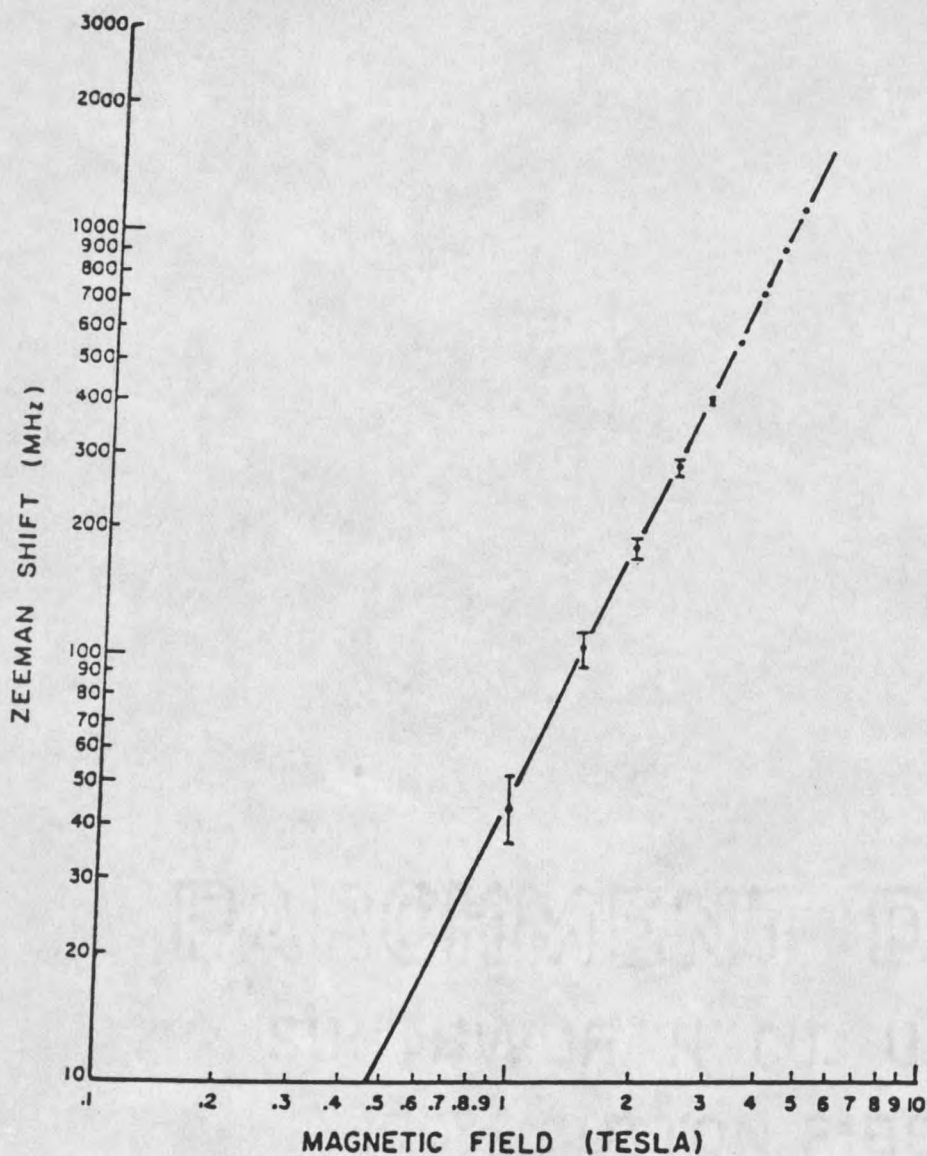


Figure 16: Electronic Zeeman shift of the ${}^7F_0 \rightarrow {}^5D_0$ absorption spectrum in $\text{Eu}(\text{OH})_3$. Data points every 0.5 Tesla between 1.0 T and 5.0 T. $B \parallel c$.

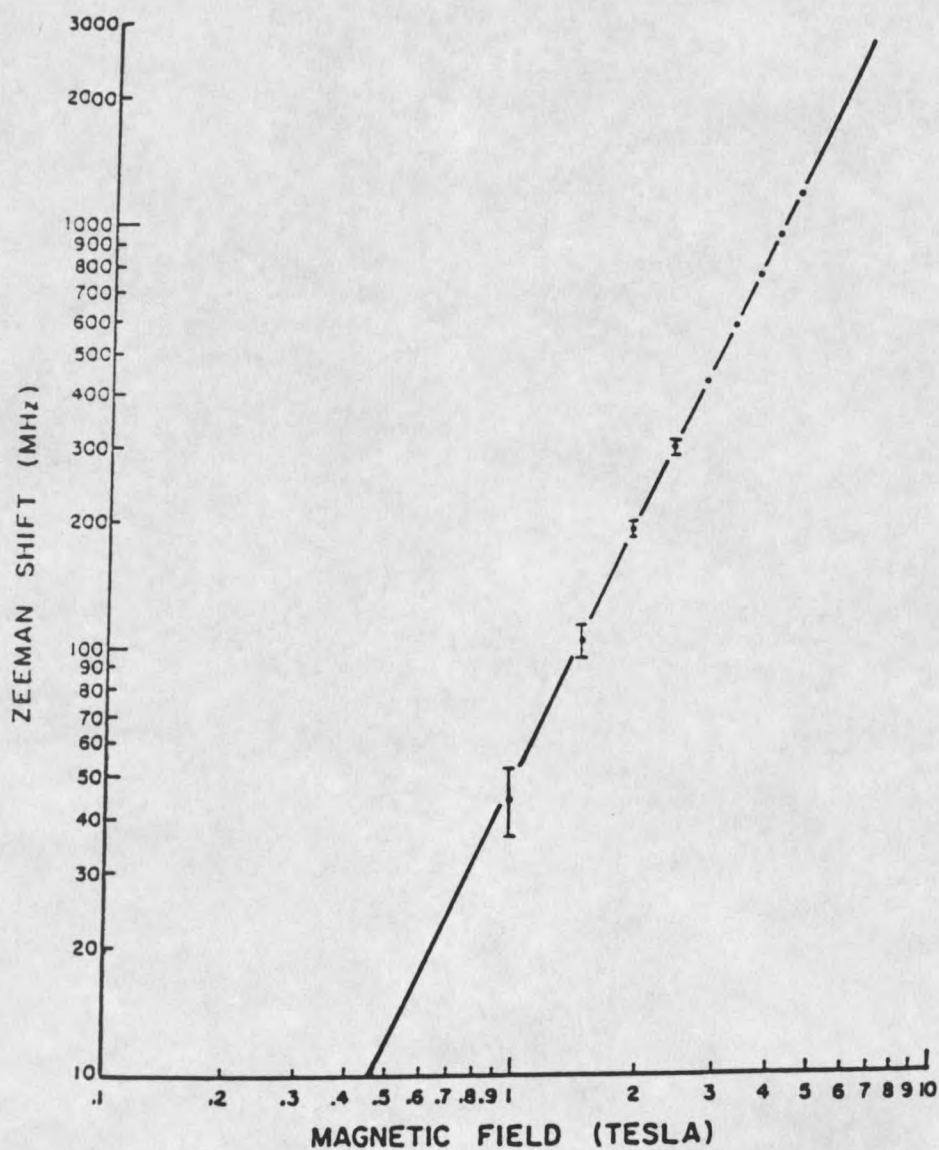


Figure 17: Electronic Zeeman shift of fluorescence excitation signal corresponding to ${}^7F_0 \rightarrow {}^5D_0$ transition. $B \parallel c$, total shift 1265 MHz.

Magnetic Field Perpendicular to c-axis

A check of the intermediate coupling matrix elements can be obtained by calculating and measuring the Zeeman shift with the magnetic field perpendicular to the c-axis of the crystal. In this case, everything is the same, except the admixture is with the ${}^7F_1 \mu=1$ state which is 339 cm^{-1} away from the ${}^7F_0$ ground state. Since it is 101.5 cm^{-1} closer to the ground state than the ${}^7F_1 \mu=0$ state it will give a larger Zeeman shift. The ${}^5D_1 \mu=1$ state is also closer to the ${}^5D_0$ state than the ${}^5D_1 \mu=0$ state but only 19 cm^{-1} closer, so the total measured Zeeman shift is larger. In each case the calculated intermediate coupling matrix elements,

$$\langle F_{00} | L_z + 2S_z | F_{11} \rangle = 1.965,$$

$$\langle D_{00} | L_z + 2S_z | D_{11} \rangle = 1.280,$$

are the same, and the Zeeman shift at 50 kilogauss is

$$\Delta E = (1.965)^2 (50)^2 / (21.42)^2 (339)$$

$$\Delta E = 1863 \text{ MHz}$$

for the ${}^7F_0$ ground state.

The change in energy for the ${}^5D_0$ excited state is

$$\Delta E = (1.2803)^2 (50)^2 / (21.42)^2 (1752)$$

$$\Delta E = 153 \text{ MHz.}$$

Thus, the total Zeeman shift is

$$\Delta E = (1863 - 153) \text{ MHz} = 1710 \text{ MHz.}$$

Again this is a confirmation of the calculated intermediate coupling matrix elements and the interpretation as a whole,

because the measured value is $1734 \text{ MHz} \pm 30 \text{ MHz}$. This value was determined from Figure 18, which is the measured Zeeman shift taken from fluorescence excitation data. Also shown in Figure 19 is the Zeeman shift of the absorption line, which is not as accurate because the change in energy can only be monitored between 10 kG and 50 kG.

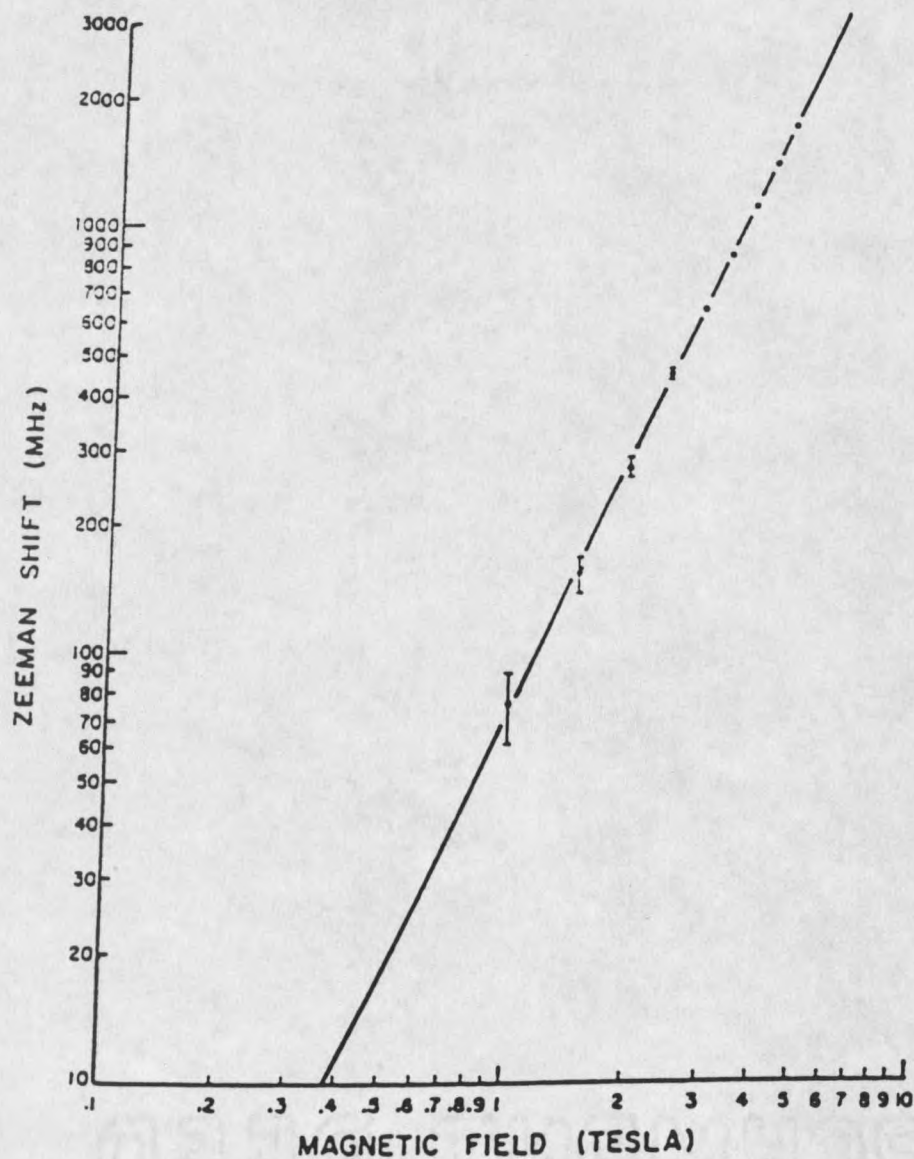


Figure 18:

Electronic Zeeman shift of fluorescence excitation corresponding to ${}^7F_0 \rightarrow {}^5D_0$ transition. $B \perp c$, total shift 1734 MHz.

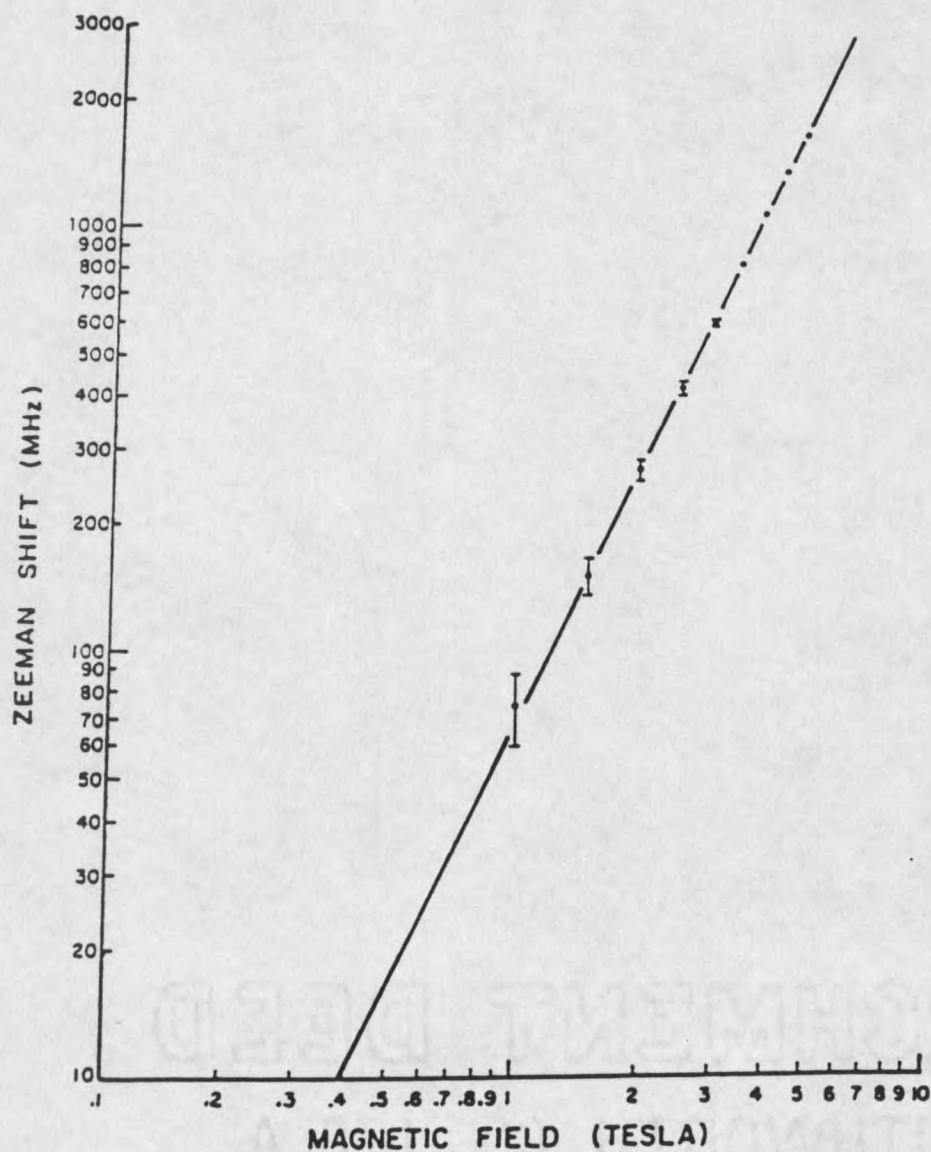


Figure 19:

Electronic Zeeman shift of ${}^7F_0 \rightarrow {}^5D_0$
absorption spectrum in $\text{Eu}(\text{OH})_3$. $B \perp c$.

Measurement of Optical Dephasing Time

The phase switch measurements of the transient relaxation time were first done on iodine vapor to characterize the response time of the system and check the results against measurements already made by Genack et al.⁴⁷ and measurements made by the use of other techniques.⁶³ The response time or rise time was measured by using an EG&G FND-100 photodiode with less than 1 nanosecond rise time to monitor the homodyne signal from the sample. The pulse to the LiTaO_3 electro-optic phase modulator was generated by a Tektronix model 109 reed relay pulser with 150 picosecond rise time. This pulse was 32 nanoseconds long, determined by the length of charging cable, and the amplitude of the pulse was 70 volts. The signal from the photodiode was monitored directly with a Princeton Applied Research Model 162 Boxcar Averager with a Model 163 Processor Module using a Tektronix Type S-2 Sampling Head with 50 Ω input resistance. This boxcar averager has a rise time limited to 100 picoseconds by internal timing uncertainties.

An example of this type of measurement in iodine vapor is shown in Figure 20. This figure also shows a schematic representation of the electro-optic modulator pulse for the sake of reference. The experimental result, shown in Figure 20, consists of two parts, the initial change in signal,

marked by T_2^* , is the linear response of the sample which is related to the inverse of the inhomogeneous linewidth of the transition. The rise time of the electro-optic phase modulator is approximately 300 picoseconds, and the measured rise time of this linear portion is 500 picoseconds, which is probably the intrinsic response of the FND-100 photodiode. The second part, marked by T_1, T_2 , is the nonlinear response of the sample which depends on T_1 and T_2 . In the limit $\chi^2 T_1 T_2 \ll 1$, this response is just a function of T_2 , and the inverse slope plotted on a semi-log plot is just $T_2/2$. A measurement of this slope gives a relaxation time of 15 nanoseconds, but more importantly it establishes that the time response of the system is 500 picoseconds, and it is able to measure transient relaxation times accurately from the subnanosecond into the microsecond range.

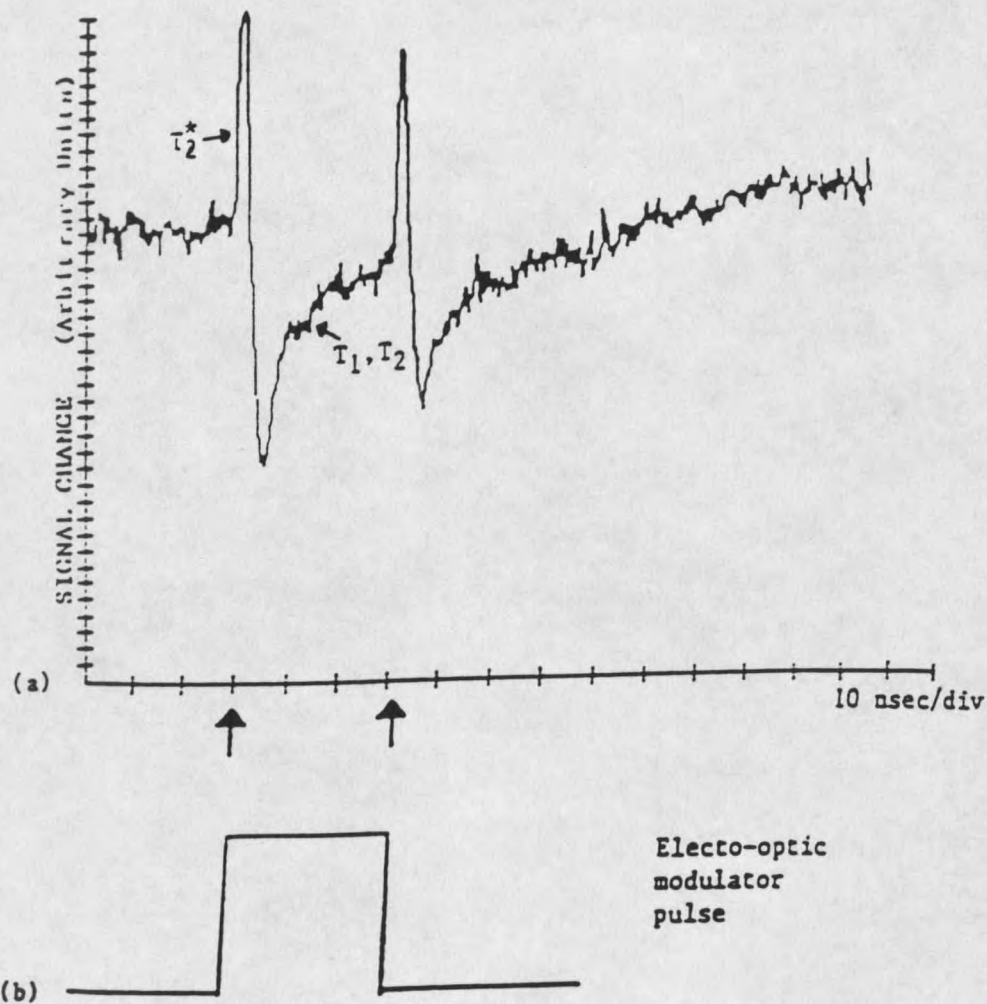


Figure 20: (a) Transient signal following a phase shift of π radians in iodine vapor. (b) Schematic representation of 70 volt electro-optic modulator pulse, 32 nsec long.

Dephasing Time in $\text{Eu}(\text{OH})_3$

The first measurements in $\text{Eu}(\text{OH})_3$ were done in the same manner, with the experimental arrangement shown in Figure 7. The Tektronix Model 109 pulser operates on a free run basis with a repetition rate of 700 Hz. Because of this free run operation, it was not possible to gate the light with the acousto-optic modulator. This resulted in long continuous exposure times. When the sample is exposed to resonant radiation for a time longer than the diagonal relaxation time, T_1 , the laser frequency jitter may prepare states with a bandwidth wider than the homogeneous linewidth. The preparation of more than one homogeneous packet then results in a measured relaxation time which is not related to the dephasing time T_2 . Exposure times much greater than T_1 can burn long lived population holes in the inhomogeneous profile. The decay of a long lived population hole will also result in a measurement of the wrong T_2 .

This situation was corrected by building a pulser which could be triggered externally, and programing the computer to scan the laser over the inhomogeneous profile between each phase switch. It was then possible to eliminate, or erase, a population hole in the profile, but it allowed a saturation hole to be burnt because the computer could generate an A/O modulator light pulse which was continuously variable between 200 nsec and 200 msec. By changing the time delay between the beginning of the A/O pulse and the

phase switch pulse, and monitoring the signal strength it was easy to determine that there was no advantage to delaying the phase switch more than 10 μsec into the A/O pulse. The time response of the $\text{Eu}(\text{OH})_3$ sample was in the 500 nsec to microsecond range and shots were averaged using a Tektronix 7912AD transient digitizer which could average up to 64 shots internally. A typical average of 16 shots for $\text{Eu}(\text{OH})_3$ is shown in Figure 21. In Figure 22, the nonlinear response is plotted on a semi-log scale with an inverse slope of 974 nsec. This implies an off diagonal relaxation time of $T_2 = 1.95 \mu\text{sec}$. A homogeneous linewidth of 163 kHz, corresponding to a 1.95 microsecond dephasing time, is of the same order of magnitude as similar measurements in other Eu^{3+} compounds. But the shot to shot variation of the signal was such that averages at the same position in the inhomogeneous profile gave results that varied unsystematically by as much as 200 nsec.

Inconsistent measurements at the same location within the inhomogeneous profile are an indication of an instrumental limit. To confirm the fact that the measurement had reached its upper instrumental limit at 2 μsec , the same experiment was repeated in $0.05\% \text{Pr}^{3+}:\text{LaF}_3$. This material, where the dephasing time, T_2 , is 5.6 μsec , has been the subject of much study in recent years.⁶⁴ The result of that experiment was the same as that for the $\text{Eu}(\text{OH})_3$ experiment, implying that the laser frequency jitter

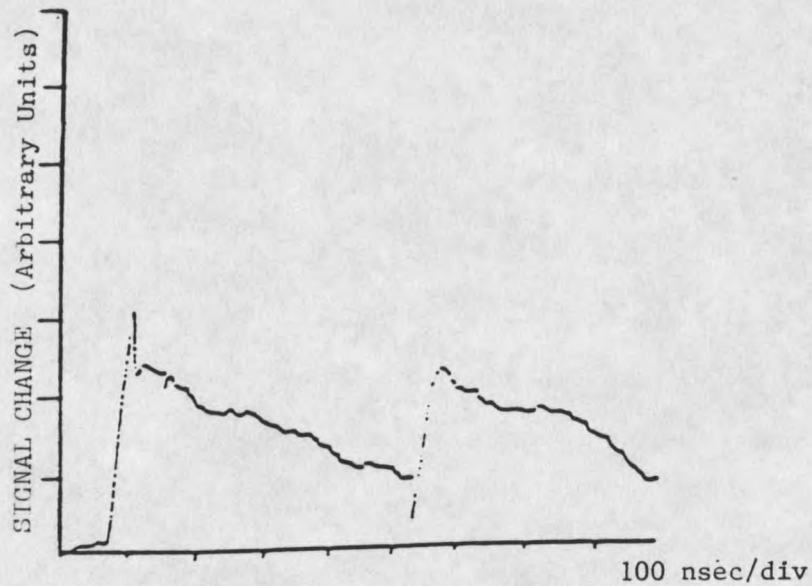


Figure 21: Phase Switch transient signal in $\text{Eu}(\text{OH})_3$.
Average of 16 shots. Magnetic field 15 kG.

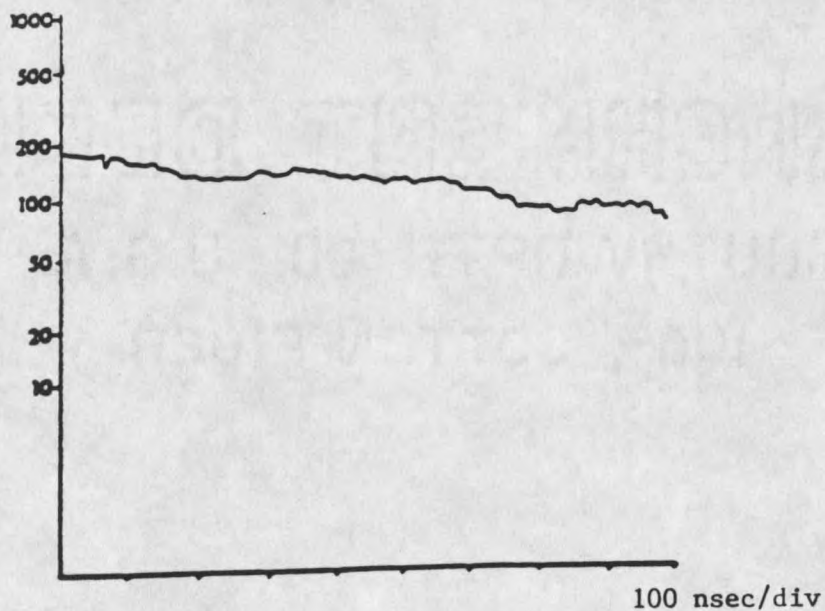


Figure 22: Semi-log plot of nonlinear response shown
in Figure 4.14. Inverse slope = 974 nsec.

was contributing to the measured decay time. One can understand this in a very simple way by considering the generation of the phase switch signal by the homodyne mixing of the sample polarization with the laser beam at a new phase. If a single homogeneous packet is excited in the burn phase, after the phase switch, it will decay at a rate $2/T_2$. But if the homogeneous width is less than the laser linewidth more than one single homogeneous packet will be excited and the decay time will be determined by the interference of more than one isochromat decaying simultaneously.

The variation of the phase switch signal on a shot to shot basis was such that one could observe the shorter decay time, generated by the laser jitter, on every third or fourth shot. This, together with results in other Eu^{3+} systems, indicates that the real transient relaxation time for $\text{Eu}(\text{OH})_3$ is probably in the range between 2 microseconds and 5 microseconds, but in order to measure it using an optical phase switching technique, the 599-21 dye laser would have to be stabilized more than the present 1 MHz linewidth, down to the 10 kHz range. This could be done with the correct equipment, but it is not possible in this laboratory on any reasonable time scale.

Several mechanisms must be considered to account for the homogeneous width in $\text{Eu}(\text{OH})_3$. The ultimate limit to the optical linewidth, set by the optical excited state lifetime, is 573 Hz, corresponding to a lifetime of 278

usec. This is insignificant compared to a homogeneous linewidth of 60 kHz or more. Hyperfine dephasing is also expected to be small because both the ground and excited states are $J = 0$ states. There was experimental evidence to support this, as the measured relaxation time apparently did not change as the external magnetic field was varied between 10 kG and 50 kG. The long lived holes burned into the inhomogeneous profile, to be discussed in the next section, also support the conclusion that hyperfine induced dephasing does not contribute to the homogeneous linewidth. Phonon assisted energy transfer could account for some of the residual linewidth but it is unlikely to be more than 1 kHz at a temperature of 1.3 K. Temperature dependent studies of the dephasing time would determine this contribution. The most likely explanation of the remaining residual linewidth is a result of the weak coupling of the europium nucleus to hydrogen spin flip-flops. The fluctuation of the local field caused by the nearby hydrogen ions can have an effect on the optical linewidth as demonstrated by nuclear spin decoupling measurements in $\text{Pr}^{3+}:\text{LaF}_3$.⁶⁴ An actively stabilized laser, of 10 kHz bandwidth, would allow one to do both of these experiments in $\text{Eu}(\text{OH})_3$ and determine specifically the contributions to the homogeneous linewidth.

It should be noted that optical phase switching is an accurate and simple technique for the measurement of optical

transient relaxation times. The simplicity and the ability to measure very fast transient signals make optical phase switching a very attractive method to be used for the measurement of dephasing times in solids as well as liquid and gas phase materials.

It has been shown that the homogeneous FWHM for the ${}^7F_0 \longleftrightarrow {}^5D_0$ transition in $\text{Eu}(\text{OH})_3$ is less than 163 kHz. This corresponds to a dephasing time, T_2 , greater than 2 microseconds. An estimate of the dephasing time on the basis of the shot to shot variation of the phase switch signal implies a homogeneous linewidth between 150 kHz and 60 kHz.

Hole Burning in $\text{Eu}(\text{OH})_3$

The experimental schematic for hole burning in $\text{Eu}(\text{OH})_3$ is shown in Figure 6 with the computer driven burn and read cycle for the CW-dye laser and A/O modulator shown at the bottom of Figure 6. Variable burn times are available, between 500 μsec and 30 seconds in 500 μsec increments, and the read time could be varied between 64 msec and 1 second, each controlled independently through the computer. A fiber-optic bundle was used to transmit the fluorescence emission from the $\text{Eu}(\text{OH})_3$ crystal to a photomultiplier located some 1.5 meters from the magnet and cryostat. The fluorescence emission to the $^7\text{F}_4$ and $^7\text{F}_2$ low lying excited states from the $^5\text{D}_0$ optically excited state was separated from the exciting laser radiation by using a Corning 2.61 filter. The signal from the photomultiplier tube was fed directly into a Northern Scientific 575 signal averager which was triggered by the computer, just as it began to generate the laser 'read' frequency sweep.

It was possible to burn holes in $\text{Eu}(\text{OH})_3$ with exposure times as small as 20 milliseconds, but by recording both the read and the burn cycle, as shown in Figure 23, it was determined that the deepest hole would burn on a time scale of about 100 milliseconds with no improvement of signal to noise for longer burn times. For this reason the burn time

was always between 100 and 300 milliseconds. Fast scan times are necessary because broadening of the hole by time dependent interactions results in a loss of detection sensitivity. The scan time was 456 milliseconds for a 400 MHz scan. In this way the tuning rate was fast enough, ~ 1 MHz/msec, that the read cycle made only a small perturbation of the level populations.

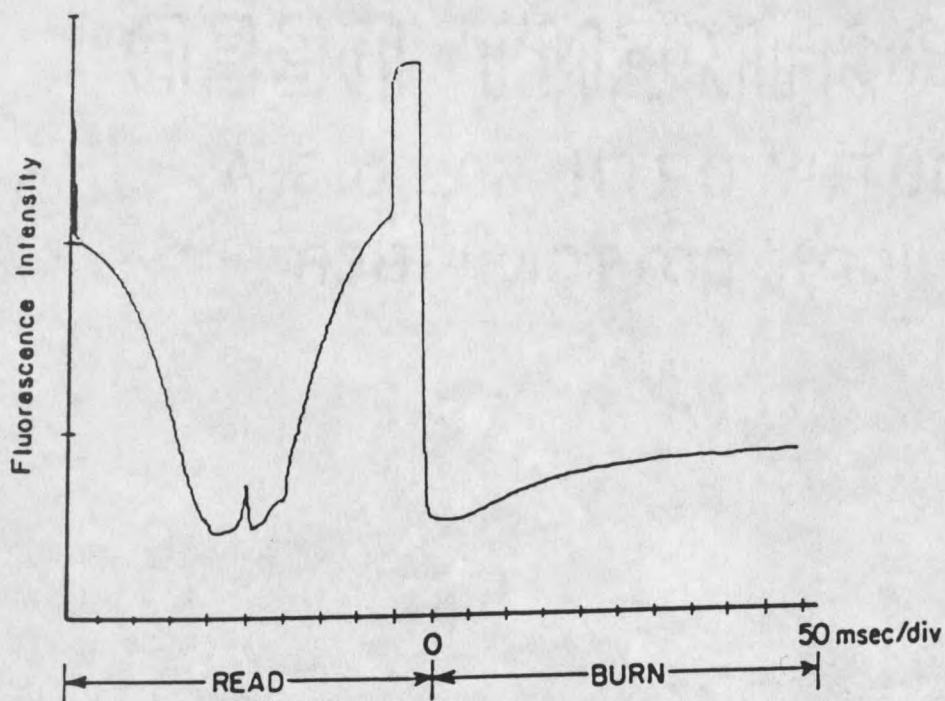


Figure 23: Read and Burn cycle for hole burning near the center of the inhomogeneous profile. Fluorescence intensity increases toward the bottom of the figure.

Quadrupole Splittings

Much can be learned from hole burning but the most effective use of this technique is the determination of splittings hidden within the inhomogeneously broadened line. These hyperfine splittings, which are usually much less than the inhomogeneous broadening, can be determined by measuring the energy separations of the side holes and the antiholes. An example of the spectral output with an average of 16 burn and read cycles is shown in Figure 24. Appendix I describes the computer control of read-burn cycle. This can be compared with Figure 25, which is a simple average of 16 scans in which the laser was controlled by the computer program in Appendix II. The fluorescence excitation signal in Figure 25 was obtained after the burn-read signal shown in Figure 24. By repetitively scanning the laser back and forth across the inhomogeneous line for 5 or 10 minutes the hole which had previously been burnt into the line was erased. Figure 25 was then recorded by averaging 16 successive scans, each 400 MHz wide.

We introduce a new technique which gives the necessary experimental resolution to see the side holes and antiholes corresponding to the energy splittings of the quadrupole levels. Comparing Figures 24 and 25, it is easy to see the hole burnt into the inhomogeneous line, but the side holes are very weak, or absent, and only one antihole shows up with enough resolution to be distinguishable.

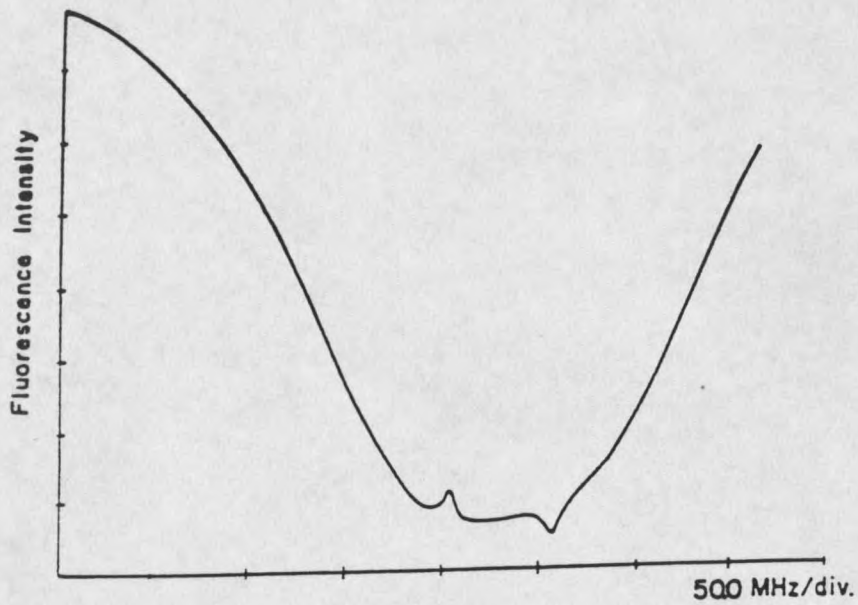


Figure 24: Average of 16 read scans of 400 MHz.
Burn time 100 msec.

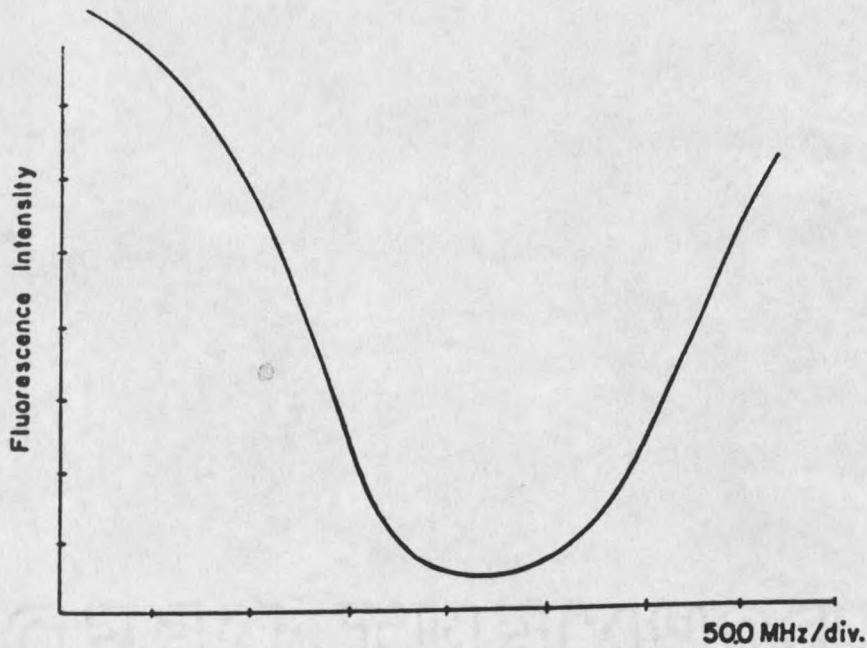


Figure 25: Average of 16 read scans of 400 MHz.
No Burn time. Fluorescence excitation signal.

By taking the ratio, or dividing the data in Figure 25 into that in Figure 24, one obtains the experimental resolving power necessary to measure the frequencies corresponding to the energy splittings of the quadrupole levels. An example of the improved resolution using this new technique is shown in Figure 26. By using this new procedure, of taking two data files and dividing to resolve the side holes, one can map out the hole frequencies, quadrupole energy splittings, as a function of magnetic field.

In zero magnetic field, the effective spin Hamiltonian,

$$H = P[I_z^2 - I(I+1)/3 + \eta(I_x^2 - I_y^2)/3],$$

describes the splitting of the quadrupole levels for each isotope. Measurements at zero field allow the determination of the quadrupole coupling parameters, P , for each isotope. In $\text{Eu}(\text{OH})_3$, however, the transitions are too weak for hole burning in zero field. Furthermore, in the axial limit the spin Hamiltonian is

$$H = P[I_z^2 - I(I + 1)/3]$$

and the zero field nuclear eigenstates are $|\pm m_I\rangle$ where $\pm m_I = \pm 1/2, \pm 3/2, \pm 5/2$. Optical transitions between these levels should satisfy the selection rule $\Delta m_I = 0$, which implies that redistribution of population among the quadrupole levels would not be expected, and hole burning would not occur. Thus hole burning, if it is observed, is presumably the result of a small admixture of the nuclear eigenstates,

$|m_I\rangle$. One can attribute the observed hole burning to two possible effects; one, a departure from true axial symmetry so that $\eta \neq 0$, or secondly, the application of a magnetic field where the field axis is not parallel to the crystallographic c-axis.

An analysis of the hole burning characteristics in $\text{Eu}(\text{OH})_3$ proves that it is the latter effect, and not the former, which is responsible for the admixture of the nuclear eigenstates. This is done by intentionally aligning the crystal so the c-axis was not parallel to the applied field direction. This last procedure would enhance the hole burning process and lead to deeper holes, which was exactly what was observed. Also, it was not possible to burn holes in zero magnetic field.

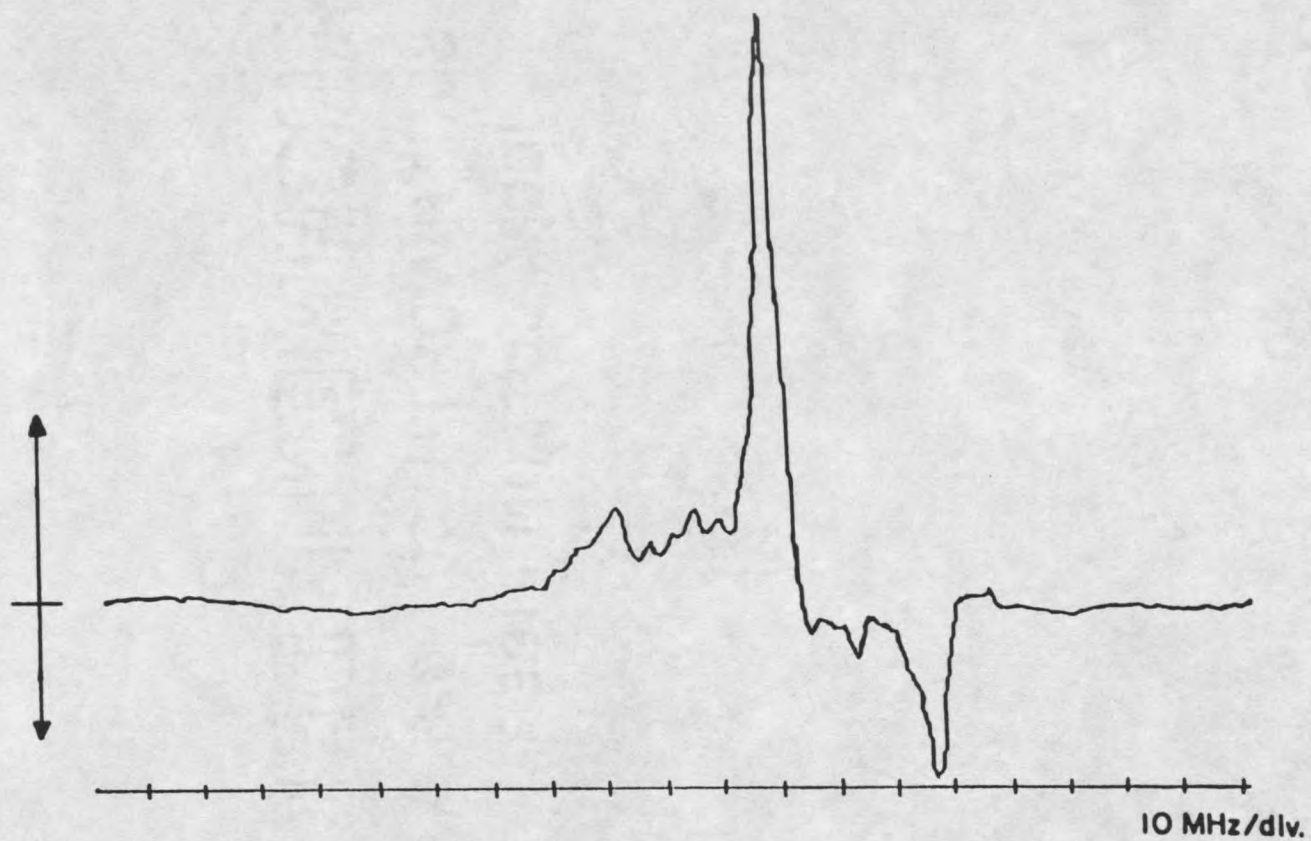


Figure 26: Data shown in Figure 24 divided by data shown in Figure 25. Hole intensity increases toward the top of the figure. Antihole intensity increases toward the bottom of the figure.

Magnetic Field Effects

The spin Hamiltonian in an axial limit, where $\eta = 0$, is

$$H = P[I_z^2 - I(I + 1)/3].$$

To obtain the parameters of primary interest, the quadrupole coupling parameters, P , one would like to burn holes in zero magnetic field where the holes would show a splitting of $2P$, $4P$, and $6P$ for each isotope. Since it is only possible to burn holes in $\text{Eu}(\text{OH})_3$ when there is a magnetic field, the nuclear Zeeman effect must also be included in the effective spin Hamiltonian. Writing the Hamiltonian as,

$$H = P[I_z^2 - I(I+1)/3] - (\gamma\mu_N/I)\vec{I} \cdot \vec{B},$$

it is easy to discern that the effect of the nuclear Zeeman interaction is to split each energy level into a pair of levels. This complicates the spectrum significantly because 14 side holes, 7 for each isotope, can appear on each side of the laser burn frequency. A further complication is the fact that the holes move as a function of the magnetic field strength, crossing through each other before the Zeeman term, $\gamma\mu_N B_z/I$, gets as large as the quadrupole coupling parameter, P .

The nuclear moment, $\gamma\mu_N$, that should be used in fitting the experimental data depends on the particular crystal field level involved. The reduced nuclear moment plays an important role in the ground state, $^7F_0$, but it is not expected to affect the $^5D_0$ nuclear moment because the $^5D_1$ energy level is much further away ($\sim 1753 \text{ cm}^{-1}$). One can

assume the bare nuclear magnetic moments as given by Fuller and Cohen,^{6s}

$$\gamma_{\mu N} = ((1.53)/(5/2))(0.762 \text{ MHz/kG}) = 0.466 \text{ MHz/kG}$$

for ^{153}Eu , and

$$\gamma_{\mu N} = (3.46/(5/2))(0.762 \text{ MHz/kG}) = 1.055 \text{ MHz/kG}$$

for ^{151}Eu .

The validity of this assumption can then be checked by comparing the experimental data and the fitted constants in two different cases.

In one case, with the magnetic field perpendicular to the crystalline c-axis, it is also possible to burn holes. Because the effective splitting does not vary as rapidly as a function of the field strength, at least for the isotope ^{153}Eu , it is easier to make measurements with the magnetic field perpendicular to the crystalline c-axis. The quadrupole splittings also show the same zero field limit given by 2P, 4P, and 6P. In this case the bare nuclear moments are used in fitting the quadrupole coupling constants.

In the other case, with the magnetic field axis parallel to the crystalline c-axis, one can check the quadrupole coupling constants and the nuclear moments used to fit the first case.

Magnetic Field Perpendicular to c-axis

To measure the value of the quadrupole coupling coefficients, P , one can measure the hole locations as a function of field for the crystallographic c -axis perpendicular to the applied field direction. This also leads to a nuclear Zeeman splitting; the Hamiltonian describing this splitting is given by the matrix below. This matrix equation can be solved in the clearest manner by first dividing by the quadrupole coupling constant P , and then diagonalizing for each value of the parameter $\gamma B/P$.

$$H = \begin{vmatrix} & 5/2 & 3/2 & 1/2 & -1/2 & -3/2 & -5/2 \\ (10/3)P & \sqrt{5/4}\gamma B & 0 & 0 & 0 & 0 \\ \sqrt{5/4}\gamma B & -(2/3)P & \sqrt{2}\gamma B & 0 & 0 & 0 \\ 0 & \sqrt{2}\gamma B & -(8/3)P & 3/2\gamma B & 0 & 0 \\ 0 & 0 & 3/2\gamma B & -(8/3)P & \sqrt{2}\gamma B & 0 \\ 0 & 0 & 0 & \sqrt{2}\gamma B & -(2/3)P & \sqrt{5/4}\gamma B \\ 0 & 0 & 0 & 0 & \sqrt{5/4}\gamma B & (10/3)P \end{vmatrix}$$

The resulting eigenvalues can then be plotted as a function of the dimensionless parameter $\gamma B/P$ as shown in Figure 27. Just as in the case with the magnetic field parallel to the crystalline c -axis, Figure 27 shows that the quadrupole splitting parameter P can be determined by monitoring the relative frequencies of the holes as a function of the magnetic field.



Figure 27: Eigenvalues of quadrupole Hamiltonian plotted as a function of the dimensionless parameter $\gamma B/P$.

Figure 28 shows the experimental results of measurements made with the magnetic field axis perpendicular to the crystallographic c-axis. The vertical bars, which are 2 MHz wide, mark the location of side holes for different fields between 2 kG and 10 kG. The solid lines through the hole positions are the energy splittings described by the eigenvalues of the diagonalized Hamiltonian shown in Figure 27. This fit is obtained with a value of $|P| = 11.6$ MHz and the bare nuclear moment of 0.466 MHz/kG for the isotope ^{153}Eu .

The ^{151}Eu isotope has a quadrupole moment $Q = 0.95$ barns which is smaller than the quadrupole moment for ^{153}Eu , $Q = 2.45$ barns. The magnetic moment for ^{151}Eu is 3.464 nuclear magnetons, μ_N , and for ^{153}Eu it is 1.53 nuclear magnetons. In a magnetic field, the energy levels of the isotope ^{151}Eu change more rapidly as the magnetic field increases, and the nuclear eigenstates admix faster. The same geometry was used for the measurement of P for the 151 isotope, but because the holes are so close to the central hole and the admixture takes place so rapidly, it is more difficult to get an accurate reading of hole position all the way from 2 kG up to 10 kG. The data does convincingly provide the quadrupole coupling constant $|P| = 4.5$ MHz, however. The solid lines in Figure 29 are calculated with the value $|P| = 4.5$ MHz and a bare moment of 1.055 MHz/kG for the 151 isotope of europium.

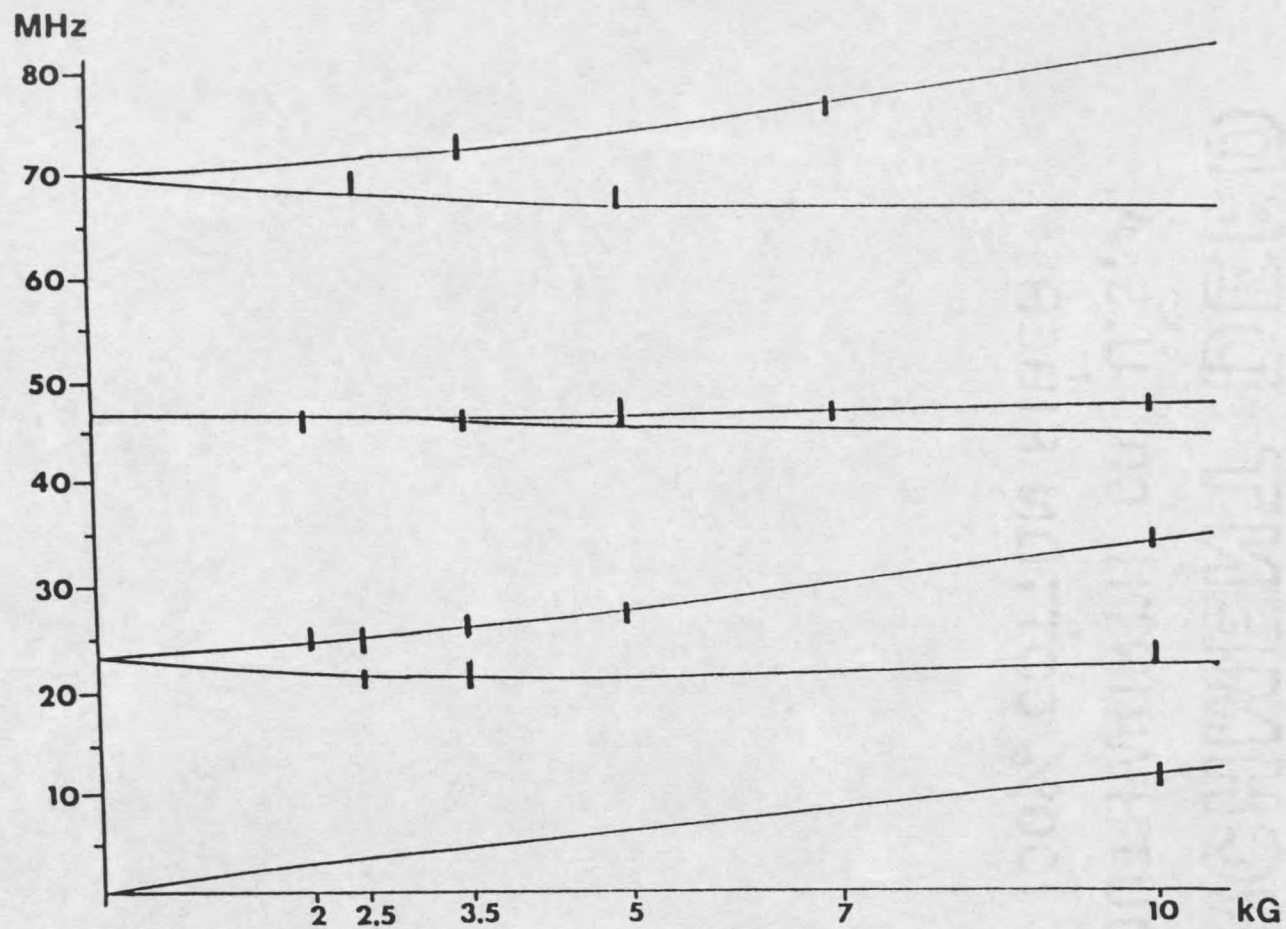


Figure 28: Nuclear Zeeman quadrupole splittings in a magnetic field perpendicular to the crystalline c-axis, $B \perp c$. Isotope ^{153}Eu ; $|P| = 11.6 \text{ MHz}$

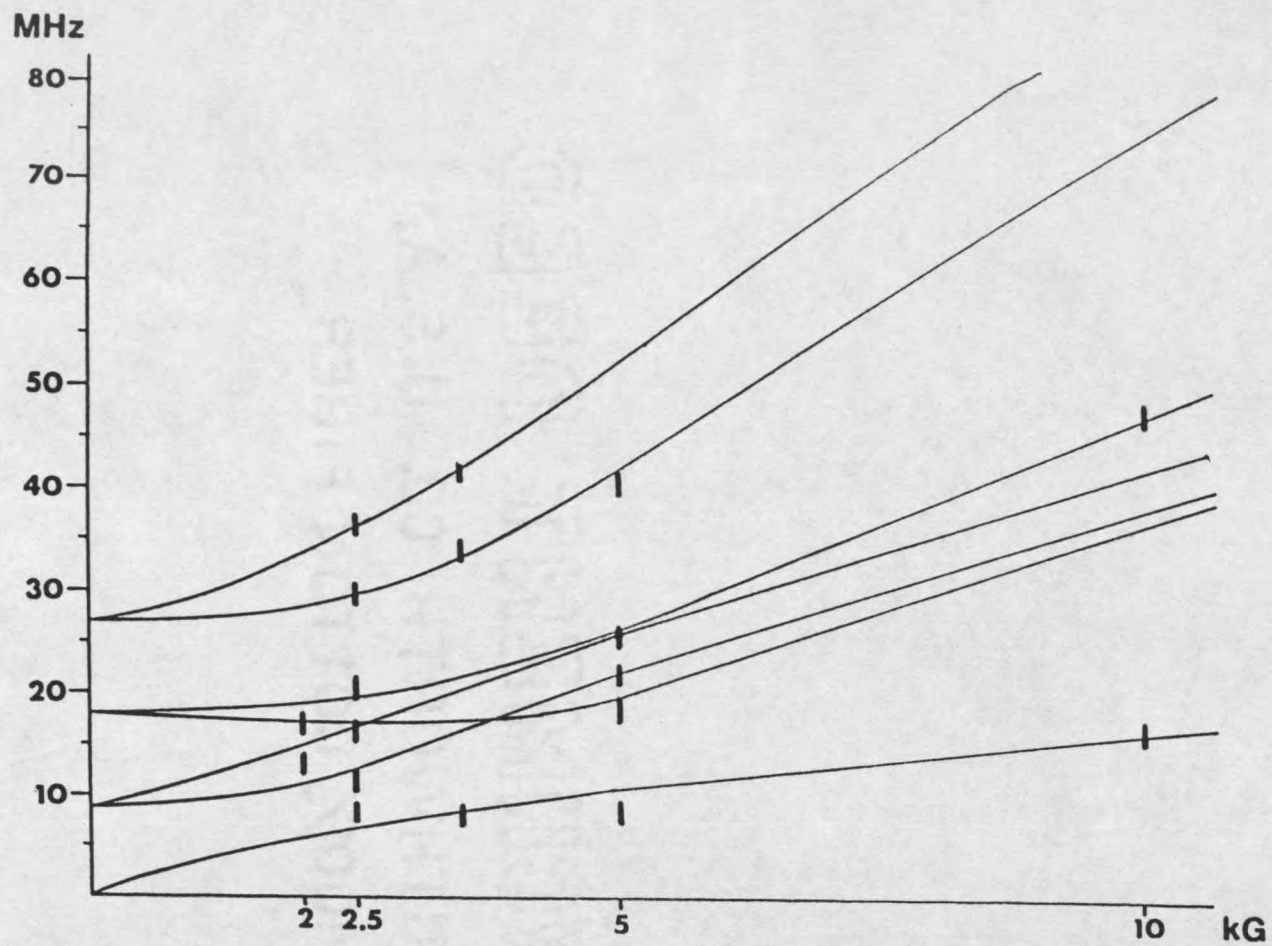


Figure 29: Nuclear Zeeman quadrupole splittings with the magnetic field perpendicular to the crystalline c-axis. Isotope ^{151}Eu ; $|P| = 4.5 \text{ MHz}$.

Magnetic Field Parallel to c-axis

Shown in Figure 30 are the measured frequencies of the side holes relative to the burn frequency of the laser with the magnetic field parallel to the crystalline c-axis. This data corresponds to measurements made at four different magnetic fields from 5kG to 20kG. Since holes do not burn in zero magnetic field, there is no data on the left axis. With the two values, $|P| = 11.6$ MHz for isotope 153 and $|P| = 4.5$ MHz for isotope 151, all the holes shown in Figure 30 can now be attached to a particular hyperfine level and isotope. Each quadrupole level splits as a function of field and the splitting is shown by the solid lines in Figure 31, with $|P| = 11.6$ MHz and $\gamma\mu_N = 0.466$ MHz/kG for ^{153}Eu .

Figure 32 shows the measured hole position as a function of field for the magnetic field parallel to the c axis of the crystal. This plot is for the ^{151}Eu isotope with quadrupole coupling coefficient, $|P| = 4.5$ MHz, and a bare nuclear moment of 1.055 MHz/kG.

The results in this chapter represent the measured quadrupole splittings in the $^5\text{D}_0$ excited state of $\text{Eu}(\text{OH})_3$. They correspond to a measurement on ions in complete axial symmetry. The splittings are entirely consistent with measurements made by Macfarlane et al. in $\text{EuP}_5\text{O}_{14}^{30}$ and $\text{YAlO}_3:\text{Eu}^{3+1}$ but the P values are more than a factor of four smaller.

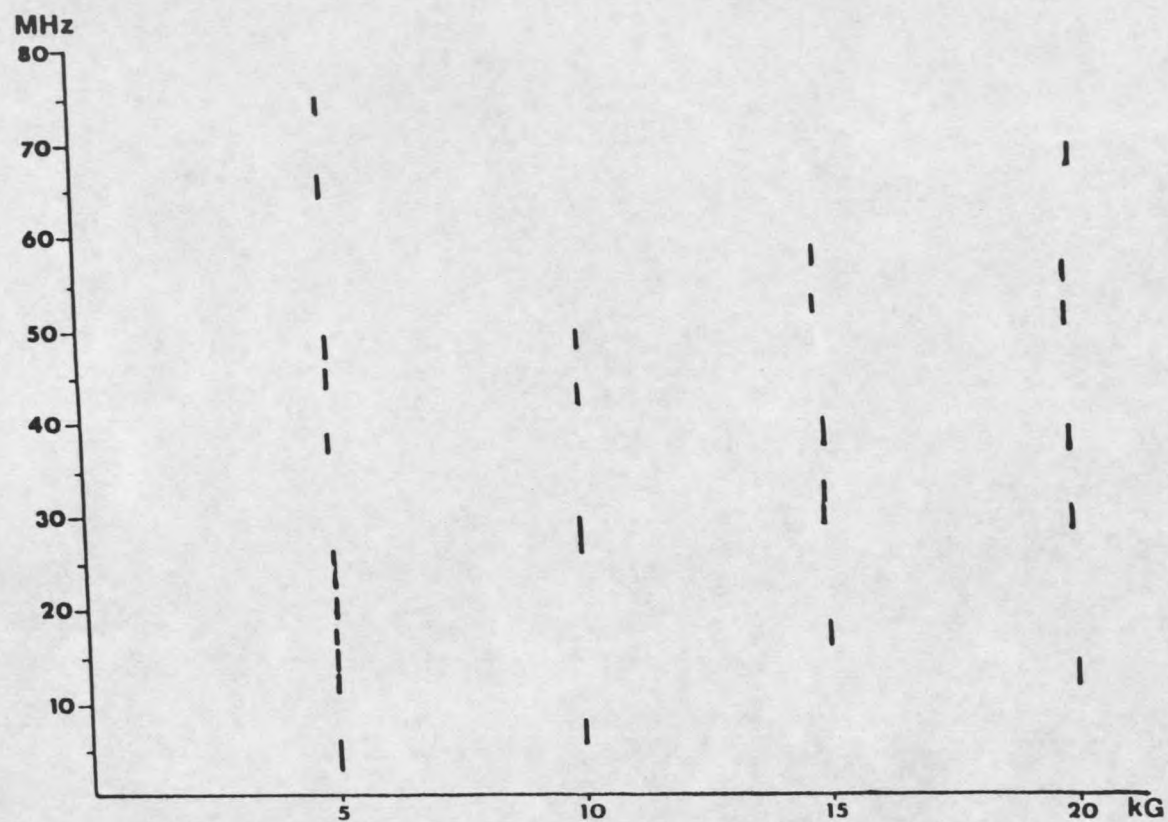


Figure 30: Side hole frequencies relative to laser burn frequency at four different magnetic fields. Magnetic field parallel to c-axis, $B \parallel c$.

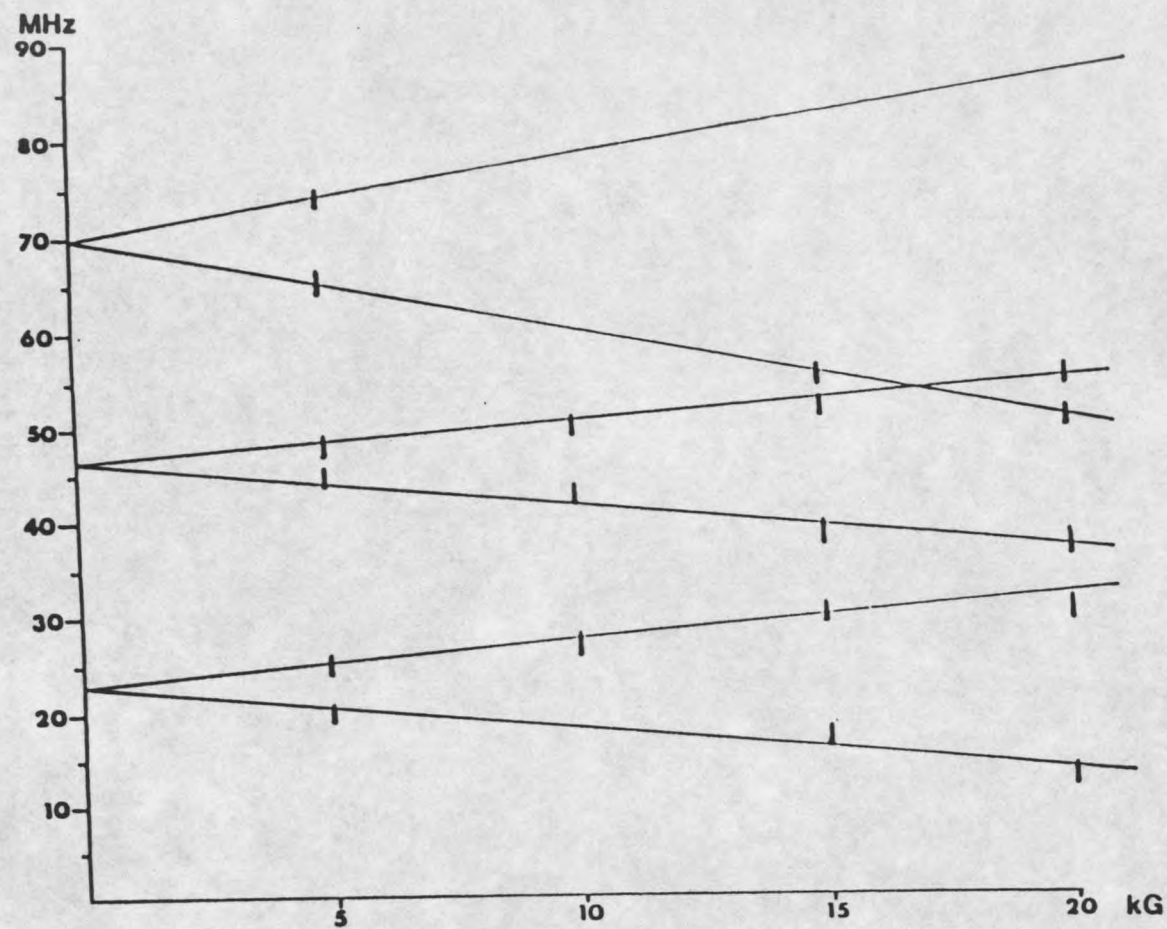


Figure 31: Nuclear Zeeman quadrupole splitting of ^{153}Eu in a magnetic field parallel to the crystalline c-axis, $B \parallel c$. $|P| = 11.6 \text{ MHz}$, $\gamma\mu_N = 0.466 \text{ MHz/kG}$.

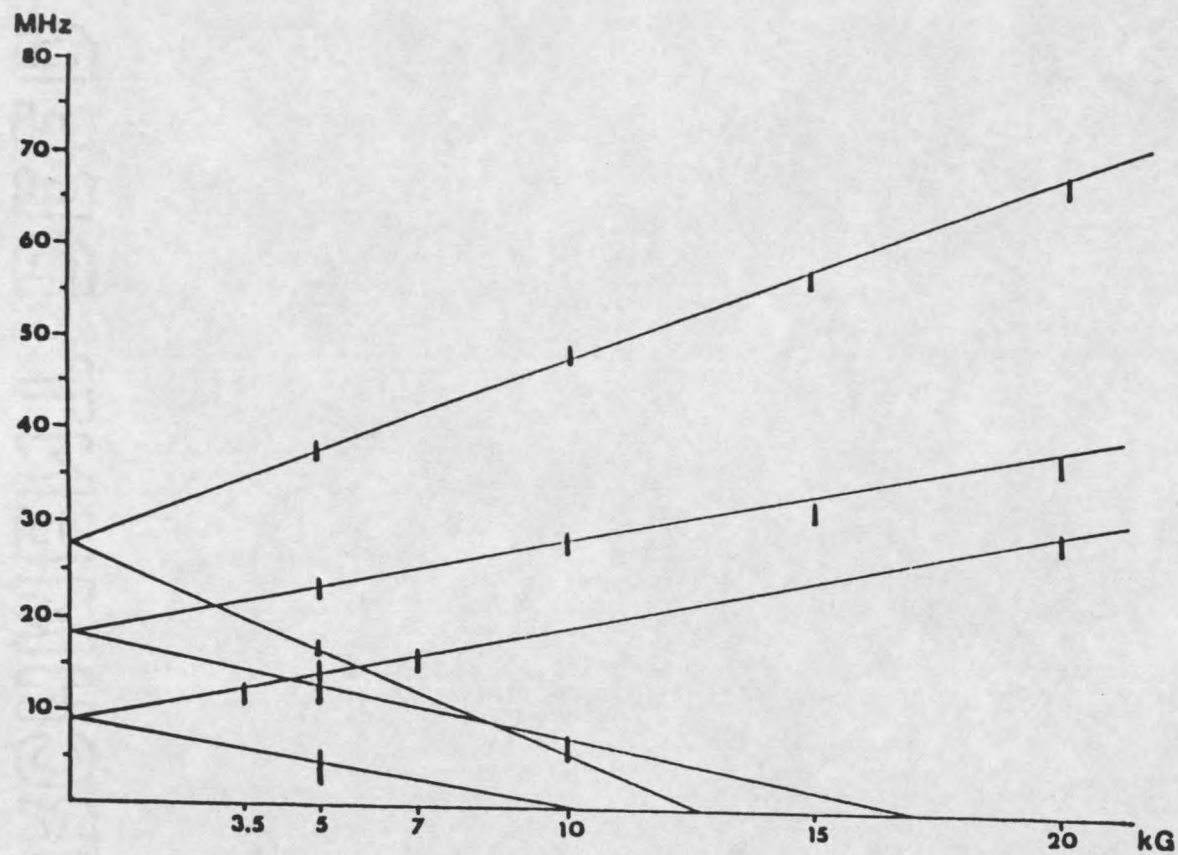


Figure 32: Nuclear Zeeman quadrupole splitting of ^{151}Eu in a magnetic field parallel to the crystalline c -axis, $B \parallel c$. $|P| = 4.5$ MHz, $\gamma\mu_N = 1.055$ MHz/kG.

A way to check the validity of the measurement is by comparing the ratio of the quadrupole coupling parameters with the known ratio of the quadrupole moments³⁸

$$Q^{153}/Q^{151} = 2.5812 \pm 0.0010.$$

This can be compared to the measurements in this work,

$$^{153}\text{P}/^{151}\text{P} = 11.6/4.5 = 2.58 \pm 0.5,$$

again confirming the accuracy of the measurements.

Although antiholes do exist, and it should be possible to measure the ground state, $^7\text{F}_0$, hyperfine splittings, the ground state splittings seem to be so small, less than 4 MHz as shown in Chapter 3, that no attempt was made to measure them with this experimental technique. It is most likely that these measurements could best be carried out using an optical rf double-resonance technique²² available in other laboratories.

Hole Lifetimes and Linewidths

A complete study of hole lifetimes and hole widths versus time was not attempted. Hole widths as small as 1-2 MHz were measured, but from the phase switching data, it was already known that the homogeneous width was less than the laser linewidth. It was observed that the spectral hole burnt into the inhomogeneous profile got wider as a function of the time delay between the burn and read cycle but this was not pursued further because the change in the hole width was not dramatic enough to make an accurate measurement, and an explanation of the dynamics does not exist at this time.⁶⁶ It was also observed that the hole lifetime was greater than 1/2 hour depending on the burn time and the position within the inhomogeneous profile. Holes on the high energy side of the transition would burn much easier and deeper than holes on the low energy side. By delaying the read cycle, it was determined that these deep holes would last at least 30 minutes and possibly much longer. These long lived holes imply that hyperfine dephasing is not important, at least on a time scale on the order of minutes, in the explanation of the transient relaxation time in the previous chapter.

Chapter 7

CONCLUSIONS

We have studied the intrinsic ${}^7F_0 \longleftrightarrow {}^5D_0$ transition of the Eu^{3+} ion in axial sites of C_{3h} symmetry in $\text{Eu}(\text{OH})_3$. A variety of linear and nonlinear techniques were used to measure and characterize the interaction of this ion with the crystalline environment in $\text{Eu}(\text{OH})_3$. This study has identified several novel effects in $\text{Eu}(\text{OH})_3$. These novel effects will also occur in other materials that contain this trivalent rare earth ion. To our knowledge, this is the first time that optical hole burning has been used to measure the quadrupole splitting of an ion in an axially symmetric crystal field potential.

Narrow Linewidth

An exceptionally narrow inhomogeneous linewidth of 167 MHz FWHM has been measured for the first time for the ${}^7F_0 \rightarrow {}^5D_0$ transition in $\text{Eu}(\text{OH})_3$. Compared with all other stoichiometric solids, this is the narrowest inhomogeneous width ever measured for an optical transition.

Isotope Shift

Line shape fitting of the ${}^7F_0 \longleftrightarrow {}^5D_0$ transition provided an indication of an isotope shift. The apparent measured isotope shift of ~ 85 MHz is about $1.5 \times 10^{-3} \text{ cm}^{-1}$

per unit mass. This shift is approximately the order of magnitude that is expected for rare earth materials,⁵⁵ but it is apparently the first case in which it may be clearly resolvable in the solid state. Further measurements including ODNMR, Optically Detected Nuclear Magnetic Resonance, and the acquisition of isotopically pure samples are planned to clarify this further.

Electronic Zeeman Shift

Measurements of the electronic Zeeman shifts of the fluorescence excitation line and the absorption line are completely explained in terms of second order perturbation theory. The measured shift of $1265 \text{ MHz} \pm 30 \text{ MHz}$ agrees exactly with the second order perturbation theory calculation of 1282 MHz . With the magnetic field perpendicular to the c-axis, the Zeeman shift of $1734 \text{ MHz} \pm 30 \text{ MHz}$ also agrees with the predicted change of 1710 MHz . This also provides a check of the calculated electronic Zeeman matrix elements,

$$\langle F_{00} | L+2S | F_{10} \rangle = 1.965,$$

$$\langle D_{00} | L+2S | D_{10} \rangle = 1.280,$$

for each of the excited $J=1$ states with the $J=0$ states. This is the highest resolution electronic Zeeman effect measured in any rare earth solid.

The same matrix elements lead to an understanding of the admixture which results in the dramatically increased oscillator strength. The three order of magnitude quadratic

variation of transition probability with magnetic field strength can be very useful in future work with rare earth materials and lasers.

Quadratic Enhancement

The quadratic enhancement of the intrinsic transition, which we pioneered, has already been used by others in two materials, EuVO_4 ^{3,4} and EuAsO_4 ,^{6,7} as a sensitive detector to distinguish (unperturbed) intrinsic sites from defect and dislocation sites commonly found in spectroscopic samples. This effect is applicable in both trivalent Europium and isoelectronic divalent Samarium compounds presently and has played a major role in the gated hole burning experiments of Macfarlane and Shelby. The quadratic enhancement may also be useful in a practical way for optical switching and energy transfer.

Dephasing Time

While it was not possible to make an exact measurement of the off diagonal dephasing time, T_2 , it was determined that it is in the range between 2 and 5 μsec . This is surprisingly long in that stoichiometric materials usually have very fast dephasing times because of the interactions between ions which lead to energy transfer and a loss of phase memory. The residual width, not accounted for by the population relaxation rate, $1/2\pi T_1 = 573 \text{ Hz}$, is probably due to the reduced nuclear moment of the ground state Eu^{3+} ion and the fluctuation of local fields which modulates the

local environment and causes dephasing.

Quadrupole Splittings

Excited state nuclear quadrupole measurements are reported for europium ions in an axial field. Using optical hole burning as a sensitive detection technique for overcoming inhomogeneous broadening, we have measured the quadrupole splittings of each of the stable isotopes of trivalent europium.

$$^{151}\text{Eu} \quad |P| = 4.5 \text{ MHz} \pm 0.5 \text{ MHz}$$

$$\eta = 0.0$$

$$^{153}\text{Eu} \quad |P| = 11.6 \text{ MHz} \pm 0.5 \text{ MHz}$$

$$\eta = 0.0$$

These measurements agree with the predicted second order contribution to the quadrupole coupling parameter. This is a distortion caused by the crystalline electric field and proportional to the nuclear electric quadrupole moment. Considering Erickson's nuclear electric quadrupole ratio of

$$^{153}\text{Q}/^{151}\text{Q} = 2.58$$

the measured ratio of quadrupole coupling parameters in this study,

$$^{153}\text{P}/^{151}\text{P} = 2.58 \pm 0.5,$$

is in exact agreement. This implies that in the $^5\text{D}_0$ excited state only, the distortion of the electronic charge cloud caused by admixtures of $J = 2$ states into the $J = 0$ state dominates the nuclear quadrupole interaction parameter P .

Chapter 8

FOUR-WAVE MIXING AND HYPERFINE SPLITTINGS

IN LiTbF_4 AND $\text{Tb}(\text{OH})_3$

INTRODUCTION

Four-wave mixing has been of considerable interest recently because of its general usefulness as an experimental technique and the possible practical applications. Four-wave mixing has been used in measurements of Doppler-free two-photon spectra,^{6,8} and in solids four-wave mixing transient-grating spectroscopy^{6,9} has been useful in characterizing exciton-transport properties. Interest is also evident in proposals concerning the use of four-wave mixing as a means of generating a phase conjugate image wave^{7,0} to overcome phase distortion in an inhomogeneous medium. Four-wave mixing has also demonstrated a potential usefulness as a narrow-band optical filter.^{7,1} Doubly Resonant Four-Wave Mixing in particular has shown some important new properties in the study of Tb^{3+} compounds in our laboratory. An explanation of these new results and their potential importance will be discussed in what follows.

Studies of hyperfine splittings in LiTbF_4 and $\text{Tb}(\text{OH})_3$ were undertaken fortuitously in trying to understand results

obtained by D. A. Ender,⁷² R. L. Cone, and M. S. Otteson,⁷³ from Doubly Resonant Four-Wave Mixing experiments in these materials. The original emphasis in this work was to understand the line narrowing observed in the four-wave mixing signal. This line narrowing has several possible explanations,⁷⁴ and all but one of these can be eliminated by the observed phase matching angle dependence of the four-wave mixing signal shown in Figure 33.

This new, additional explanation is developed by including the dispersion due to the index of refraction and its effect on the phase matching conditions. The anomalous index dispersion has been ignored in other treatments because there is negligible contribution in Nonresonant Four-Wave Mixing. But in the following, a Doubly Resonant Four-Wave Mixing process is considered, and the anomalous index dispersion must be considered in all four-wave mixing experiments where single or double resonances occur.

Schematically, a four wave mixing experiment is shown in Figure 34(a). The three input beams, at frequencies ω_1 , ω_2 , and ω_3 , generate a coherent fourth beam at frequency ω_4 , where

$$\omega_4 = \omega_1 + \omega_2 - \omega_3.$$

The beam at frequency ω_4 is, unlike degenerate four-wave mixing, both spatially and spectrally distinct from the other three. The sample polarization $P(\omega_4)$ is related to

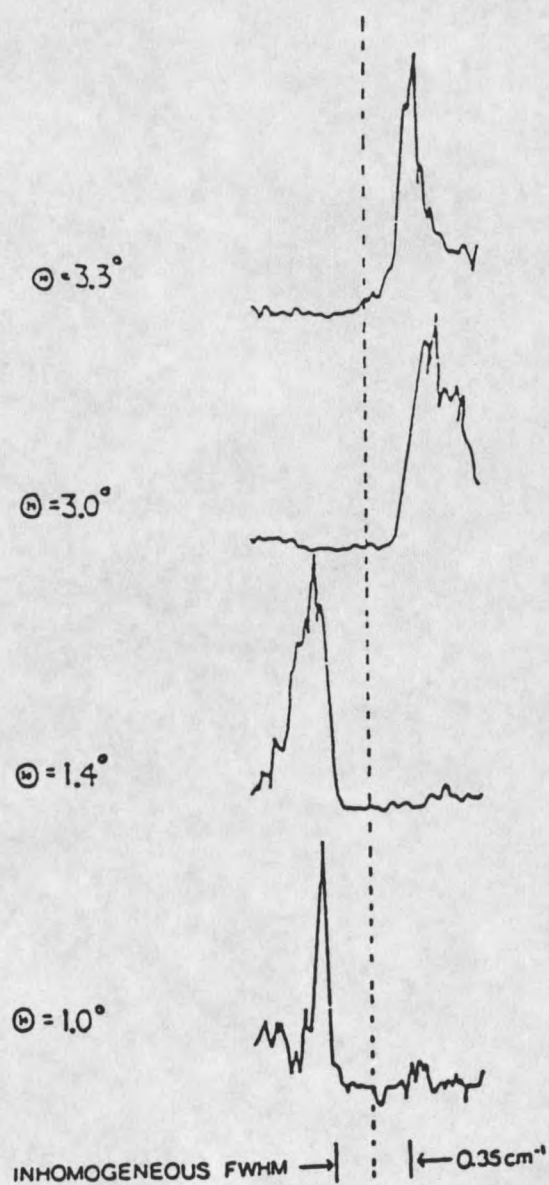
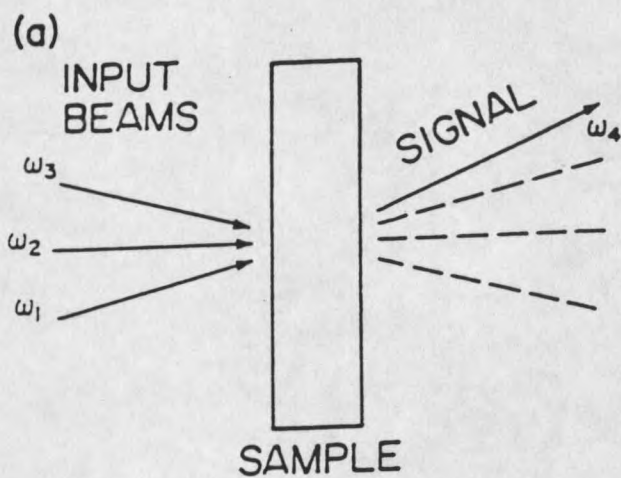


Figure 33: Four-wave mixing signal in LiTbF_4 . Signal shown is at frequency $\omega_4 = 2\omega_1 - \omega_3$ for different crossing angles, θ . $\omega_3 = 17422 \text{ cm}^{-1}$.



$$\omega_4 = \omega_1 + \omega_2 - \omega_3$$

$$\vec{P}(\omega_4) \propto \vec{\chi}^{(3)}(-\omega_4, \omega_1, \omega_2, -\omega_3) \vec{E}(\omega_1) \vec{E}(\omega_2) \vec{E}^*(\omega_3)$$

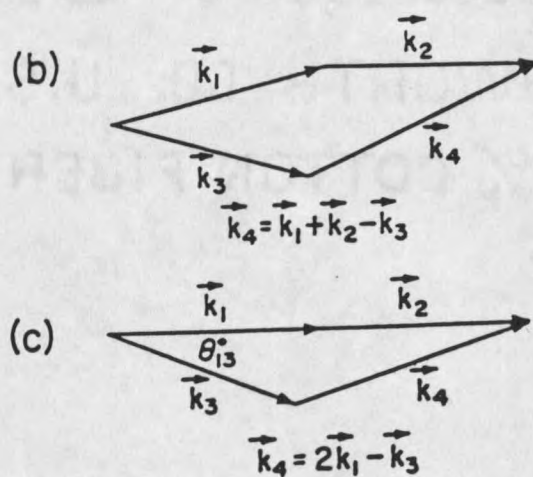


Figure 34: (a) Schematic diagram of four-wave mixing experiment.
 (b) General three beam phase matching diagram.
 (c) Two beam phase matching diagram with beam crossing angle θ_{13} .

the input laser fields $E_1(\omega_1)$, $E_2(\omega_2)$, and $E_3(\omega_3)$, by the third order electric susceptibility $\chi^{(3)}(-\omega_4, \omega_1, \omega_2, -\omega_3)$.⁷⁵

$$P(\omega_4) \propto \chi^{(3)}(-\omega_4, \omega_1, \omega_2, -\omega_3) E_1(\omega_1) E_2(\omega_2) E_3^*(\omega_3). \quad 6.1$$

The possible resonances which occur in $\chi^{(3)}$ can be both single and double photon resonances, but in nonlinear mixing experiments, whenever there are single or double photon resonances, phase matching induced frequency selectivity plays a major role in the interpretation.⁷⁴ The inadequacy of existing theories in accounting for the phase matching induced frequency selectivity was the original reason for this study.

Theory and Experiments

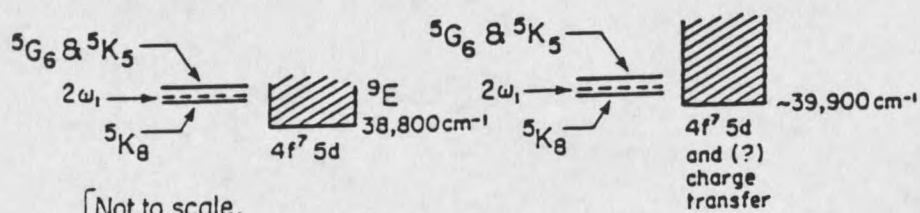
In the terbium compounds, LiTbF_4 and $\text{Tb}(\text{OH})_3$, multiple resonances occur, but for the purpose of analyzing the experiments here it is sufficient to consider a single inhomogeneously broadened resonance.^{7,3} Also without loss of generality, the simplest phase matching condition can be assumed, with $k_1=k_2$ and the beams parallel to each other. In this geometry, the phase matching condition is set by the choice of ω_3 and the angle θ_{13} , as shown in Figure 34(c).

$$\omega_4 = 2\omega_1 - \omega_3 \quad 6.2$$

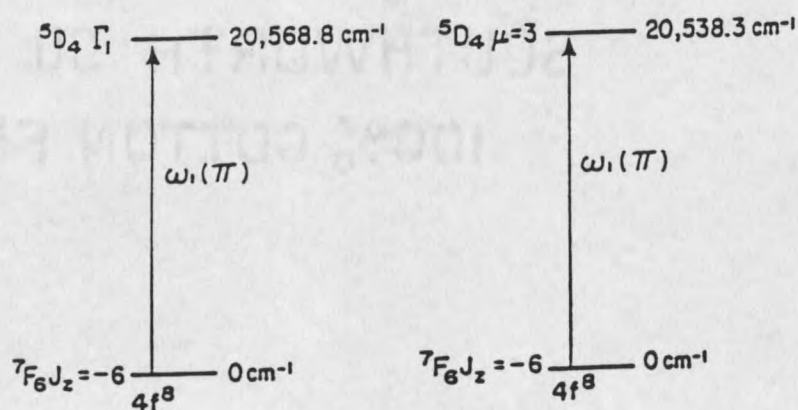
The more general case is shown in Figure 34(b).

Two photon fluorescence excitation studies by Cone and Freidmann, Figure 35, have located the excited $^5\text{K}_8$, $^5\text{K}_5$, and $^5\text{G}_6$ manifolds of the $4f^8$ electronic configuration, in the vicinity of twice the $^7\text{F}_6 \rightarrow ^5\text{D}_4$ energy. $^5\text{K}_8$ is close enough, $\sim 68 \text{ cm}^{-1}$, to yield multiresonant enhancement to $\chi^{(3)}$, but far enough away to show no structure when ω_1 is scanned over 5 or 10 wavenumbers.

In any four-wave mixing experiment, the observed signal is proportional to the product of $|\chi^{(3)}|^2$ and a phase matching factor which takes into account the interference of coherently generated waves at different points along the optical path. A change in the frequency ω_1 causes an individual wave vector to change in the manner shown in equation 6.3.



[Not to scale,
Spacing $\sim 68 \text{ cm}^{-1}$ between
twice $5D_4 (2\omega_1)$ and $5K_8$]



LiTbF_4

Tb(OH)_3

(a)

(b)

Figure 35: Excited states identified by two photon fluorescence excitation.
(a) LiTbF_4 ; (b) Tb(OH)_3

$$\Delta k_i / k_i = \Delta \omega_i / \omega_i + \Delta n_i / n_i \quad 6.3$$

Over the narrow linewidths in these materials, 0.35 cm^{-1} FWHM for LiTbF_4 , 0.8 cm^{-1} FWHM for Tb(OH)_3 , $\Delta \omega_1$ gives negligible changes in k_1 . So changes in n_1 must provide the $\Delta k = 2\pi/L$ which is necessary for phase matching selectivity.

The terms in equation 6.4 can be rewritten, using $k_i = n_i \omega_i / c$, as

$$\Delta k_i = (n_i / c) \Delta \omega_i + (\omega_i / c) \Delta n_i \quad 6.4$$

where it is easy to see that the dominant term off resonance will be the term $(n_i / c) \Delta \omega_i$. But on resonance the other term, $(\omega_i / c) \Delta n_i$, will be dominant.

In the plane wave approximation, which is applicable in these experiments, one can integrate along the path length and obtain an expression for the four-wave mixing signal intensity. This intensity is proportional to the square of the third order susceptibility and a phase matching factor $G(\Delta k)$.

$$I_{\omega_4}(\omega_1) \propto |\chi^{(3)}|^2 G(\Delta k) \quad 6.5$$

A general form the phase matching factor can be written in the following way.

$$G(\Delta k) = \frac{1 + \exp[-(2a_1 + a_3 - a_4)L] - 2 \exp[-(2a_1 + a_3 - a_4)L/2] [\cos \Delta k L]}{[\Delta k]^2 + (2a_1 + a_3 - a_4)^2/4}$$

In the experiments described here, ω_3 was tuned away from any electronic or raman resonances such that $a_3 = a_4 = 0$.

and with $\alpha_1 = \alpha_2 = \alpha$,

$$G(\Delta k) = \frac{1 + \exp[-2\alpha(\omega_1)L] - 2\exp[-\alpha(\omega_1)L]\cos(\Delta kL)}{[\Delta k]^2 + [\alpha(\omega_1)]^2} \quad 6.6$$

Two things should be noted in this factor $G(\Delta k)$. One, it reduces to the familiar form $\text{sinc}^2(\Delta kL/2)$ as $\alpha(\omega)$ goes to zero, and secondly, $G(\Delta k)$ depends on only two parameters. One being $\alpha(\omega_1) \cdot L$ and the other the line shape. To understand this dependence on line shape, one must determine how Δk depends on the frequency ω_1 .

This is easily done by expressing the phase matching condition in terms of the law of cosines.

$$\bar{k}_4^2 = 4k_1^2 + k_3^2 - 4k_1k_3\cos\theta_{13} \quad 6.7$$

Now for phase matching at ω_{10} , $\Delta k = 0$, within the resonance line.

$$\bar{k}_{40} = (4k_{10}^2 + k_3^2 - 4k_{10}k_3\cos\theta_{13}^0)^{1/2} \quad 6.9$$

where k_3 , θ_{13}^0 , k_{10} , and k_{40} are constants fixed for a given resonance profile.

$$k_4 = k_{40} + \Delta k_4 = k_{40} + (\omega_{40}/c)\Delta n_4 + (n_{40}/c)\Delta\omega_4$$

$\Delta n_4 = 0$ for the small scan range used in these experiments, $\sim 5 \text{ cm}^{-1}$, and from equation 6.2, $\Delta\omega_4 = 2\Delta\omega_1$ for fixed ω_3 .

Then

$$k_4 = k_{40} + (2n_{40}/c)\Delta\omega_1,$$

and in equation 6.7 with $k_1 = k_{10} + \Delta k_1$,

$$\bar{k}_4 \simeq k_{40} + 2(2k_{10} - k_3\cos\theta_{13}^0)/k_{40} \Delta k_1 + \mathcal{O}(\Delta k_1^2)$$

$$\bar{k}_4 \simeq k_{40} + 2\Delta k_1 = k_{40} + 2\omega_{10}/c \Delta n_1 + 2n_{10}/c \Delta\omega_1$$

$$\Delta k = k_4 - \bar{k}_4 = (2\omega_{10}/c)\Delta n_1 + (2\Delta\omega_1/c)(n_{10} - n_{40}).$$

The final result is

$$\Delta k \simeq (2\omega_{10}/c)\Delta n_1. \quad 6.10$$

This result implies that as the laser scans through an intermediate resonance, the signal will display a width characteristic of the dispersive change in the index. This change in index, $dn_1/d\omega_1$, is related to the homogeneous width of the transition in some cases. This also leads to a phase matching condition which is over a thousand times more selective than in the case of nonresonant four wave mixing.

As an example of this, consider again the experimental four-wave mixing signals at different phase matching angles shown in Figure 33. As the phase matching angle increases the value of k_1 which satisfies the phase matching condition gets smaller, and the signal broadens as it moves away from line center. Then by increasing the angle to 3.0° the signal moves to the high energy side of the line, where phase matching occurs for smaller index. By increasing the angle more, the signal is again driven toward line center, where the index change is steeper and the signal gets narrower.

To understand this dependence on the anomalous dispersion and the phase matching angle, one must know the absorption coefficient and the dispersion for the resonant transition. To that end, very thin samples of LiTbF_4 and

$\text{Tb}(\text{OH})_3$ were polished using diamond polishing techniques. With patience, a $\text{Tb}(\text{OH})_3$ sample was polished to a thickness of 26 microns, and a LiTbF_4 crystal was polished to a thickness of 78 microns.

The absorption profiles were obtained using a pressure scanned dye laser with 1 GHz bandwidth. The result of this experiment for LiTbF_4 is shown in Figure 36, where standard techniques have been used to convert the transmitted intensity into absorption coefficient using Beer's law. The asymmetric shape and apparent structure in this absorption profile are important, but the discussion will return to that later.

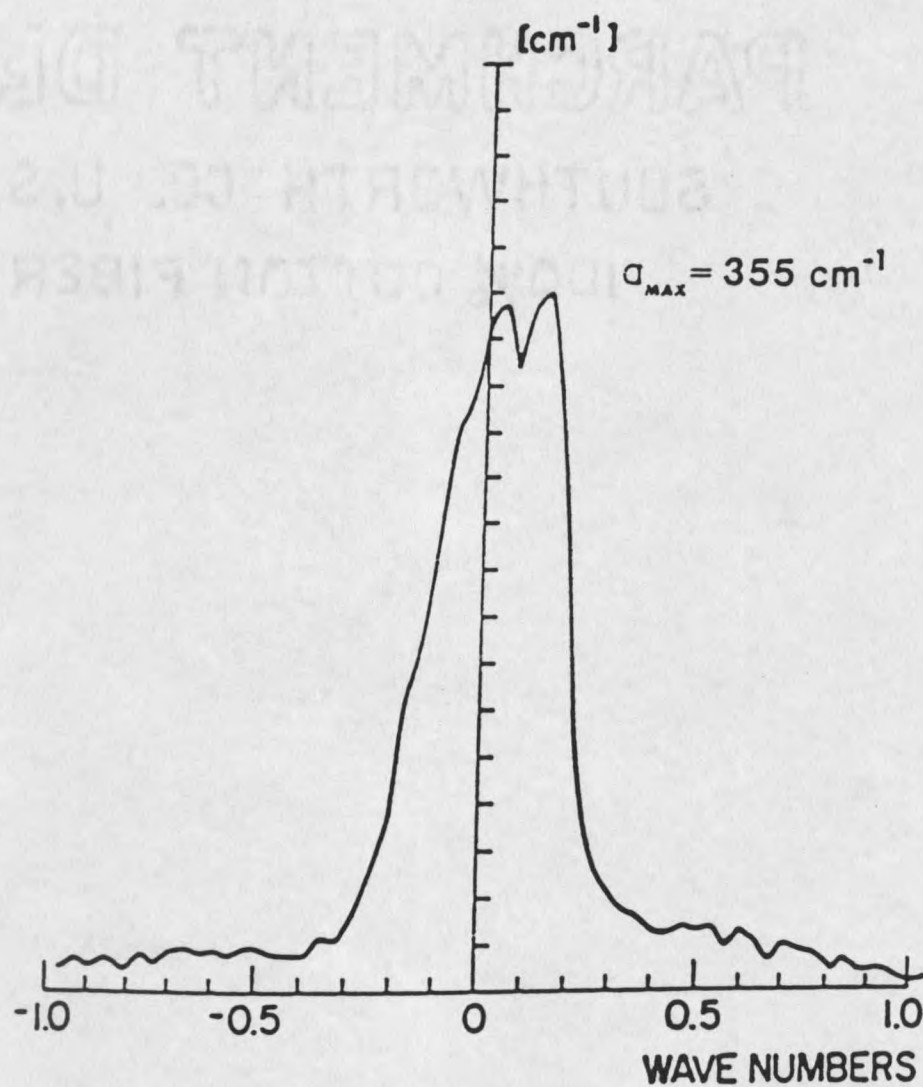


Figure 36: Experimental absorption coefficient. LiTbF_4 crystal 78 microns thick.
 $\text{FWHM} = 0.35 \text{ cm}^{-1}$

Simulation Studies

Using the plasma dispersion function, or Voigt profile, this experimental profile was fit to an approximate gaussian line shape, with a FWHM of 0.35 wavenumbers, 10.5 GHz. Then by using the absorption coefficient and index profiles obtained from the fitted complex plasma dispersion function, one can calculate the four-wave mixing signal which is shown in Figure 37. This fit shows the same type of behavior as was observed experimentally as a function of phase matching angle. It shows the characteristic line narrowing also, but it does not show the line narrowing that was observed experimentally, 0.056 cm^{-1} , 1.68 GHz, which was the narrowest signal detected in LiTbF_4 .

It was then necessary to reconsider the absorption profile. If one believes that there was really structure hidden within the inhomogeneous line, one is forced to consider the possibility of hyperfine levels, with a splitting on the order of the inhomogeneous width for each individual hyperfine component. This would also explain the asymmetric shape of the absorption line, because this data was taken at 1.3 K, where the higher energy hyperfine components would have a reduced population proportional to the Boltzman distribution $\exp(-E/kT)$.

The original experimental absorption profile, Figure 36, was then fit with a superposition of 4 gaussian lines with inhomogeneous widths of 0.08 cm^{-1} , 2.4 GHz, and

hyperfine splittings of 0.106 cm^{-1} , 3.18 GHz. This fit which took into account the temperature dependence of the hyperfine level populations is shown in Figure 38. This superposition of four hyperfine energy levels within the the ground state absorption profile reproduces the experimental data almost exactly.

The complex plasma dispersion function which resulted from this fit was then used to generate the model simulations of the four-wave mixing signal. An example of the simulated four-wave mixing signal is shown in Figure 39. This simulation reproduces the line narrowing observed in the experiments, and it also displays the correct behavior with respect to phase matching position within the inhomogeneous profile.

Comparison of the inverse FWHM of the four-wave mixing signal for each of the two cases is shown in Figure 40. For the curve marked (a), the inverse FWHM of the four-wave mixing signal is plotted for the gaussian fit to the absorption profile. The curve (b) is the same thing plotted for the fit of four hyperfine components, where the inhomogeneous width of each component is 2.4 GHz and the splitting between components is 3.18 GHz. As this figure shows, the signal is a factor of four narrower in the latter case. This factor of 4 narrowing is exactly the amount needed to duplicate the experimental results shown in Figure 33.

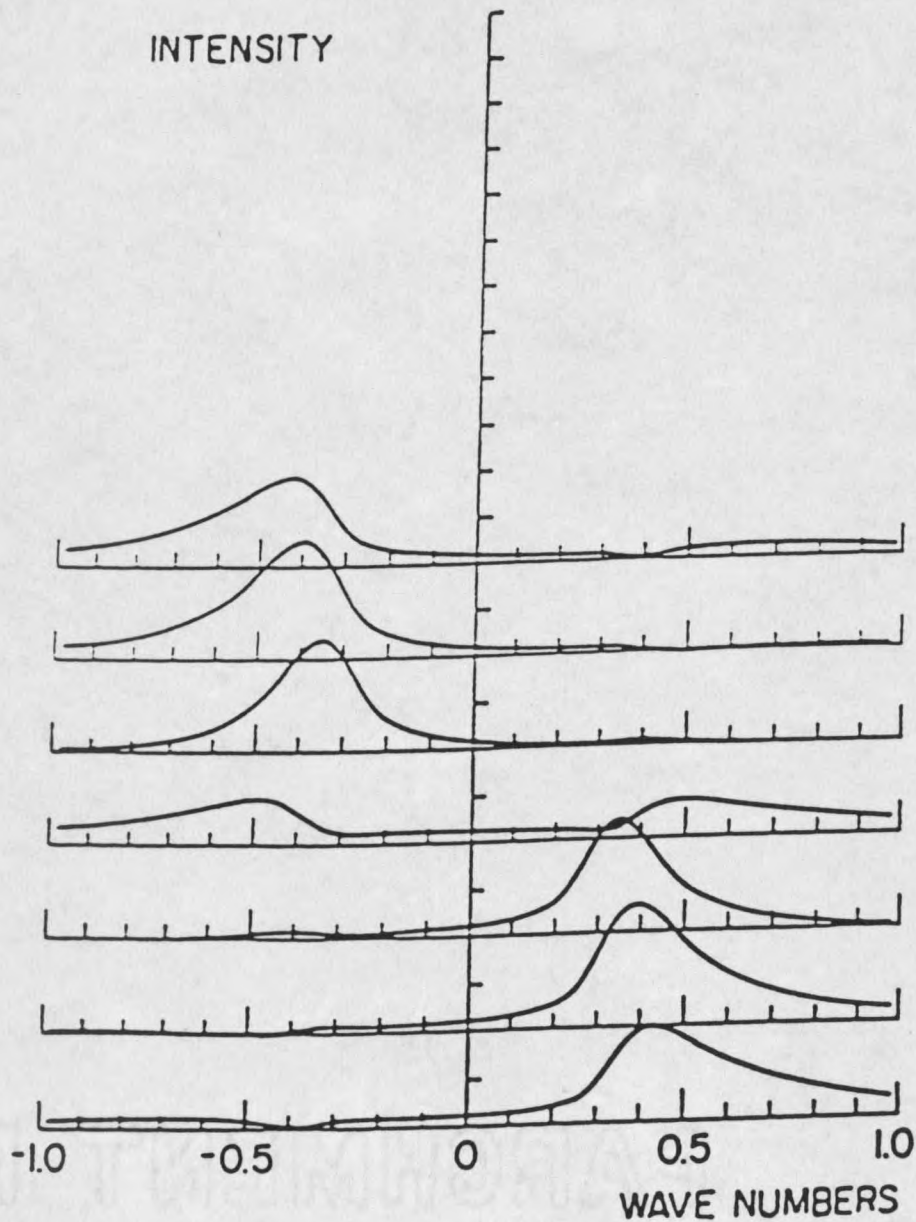


Figure 37: Model simulation of four-wave mixing signal as a function of phase matching angle for a gaussian fit to the complex plasma dispersion function.

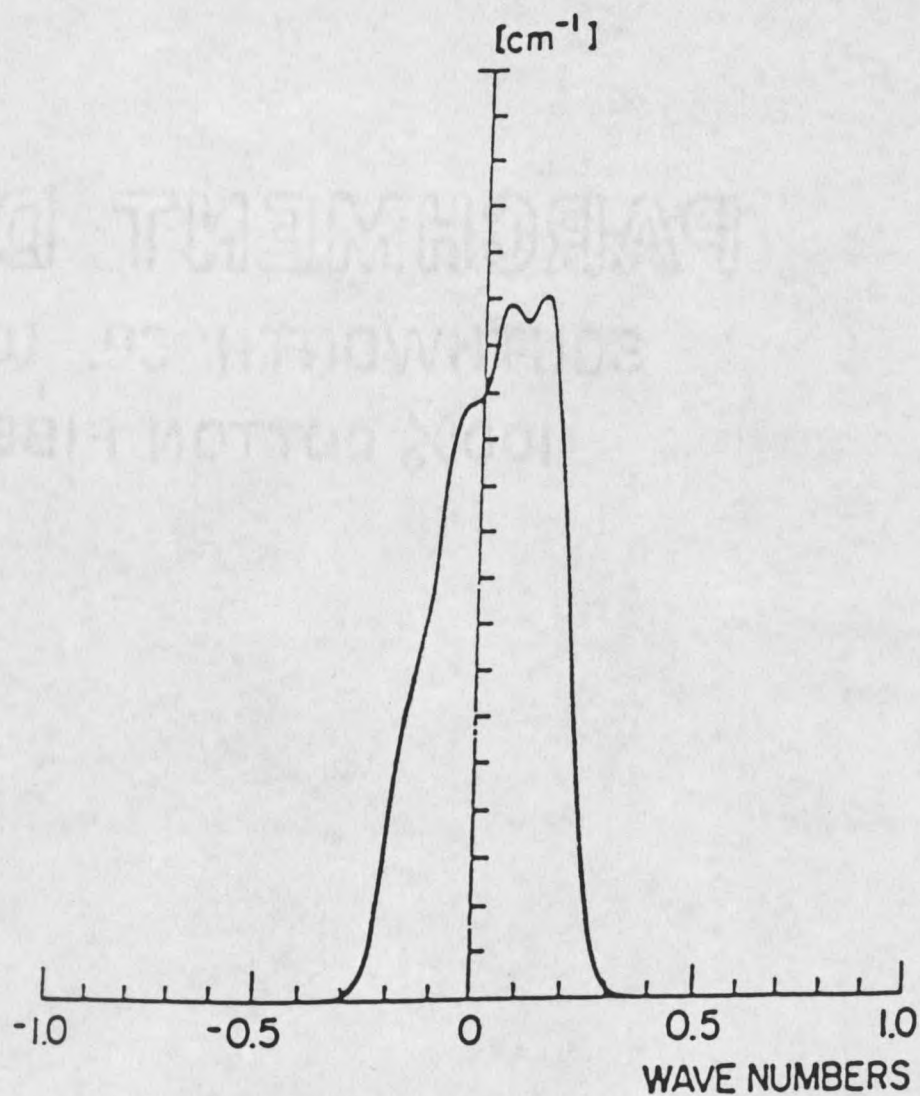


Figure 38: Superposition of four gaussian lines, each with an inhomogeneous width of 0.08 cm^{-1} , with hyperfine splitting of 0.106 cm^{-1} .

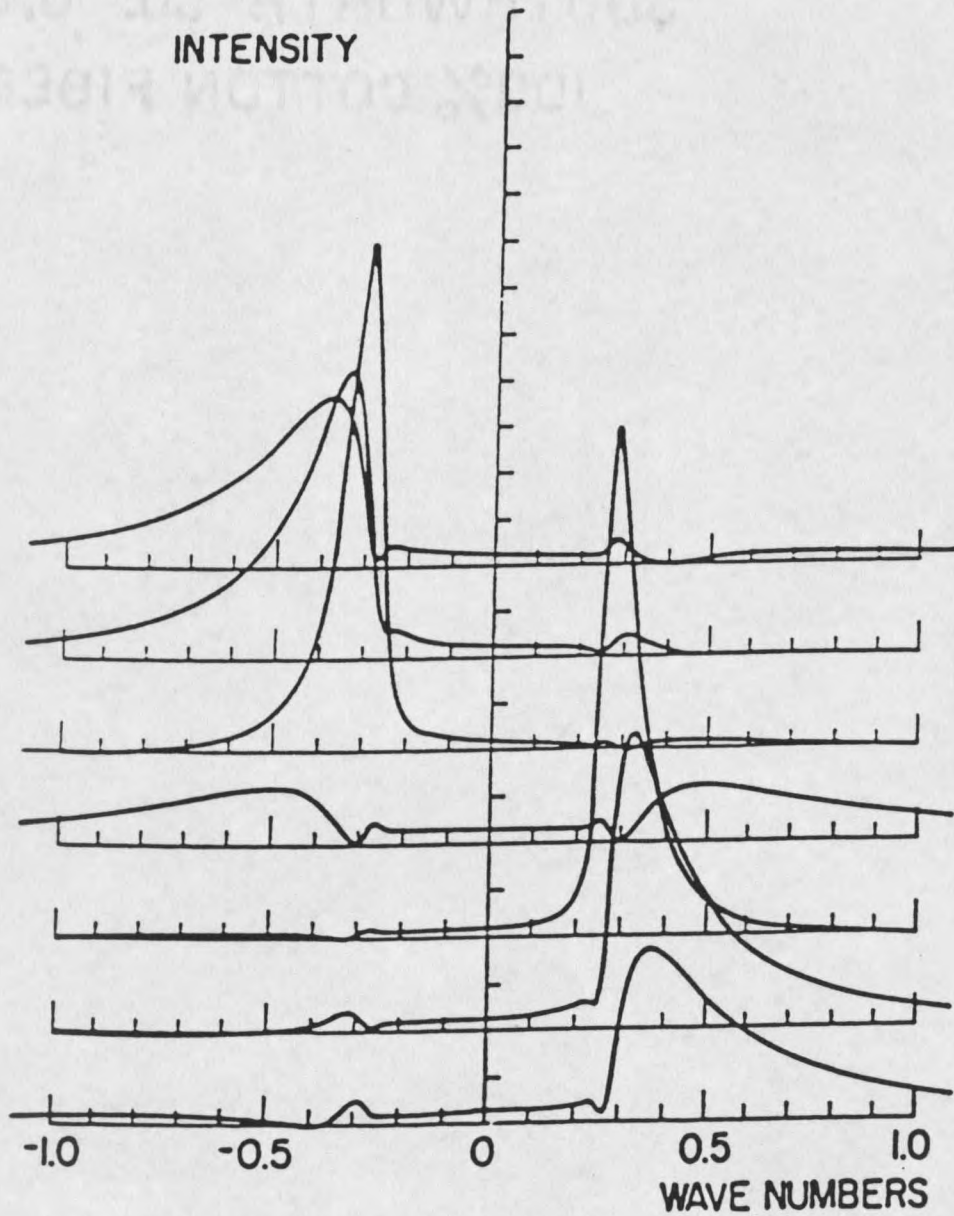


Figure 39: Model simulation of four-wave mixing signal as a function of phase matching angle. Complex plasma dispersion function fit to a superposition of four gaussian lines.

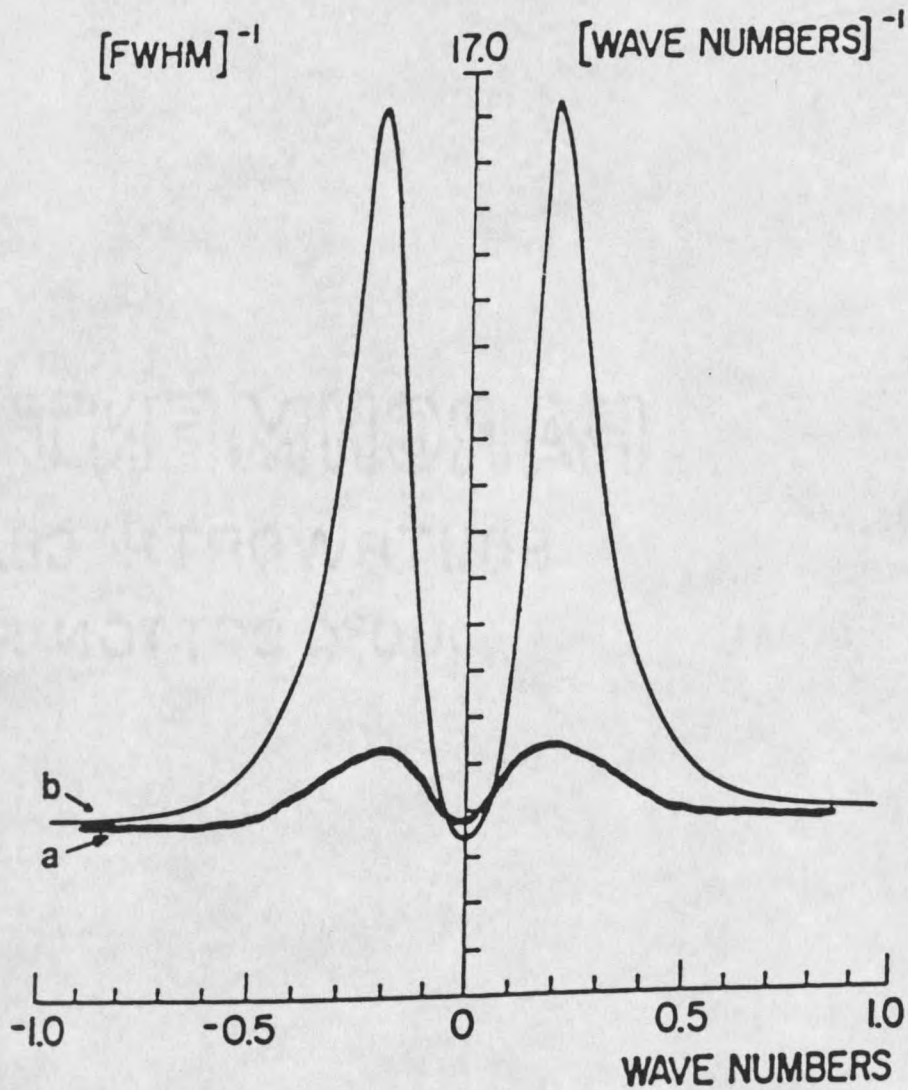


Figure 40: Comparison of inverse Full Width at Half Maximum of four-wave mixing signal.
 (a) Single gaussian.
 (b) Superposition of four gaussian lines.

The important point to be made in these simulation studies, is that the four-wave mixing signal, which was simulated, depends on only two experimental parameters. One is the absorption coefficient, $\alpha(\omega_1)$, which was fit to duplicate the experimental absorption profile, and the other is the dispersion profile. This last parameter, which determines line shape, was fit with in a range of values to duplicate the structure and width of the inhomogeneous absorption profile. Thus there are no free parameters and the resulting fit gives an accurate simulation of the signal observed experimentally. This implies that one can obtain a great deal of information by analyzing the four-wave mixing signal in terms of its phase matching dependence and narrowing. For example, the fitted parameter for the hyperfine splitting was 3.18 GHz, writing the hyperfine Hamiltonian in the familiar form with no external magnetic field.⁷⁶

$$H = A_J (\vec{J} \cdot \vec{I})$$

The splitting between hyperfine levels for Tb^{3+} is then

$$\Delta E = 6A_J,$$

where $J=6$ and $I=3/2$. This implies a value $A_J = 530$ MHz in $LiTbF_4$. In checking previous measurements, it was discovered that this is the exact value obtained by Bleaney,⁷⁷ in measurements in rare earth salts, using electron spin resonance techniques.

Conclusions

The most interesting and useful application of four-wave mixing may be in the measurement of the homogeneous linewidth. These studies indicate that the phase matching restrictions will approach the fundamental limit imposed by the homogeneous linewidth. If that holds, the homogeneous linewidth could be measured by doing a four-wave mixing experiment and measuring the linewidth of the narrowest signal as the phase matching angle was changed. To realize this, one must have a sample that is big enough to produce the narrowing necessary to reach this fundamental limit. But this is not a severe restriction, because the oscillator strength also plays a role, since the important parameter is $\alpha(\omega) \cdot L$. The simulated signal shown in Figure 41 is the four-wave mixing signal from a crystal one centimeter thick, with the same fit parameters as the LiTbF_4 crystal discussed previously. The extreme narrowing of the signal and the signal strength both scale with the thickness dimension, so thick crystals with strong absorptions will produce very strong and very narrow signals limited only by the homogeneous linewidth in the particular material. Although oscillator strengths for Tb^{3+} f-f transitions are quite small, 9×10^{-9} for the ${}^7\text{F}_6 \longleftrightarrow {}^5\text{D}_4$ transition in LiTbF_4 , many rare earth materials have oscillator strengths which are larger by 2 or 3 orders of magnitude. These materials may be prime candidates for testing this hypothesis and

reaching the homogeneous limit of the material transition.

Further simulations, which have not been done in detail, have demonstrated that the fundamental limit is the homogeneous linewidth. By varying the crystal length in the simulation and varying the homogeneous width of the inhomogeneous profile, the simulations predict that, as expected, the homogeneous width is the fundamental limit in this Doubly Resonant Four-Wave mixing. This prediction will have to wait for experimental verification, but it will have far reaching implications and many practical applications in future four-wave mixing experiments, if it is confirmed.

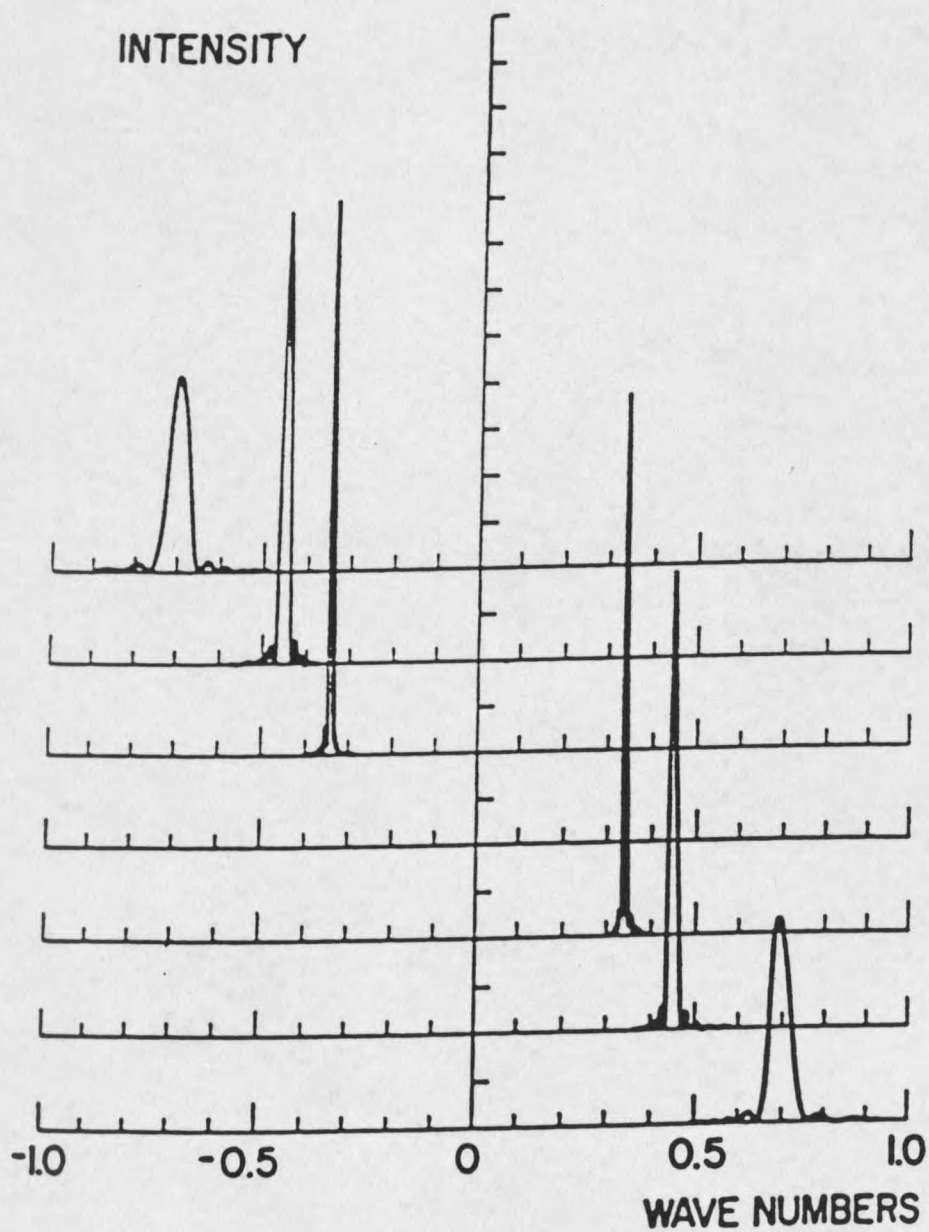


Figure 41: Model simulation of four-wave mixing signal as a function of phase matching angle.
 $L = 1.0$ cm.

APPENDICES

APPENDIX I

```
/* HOLE BURNING PROGRAM TO REPETITIVELY
   SCAN LASER IN BURN-READ CYCLE */
```

```
#include      <std.h>
#include      <rt11.h>
#include      "da.c"

main()
{
    int      scan, rdly, volt, hbtime;
    int      i, j, k, l, m, s, t;

    /* SET HOLE BURN TIME */
    printfmt("Hole burning time, integer\n");
    getfmt("%i\n", &hbtime);
    /* SET SCAN SPEED */
    printfmt("scan speed, ramp increment\n");{
    getfmt("%i\n", &scan);
    printfmt("ramp delay\n");
    getfmt("%i\n", &rdly);
    /* SET ACOUSTO-OPTIC MODULATOR VOLTAGE */
    printfmt("voltage, A/O modulator, 1843<=voltage<=2047\n");
    getfmt("%i\n", &volt);
    /* NUMBER OF SCANS TO AVERAGE */
    printfmt("How many scans do you want?\n");
    getfmt("%i\n", &j);
    /* SET START POSITION */
    printfmt(" 0 => mid freq., 1 => low freq.\n");
    getfmt("%i\n", &m);
    if(m == 1){
        for(s=3071;s>=2047;s-=16)
        {
            putvolt(2,2047);
            putvolt(0,s);
        }
    }
    /* START SCAN */
    printfmt("hit return key to start\n");
    getfmt("\n");
```

```

for(k=1;k<=j;k+=1)
{
    for(s=1;s<=hbtime;s+=1)
    {
        putvolt(0,2047);
        /* SET A/O MODULATOR VOLTAGE TO 1 VOLT TO BURN HOLE */
        putvolt(2,1844);
    }
    for(i=2047;i<=3071;i+=16)
    {
        putvolt(2,2047);
        putvolt(0,i);
    }
    putvolt(1,1024);
    for(l=0;l<=25;l+=1){} /* TRIGGER PULSE */
    putvolt(1,2047);
    /* LASER SCAN VOLTAGE */
    for(s=3071;s>=1023;s-=scan)
    {
        putvolt(0,s);
        putvolt(2,volt);
        for(l=0;l<=rdly;l+=1){}
    }
    for(s=1023;s<=2047;s+=16)
    {
        putvolt(2,2047);
        putvolt(0,s);
    }
}
for(s=2047;s<=3071;i+=16)
{
    putvolt(2,2047);
    putvolt(0,s);
}

putvolt(0,3071);
putfmt("done\n");
}

```

APPENDIX II

```
/* PROGRAM TO ERASE HOLE IN THE INHOMOGENEOUS LINE */
```

```
#include      <std.h>
#include      <rt11.h>
#include      "da.c"

main()
{
    int      scan, rdly, volt;
    int      j, k, l, m, n, s;

    /* INITIALIZE ALL D/A OUTPUTS TO ZERO */
    printfmt("Should scan be initialized? 0 => yes \n");
    getfmt("%i\n", &n);
    if(n == 0){
        putinit();
    }

    /* NUMBER OF SCANS TO ERASE HOLE */
    printfmt("How many scans do you want?\n");
    getfmt("%i\n", &j);
    /* SET SCAN SPEED */
    printfmt("scan speed, ramp increment\n");{
        getfmt("%i\n", &scan);
        printfmt("ramp delay\n");
        getfmt("%i\n", &rdly);
    }
    /* SET ACOUSTO-OPTIC MODULATOR VOLTAGE */
    printfmt("voltage, A/O modulator, 1843<=voltage<=2047\n");
    getfmt("%i\n", &volt);

    /* SET START POSITION */
    printfmt(" 0 => mid freq., 1 => low freq.\n");
    getfmt("%i\n", &m);
    if(m == 0){
        for(s=2047; s<=3071; s+=16)
        {
            putvolt(2, 2047);
            putvolt(0, s);
        }
    }

    /* START SCAN */
    printfmt("hit return key to start\n");
    getfmt("\n");
```

```

for(k=1;k<=j;k+=1)
{
    putvolt(1,1024);
    for(l=0;l<=25;l+=1){}          /* TRIGGER PULSE */
    putvolt(1,2047);
    /* LASER SCAN VOLTAGE */
    for(s=3071;s>=1023;s-=scan)
    {
        putvolt(0,s);
        putvolt(2,volt);
        for(l=0;l<=rdly;l+=1){}
    }
    for(s=1023;s<=2047;s+=16)
    {
        putvolt(2,2047);
        putvolt(0,s);
    }
    putvolt(0,2047);
    putvolt(3,1535);
    putvolt(3,2047);

    for(s=2047;s<=3071;i+=16)
    {
        putvolt(2,2047);
        putvolt(0,s);
    }
}

putvolt(0,3071);
putvolt(2,2047);
putvolt(3,2047);
putfmt("done\n");
}

```

APPENDIX III

```
/*PROGRAM TO SCAN LASER AND ACCEPT PHASE SWITCH DATA FROM
TEKTRONIX 7912AD TRANSIENT DIGITIZER */
```

```
#include <std.h>
#include <rt11.h>
#include "da.c"

main()
{
    int IBUP();
    int write = 0;
    int read = 1;
    int remote = 4;
    int local = 5;
    int digitizer = 1;
    char *comd1;
    char *comd2;
    char *comd3;
    int lenst1;
    int lenst2;
    int lenst3;
    char strip[3];
    unsigned char array[1024]
    long sumaray[512]
    int three = 3;
    int size = 1024;
    int two = 2;
    int one = 1;
    int bit9 = 256;
    int i, j, k, l, s;
    int scan, rdly, volt;
    int shot = 1;
    char filnam[20];
    FIO fio;
    int shots, save;

    putfmt("What is the name of the data file?\n");
    getfmt("%p\n", filnam);
    if(!fcreate(&fio, filnam, 1))
    {
        putfmt("Error: can't open %p\n", filnam);
        return;
    }
}
```

```

/* NUMBER OF SHOTS TO AVERAGE */
putfmt("How many shots do you want?\n");
getfmt("%i\n",&shots);
comd1 = "DIG SA,\0";
i = itob(comd1+7,shot,10);
comd1[7+i] = '\0';
comd2 = "READ SA \0";
comd3 = "MOD TV\0";
lenst1 = lenstr(comd1);
lenst2 = lenstr(comd2);
lenst3 = lenstr(comd3);
fcall(IBUP,2,&remote,&digitizer);
fcall(IBUP,4,&write,&digitizer,comd1,&lenst1);

/* SET SCAN SPEED */
putfmt("scan speed, ramp increment\n");{
getfmt("%i\n",&scan);
putfmt("ramp delay\n");
getfmt("%i\n",&rdly);

/* SET ACOUSTO-OPTIC MODULATOR VOLTAGE */
putfmt("voltage, A/O modulator, 1843<=voltage<=2047\n");
getfmt("%i\n",&volt);

/* START SCAN */
putfmt("hit return key to start\n");
getfmt("\n");
for(k=1;k<=shots;k+=1)
{
    putvolt(1,1024);
    for(l=0;l<=25;l+=1){}          /* TRIGGER PULSE */
    putvolt(1,2047);
    /* LASER SCAN VOLTAGE */
    for(s=3071;s>=1023;s-=scan)
    {
        putvolt(0,s);
        putvolt(2,volt);
        for(l=0;l<=rdly;l+=1){}
    }
    for(s=1023;s<=2047;s+=16)
    {
        putvolt(2,2047);
        putvolt(0,s);
    }
    putvolt(0,2047);
    putvolt(3,1535);
    putvolt(3,2047);
    for(s=2047;s<=3071;s+=16)
    {
        putvolt(2,2047);
        putvolt(0,s);
    }
}

```

```

    }
    shots = shots + 1;

    fcall(IBUP,4,&write,&digitizer,comd2,&lenst2);
    fcall(IBUP,4,&read,&digitizer,strip,&three);
    fcall(IBUP,4,&read,&digitizer,array,&size);
    fcall(IBUP,4,&read,&digitizer,strip,&two);

    printf("SAVE? 0 => YES\n");
    getfmt("%i\n", &save);
    if(save == 0)
    {
        shots = shots-1;
        for(i=1;i<7;i+=1)
        {
            array[159+i]=(array[157+i] + array[163+i])/2;
            array[251+i]=(array[247+i] + array[249+i] +
            array[257+i] + array[259+i])/4;
        }
        for(j=0;j<512;j++)
        {
            sumaray[j] = sumaray[j] + array[2*j]*bit9 +
            array[2*j+1]*one;
        }
        fcall(IBUP,4,&write,&digitizer,comd1,&lenst1);
    }
    printf(&fio,"%\n");
    for(i=0;i<64;i++)
    {
        printf(&fio,"%+\06041 %+\06061 %+\06061 %+\06061
        %+\06061 %+\06061 %+\06061
        %+\06061 %+\06061\n"
        (long)(8*i),sumaray[8*i], sumaray[8*i+1], sumaray[8*i+2],
        sumaray[8*i+3], sumaray[8*i+4], sumaray[8*i+5],
        sumaray[8*i+6], sumaray[8*i+7]);
    }
    fclose(&fio);
    putvolt(3,1535);
    putvolt(3,2047);
    fcall(IBUP,4,&write,&digitizer,comd3,&lenst3);
    putvolt(0,3071);
    putvolt(2,2047);
    putvolt(3,2047);
    fcall(IBUP,2,&local,&digitizer);
    printf("done\n");
}

```

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