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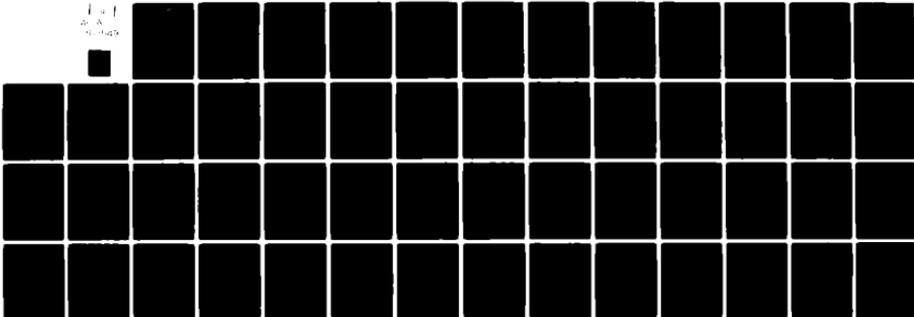
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LASER HOLE BURNING SPECTROSCOPY: A HIGH RESOLUTION PROBE OF MOL--ETC(U)  
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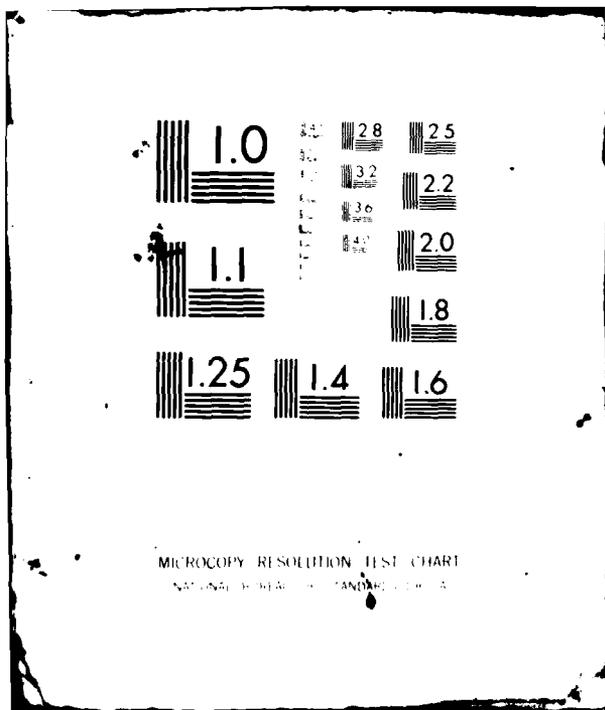
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>AFOSR-TR- 81 -0790</b>	2. GOVT ACCESSION NO. <b>AD-A108549</b>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) <b>LASER HOLE BURNING SPECTROSCOPY: A HIGH RESOLUTION PROBE OF MOLECULAR ENVIRONMENTS</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Final</b>
7. AUTHOR(s) <b>R. M. Macfarlane and R. M. Shelby</b>		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>IBM Research Laboratory 5600 Cottle Road, K32/281 San Jose, CA 95193</b>		8. CONTRACT OR GRANT NUMBER(s) <b>F49620-79-C-0108</b>
11. CONTROLLING OFFICE NAME AND ADDRESS <b>Air Force Office of Scientific Research/NC Bolling Air Force Base, Washington, DC 20332</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>611025 2305/AB</b>
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <b>6/1/79 - 6/1/81</b>
16. DISTRIBUTION STATEMENT (of this Report) <p style="text-align: center;">12 57</p>		13. NUMBER OF PAGES <b>60</b>
		15. SECURITY CLASS. (of this report) <b>Unclassified</b>
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION, DOWNGRADING, SCHEDULE <b>S DTIC ELECTE DEC 15 1981 D</b>
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <b>Laser hole burning, high resolution spectroscopy, organic molecules, rare earth ions.</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>Laser induced hole burning in optical bands of low temperature solids has been investigated with emphasis on mechanisms for population hole burning, the interactions with the environment which limit the hole widths and the use of hole burning for ultra high resolution spectroscopy. Hole burning was observed in a wide range of solids including organic and organometallic molecules in crystals and rare earth ions in crystals and glasses. The mechanisms for hole burning also varied widely and a new mechanism involving optically induced nuclear spin flips of near neighbor</b>		

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nuclei was discovered. Examples of hole burning in new classes of materials are presented here for the first time, namely inorganic glasses (silicate glasses containing  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$  or  $\text{Eu}^{3+}$ ) and undoped stoichiometric compounds (e.g.,  $\text{EuP}_{514}\text{O}_{14}$ ). Hole recovery was used to determine nuclear spin lattice relaxation rates in praseodymium doped crystals. For allowed optical transitions (e.g., singlet states of zinc, porphyrin, dibromoindigo and color centers in alkali halides) the hole widths at 2K are limited by population decay to approximately 50MHz. For longer lived optical levels in crystalline materials, e.g., those containing rare earth ions, the hole widths are narrower (less than 10MHz) and are limited by dynamical interactions with surrounding nuclei. In amorphous materials such as europium doped silicate glass, hole widths are much broader, being limited by low frequency tunneling motions. Hole burning measurements were complemented by time domain coherent transient (photon echo, and optical free decay) measurements of homogeneous linewidths which enabled us to measure optical resonances as narrow as 760Hz in  $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ . In cases where hole burning involved optical pumping of nuclear hyperfine levels, optically detected nuclear resonance was used to investigate the dynamics of nuclear spins which were responsible for hole broadening and optical dephasing.

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**AFOSR-TR- 81 -0790**

**LASER HOLE BURNING SPECTROSCOPY:  
A HIGH RESOLUTION PROBE OF MOLECULAR ENVIRONMENTS**

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**Final Report for Contract F49620-79-C-0108**

**For the Period: 6/1/79 - 6/1/81**

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## ABSTRACT

Laser induced hole burning in optical absorption bands of low temperature solids has been investigated with emphasis on mechanisms for population hole burning, the interactions with the environment which limit the hole widths and the use of hole burning for ultra high resolution spectroscopy.

Hole burning was observed in a wide range of solids including organic and organometallic molecules in crystals and rare earth ions in crystals and glasses. The mechanisms for hole burning also varied widely and a new mechanism involving optically induced nuclear spin flips of near neighbor nuclei was discovered. Examples of hole burning in new classes of materials are presented here for the first time, namely inorganic glasses (silicate glasses containing  $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$  or  $\text{Eu}^{3+}$ ) and undoped stoichiometric compounds (e.g.,  $\text{EuP}_5\text{O}_{14}$ ). Hole recovery was used to determine nuclear spin lattice relaxation rates in praseodymium doped crystals. For allowed optical transitions (e.g., singlet states of zinc porphyrin, dibromindigo and color centers in alkali halides) the hole widths at 2K are limited by population decay to approximately 50 MHz. For longer lived optical levels in crystalline materials, e.g., those containing rare earth ions, the hole widths are narrower (less than 10 MHz) and are limited by dynamical interactions with surrounding nuclei. In amorphous materials such as europium doped silicate glass, hole widths are much broader, being limited by low frequency tunneling motions. Hole burning measurements were complemented by time domain coherent transient (photon echo, and optical free decay) measurements of homogeneous linewidths which enabled us to measure optical resonances as narrow as 760 Hz in  $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ . In cases where hole burning involved optical pumping of nuclear hyperfine levels, optically detected nuclear resonance was used to investigate the dynamics of nuclear spins which were responsible for hole broadening and optical dephasing.

## INTRODUCTION

Spectral hole burning is a process whereby a narrow "hole" is bleached in an inhomogeneously broadened line following irradiation by a narrow band laser (Fig. 1). This is caused by the removal of a subset of ions or molecules from their ground state to a level where they no longer absorb the laser light. In cases where there is a fine structure in the electronic excited state (e.g., due to hyperfine interactions, external fields, etc.) this structure shows up as subsidiary side holes. The width of these holes, their dynamics and their behavior under applied perturbations gives valuable spectroscopic information relating to the environments of the active species. In addition, the phenomenon of hole burning provides the basis for frequency domain optical information storage.<sup>1</sup>

We are interested in understanding mechanisms giving rise to hole burning in solids and in using it to obtain very high resolution spectroscopic information. These measurements are limited in resolution by the homogeneous linewidth rather than the inhomogeneous linewidth which is much larger and due to crystal strains. While there was emphasis on organic solids in the earlier part of this work, it became clear that many of the important phenomena associated with hole burning could be more easily and more definitively studied in solids containing rare earth ions. The results of these studies are of wide applicability, and in particular can be applied to analogous organic molecular solids.

## **RESEARCH OBJECTIVES**

### **I. Mechanisms for Hole Burning**

- a) Investigate the use of long lived optical metastable states, such as triplet states of organic molecules, as population reservoirs for hole burning.
- b) Investigate the use of nuclear quadrupole levels as population reservoirs in rare earth solids and organic molecules and investigate mechanisms limiting hole lifetimes.
- c) Investigate hole burning in impurity doped glasses and compare with that in crystalline media.

### **II. Mechanisms Determining the Limiting Hole Widths**

- a) What processes limit the width of holes in low temperature solids?
- b) Use time domain coherent transient techniques (e.g., free decay, photon echo) to measure intrinsic homogeneous linewidths and compare these with the results of hole burning.
- c) Extend study of impurity systems to stoichiometric materials and investigate the role of energy transfer in determining hole widths.

### **III. Hole Burning Spectroscopy**

- a) Use the high resolution capabilities of hole burning to measure the effect of applied fields on the energy levels of hole burning species, e.g., use magnetic fields to measure nuclear magnetic moments.
- b) Measure hyperfine structure in electronic excited states using hole burning.
- c) Use hole burning via optical pumping of nuclear hyperfine levels as a basis for rf optical double resonance studies.

## I. MECHANISMS FOR HOLE BURNING

### Hole Burning Using Metastable Optical Levels as Population Reservoir

The simplest method of population hole burning involves two level saturation. For short lived states this is difficult to achieve and a third metastable population reservoir is desirable. The triplet states of organic molecules can, in general, provide such a level. We showed for zinc porphyrin (ZnP) in n-octane at 2K, that hole burning in the  $S_1 \leftrightarrow S_0$  transition could be observed using the lowest triplet state as a reservoir.<sup>2</sup> Hole recovery was limited by the triplet lifetime of 118 msec. The hole width for one of two crystallographic sites at 2K was 115 MHz corresponding to a dephasing time ( $T_2$ ) of 2.1 nsec. This hole width was limited by the population decay time ( $T_1$ ) of  $S_1$ . As temperature increased to 4.5K the hole width increased with an activation energy of  $14 \text{ cm}^{-1}$  which is just the splitting between the two lowest electronic states due to the asymmetric crystalline environment. Hole broadening, therefore, appears to be due to phonon absorption between these states. Molecules in another crystallographic site where the  $S_1$  splitting is  $109 \text{ cm}^{-1}$  show temperature independent hole widths up to 4K. The hole widths are therefore seen to be sensitive to the strength of the distortion at the sites which the molecules occupy.

### Hole Burning Using Nuclear Quadrupole Levels as a Population Reservoir

It has been shown in  $\text{Pr}^{3+}$  doped solids that hole burning can occur due to optical pumping effects which transfer population among nuclear quadrupole levels.<sup>3</sup> In order for this to happen the hole width must be narrower than the difference between ground and excited state quadrupole splittings ( $Q_g, Q_e$ ). Our approach was to investigate molecules with bromine replacing protons because bromine has a large quadrupole moment with  $Q_g \approx 300 \text{ MHz}$ . The difference  $Q_g - Q_e$  is expected to be several percent of this. Measurements were made on 6-6' dibromoindigo in n-octane at 2K, and hole burning was

observed with a width of  $\sim 120$  MHz. This width corresponds to a dephasing time of 5 nsec or a population decay time of 2.5 nsec which is reasonable for this material. The hole recovery was very long ( $> 1$  hour) and since the holes were broader than the expected difference between  $Q_g$  and  $Q_e$  the hole burning mechanism probably involves a photochemical isomerization. This has not yet been established. We note, however, that hole burning did not occur in the indigo which was not bromine substituted.

We studied the quadrupole hole burning mechanism in more detail in  $\text{Pr}^{3+}:\text{LaF}_3$  where the hole recovery was fairly long ( $\sim$  minutes). We recognized that this recovery was due to nuclear spin lattice relaxation and could be used to accurately measure nuclear spin lattice relaxation rates of these dilute (0.01 to 2.0 at. %) nuclei.<sup>4</sup> The relatively complicated relaxation dynamics of the  $I=5/2$  system were simplified by rf saturation of one of the three zero field hyperfine transitions to effectively produce two level behavior. In this way, the relaxation rates  $K_{12}$ ,  $K_{23}$ ,  $K_{31}$  for each of the three hyperfine transitions (1,2,3) could be determined. The temperature dependent relaxation was shown to be due to a resonant two phonon (Orbach) relaxation process involving the first excited crystal field level  $57 \text{ cm}^{-1}$  above the ground state (Fig. 2). The phonon absorption and emission processes couple to the Pr nuclear spins through the hyperfine interaction which admixes the spin states differently in the ground and excited crystal field states. Theoretical estimates of the phonon induced relaxation rates come within an order of magnitude of the experimentally observed rates.

A concentration dependent hole filling process was observed and interpreted in terms of Pr-Pr flip-flops due to homonuclear dipolar interactions. This experiment thus offers a rather direct probe of these weak interactions between dilute nuclei.

The use of nuclear quadrupole levels as population reservoirs was extended to several  $\text{Eu}^{3+}$  systems which are discussed later in this report.

#### Hole Burning Via Superhyperfine Interactions with near Neighbor Nuclei

A new mechanism for hole burning was demonstrated on the 5941A transition of  $\text{Pr}^{3+}$  in a charge compensated tetragonal site of  $\text{CaF}_2$ .<sup>5</sup> In this case there is a large electronic magnetic moment in the ground state and a small moment in the excited state. When the  $\text{Pr}^{3+}$  ion is excited, nuclear spin flips on neighboring  $^{19}\text{F}$  nuclei occur which shift the optical resonance frequency outside of its homogeneous linewidth and hole burning results (Fig. 3). However, in the ground state, the neighbor  $^{19}\text{F}$  nuclei are perturbed strongly by the  $\text{Pr}^{3+}$  ion and their return to equilibrium through mutual spin flips with surrounding  $^{19}\text{F}$  spins is retarded. The hole lifetime of several seconds is determined by this relaxation. This mechanism was confirmed by hole filling optical rf double resonance experiments in which individual near neighbor  $^{19}\text{F}$  nuclei were irradiated with rf.<sup>6</sup> When the rf frequency is resonant with a near neighbor  $^{19}\text{F}$  splitting, the resulting nuclear spin transitions cause the hole to be partially filled, thus increasing the fluorescence intensity.

Two important consequences of these findings are that it extends the number of systems in which hole burning can be observed, and it provides a mechanism for optically detecting NMR transitions on nuclear spins perturbed by an impurity electron spin (Fig. 4). The dynamics of these perturbed nuclear spins play a very important role in hole broadening and optical dephasing processes. (See "mechanisms determining hole broadening.")

**Hole Burning in Stoichiometric Compounds:  $\text{EuP}_5\text{O}_{14}$** 

Hole burning has previously only been observed in materials where the optically active center is present in a host material as a dilute impurity. This is to be expected since fast energy transfer, either optical or within a populated ground state level will normally lead to spectral diffusion and hole filling. Concentration dependent spectral diffusion is very important in potential applications of hole burning to information storage, since it is desirable to work with high concentrations where there is sufficient optical density for thin films of material to be used.

We have made the first observation<sup>7</sup> of hole burning in a stoichiometric, undoped system,  $\text{EuP}_5\text{O}_{14}$ , which has long hole lifetimes of ~60 min. This result sets a surprisingly small upper limit to the europium nuclear spin diffusion rate. We conclude that Eu-Eu nuclear flip-flops are quenched by several factors, which include the anomalously small ground-state nuclear moment and inhomogeneously broadened quadrupole levels. Hole burning also provides a direct measurement of the quadrupole splittings of the two isotopes of  $\text{Eu}^{3+}$  in the excited electronic state and permits sensitive nuclear quadrupole resonance measurements of the ground state splittings. Whereas conventional nuclear magnetic resonance (NMR) or nuclear-quadrupole-resonance (NQR) measurements of  $^{151,153}\text{Eu}^{3+}$  have not been reported because of limited sensitivity, the present technique is applicable even to dilute  $\text{Eu}^{3+}$  systems. The lifetime of the holes was measured by probing with an attenuated laser beam at 5 min intervals and was found to be 60 min at 1.6K. This lifetime is determined by both nuclear-spin-lattice relaxation ( $T_1$ ) and mutual spin flips. These  $T_2$  processes lead to hole filling because nuclear-spin flip-flops (i.e., spin diffusion) occur between ions that can have different optical splittings.<sup>4</sup> If the optical inhomogeneous broadening in  $\text{EuP}_5\text{O}_{14}$  is microscopically random or approximately so, one is forced to

conclude that the average flip-flop time is  $\geq 60$  min. It is interesting to ask why this hole filling rate can be so slow in a stoichiometric material.

There are several important factors which contribute to the quenching of spin diffusion. In the  $\text{EuP}_5\text{O}_{14}$  crystal structure, each  $\text{Eu}^{3+}$  has only two near  $\text{Eu}^{3+}$  neighbors at relatively large distances of 5-6 Å. Using the intrinsic nuclear moments<sup>8</sup> of  $3.46 \mu_N$  ( $^{151}\text{Eu}$ ) and  $1.53 \mu_N$  ( $^{153}\text{Eu}$ ), one estimates the homonuclear-dipolar interaction  $(\Delta\nu)_d$  to be  $\mu^2/r^3 = 30-150$  Hz. However, as originally pointed out by Elliott,<sup>9</sup> the second order hyperfine interaction with the  $^7F_1$  level, which is  $\sim 400 \text{ cm}^{-1}$  above the ground state, gives a contribution to the nuclear  $g$  value whose sign is opposite that of the intrinsic moment and which reduces the net magnetic moment by about a factor of 10. The corresponding reduction in the dipolar interaction gives  $(\Delta\nu)_d \simeq 1$  Hz. In addition, the quadrupole levels are inhomogeneously broadened by random variations in the electric field gradient caused by crystal strains. In the optically detected NQR measurements discussed above, we found that the inhomogeneous linewidth  $(\Delta\nu)_i$  of the NQR transitions was  $\simeq 100$  kHz. The rate of mutual spin flips  $T_f^{-1}$  may be estimated by using Fermi's golden rule, by taking  $1/2(\Delta\nu)_i$  as the density of states in the center of the line:  $T_f^{-1} \simeq (\Delta\nu)_d^2 / (\Delta\nu)_i \simeq 10^{-5} \text{ sec}^{-1}$ . Because the homonuclear interaction  $(\Delta\nu)_d$  is so weak, it may be important to include a higher order process in which energy is exchanged with the  $^{31}\text{P}$  dipolar reservoir. The presence of the two equally abundant isotopes (48%  $^{151}\text{Eu}$  and 52%  $^{153}\text{Eu}$ ) and the multilevel  $I=5/2$  spin system further reduces the probability that neighboring ions are in the right constellation to flip flop. The observed hole filling rate of  $3 \times 10^{-4} \text{ sec}^{-1}$  is consistent with these considerations. This rate also contains contributions from nuclear  $T_1$  processes. Our present measurements cannot determine which of these limits the hole lifetime.

### Hole Burning in Color Center Systems

We earlier showed<sup>10</sup> that hole burning can be observed in the zero phonon line of the  $F_3^+$  center in NaF at low temperatures. This center consists of two electrons trapped in the vicinity of three  $F^-$  vacancies, i.e., is a singly ionized aggregate of three F centers. Two mechanisms are responsible for the hole burning. The first uses a metastable optical triplet level as a population reservoir and leads to a recovery time of  $\sim 2$  secs. The second involves electron transfer and is much longer lived ( $\geq 1$  hour). At the lowest temperatures ( $\sim 2K$ ) the hole width of 45 MHz is limited by the population decay time. A similar behavior was observed more recently for the  $N_1$  center in NaF which is an aggregate of four F centers.<sup>11</sup> Since color centers are of some interest as materials for information storage we made a study of the temperature dependence of the hole width of  $N_1$  center. In these measurements<sup>11</sup> holes were detected by a sensitive optical transmission technique in which optical birefringence and dichroism are induced by hole burning in an otherwise isotropic medium (Fig. 5). The hole width showed an interesting temperature dependence being activated with an energy of  $44 \text{ cm}^{-1}$ . This is not expected from the phonon spectrum of the intrinsic material and appears to be due to the excitation of a local vibrational mode associated with the  $N_1$  defect center.

### Hole Burning in Inorganic Glasses

In recent years it has become clear that the low temperature dynamical properties of glasses are quite different from those of crystals and that this has a profound effect on the relaxation behavior of ions and molecules in glassy environments.<sup>12,13</sup> In particular, the presence of "two level systems" (TLS) — double well potentials associated with defects in glasses with a wide range of tunneling splittings — has been proposed<sup>14</sup> to explain the generally much broader linewidths seen in optical and NMR experiments at low temperatures.

Our first hole burning measurements were made on 0.25%  $\text{Eu}^{3+}$  doped silicate glass obtained from Dr. M. J. Weber, Lawrence Livermore Laboratories. An absorption band was observed around  $5800\text{\AA}$  associated with the  ${}^7\text{F}_0 \leftrightarrow {}^5\text{D}_0$  transition. Its inhomogeneous linewidth ( $\sim 100\text{ cm}^{-1}$ ) was much broader than found in crystals ( $0.5\text{ cm}^{-1}$ ). This is typical for glasses where a wide range of local environments is found. Hole burning was observed following irradiation with  $\sim 10\text{ mW}$  of cw laser light for  $\sim 1/2$  sec. The hole widths measured ( $\sim 50\text{ MHz}$ ) were much greater than in crystals ( $\sim 2\text{ MHz}$ ) and unlike the latter were not limited by laser frequency jitter. The recovery time of these holes was  $\sim 20$  sec.

Since the hole width is no greater than typical  $\text{Eu}^{3+}$  quadrupole splittings, and the holes are not permanent, it is proposed that this hole burning takes place by optical pumping of the nuclear quadrupole levels in the same way as in a crystal. This picture is consistent with the observation of anti-holes (increased absorptions) adjacent to the hole, a feature which is characteristic of the nuclear quadrupole mechanism. The recovery time of these holes is, however, much shorter than in crystals due to enhanced nuclear spin-lattice relaxation rates in the glass. This observation is in agreement with NMR measurements and is thought to be due to nuclear spin - TLS interactions.

Another mechanism for hole burning has been reported to take place in organic glasses (e.g., alcohol glasses, polymers) namely a process involving a photo-induced rearrangement of the local environment of excited molecules.<sup>16</sup> The change in environment shifts the optical absorption frequency within the broad inhomogeneous line. This type of hole burning is facilitated in glasses by the relative ease of conversion among a wide range of available environments. It has been suggested that the double well potentials mentioned above in connection with optical dephasing are also involved in this hole burning process.<sup>17</sup>

The potential barrier associated with the relaxation of the local environment is sufficiently large that at liquid helium temperatures the hole lifetimes are very long, i.e., of the order of days. This is a very desirable characteristic for hole burning information storage so we were interested to find out whether inorganic glasses with their superior optical properties and mechanical stability showed the same phenomenon.

Our experiments showed for the first time that this type of hole burning does, in fact, occur in inorganic glasses. Our first measurements were on the  ${}^3\text{H}_4 \leftrightarrow {}^3\text{P}_0$  transition of  $\text{Pr}^{3+}$  at a concentration of 0.1% in a silicate glass. Holes were burned with 100 mW from a  $\text{Kr}^+$  laser at 4825Å, and were observed in absorption with a white light source and monochromator. The observed hole width at 1.3K was 12 GHz and was limited by the resolution of the monochromator. No hole recovery was observed within 30 mins suggesting that a similar mechanism (i.e., a photophysical rearrangement of the environment) is operating here. The burning rate was not strikingly different from that observed in organic systems, i.e., a 20% deep hole was produced after ~10 min irradiation with a power density of  $10^3 \text{ W/cm}^2$  or in ~40 min with  $10 \text{ W/cm}^2$ .

Similar hole burning was observed in Nd laser glass (silicate) at 5900Å. In this case we could use a tunable dye laser with a linewidth of 1 MHz and we observed a 6 GHz hole width. Since this showed no temperature dependence between 1.3 and 3.5K, the mechanism for hole broadening appears to be a fast population relaxation to the next lowest level. From absorption measurements this is less than  $1000 \text{ cm}^{-1}$  away so that spontaneous phonon emission can be quite fast. The hole width corresponds to a 100 psec relaxation time.

The observation of hole burning in this material by the same mechanism as in organic glasses and polymers suggests that photophysical hole burning in glasses is a universal phenomenon and is a characteristic of the amorphous state, independent of dopant.

## II. MECHANISMS OF HOLE BROADENING

In the simplest picture the width of a shallow hole ( $H$ ) is twice the homogeneous linewidth ( $\Gamma$ ) which can be determined independently in the time domain by coherent transient measurements of the transverse relaxation time  $T_2$ , i.e.,

$$H = 2\Gamma(\pi T_2)^{-1} = (\pi T_1)^{-1} + 2(\pi T_2^\varphi)^{-1} . \quad (1)$$

The first term is the contribution from population decay and the second from pure dephasing due to modulation of the optical transition frequency. There are, however, complications which arise because hole burning times are normally much longer than  $T_2$  and this can introduce extra contributions to the hole width from two main sources. The first is frequency jitter of the laser. In time domain measurements of  $T_2$  we have essentially eliminated laser jitter contributions by using a photon echo technique. We modified standard optical heterodyne detection by delaying the onset of the heterodyne field until the echo arrival time.<sup>18</sup> This was necessary in order to measure the true value of  $T_2$ . The second additional contribution arises due to slow spectral diffusion which would not contribute to a time domain measurement of  $T_2$ , but can contribute during the relatively long hole burning process.

### Hyperfine Dephasing

For metastable levels of many rare earth systems  $T_2^\varphi$  is determined by the fluctuating fields from neighboring magnetic nuclei. Typical linewidths due to this mechanism are

~1 kHz to 1 MHz, and the high resolution of time domain techniques (photon echo and optical free induction decay) were necessary to measure them.

In  $\text{Pr}^{3+}:\text{LaF}_3$  we found<sup>18</sup>  $\Gamma = 56$  kHz for the  $^1\text{D}_2 \leftrightarrow ^3\text{H}_4$  transition at  $5925\text{\AA}$ , (Fig. 6) which was much greater than the  $T_1$  limit of 300 Hz. The most likely cause of this linewidth is the randomly fluctuating hyperfine field at the  $\text{Pr}^{3+}$  site due to the  $^{19}\text{F}$  nuclei. This was supported by our observation of 4 kHz linewidths in  $\text{Pr}^{3+}:\text{YAlO}_3$ <sup>18</sup> (Fig. 7) where the  $\text{Pr}^{3+}$  ion is surrounded by nonmagnetic oxygens. Further support was obtained by coherently averaging the hyperfine fields of the  $^{19}\text{F}$  nuclei in  $\text{LaF}_3$  by driving them with externally applied radio frequency fields.<sup>19</sup> This reduced the 56 kHz linewidth to 4 kHz (Fig. 6), comparable to that in  $\text{Pr}^{3+}:\text{YAlO}_3$ . The remaining width is due either to  $^{139}\text{La}$  fields or to incomplete decoupling of  $\text{Pr}^{3+}-\text{F}$  interactions. These experiments show that elimination of hyperfine interactions at low temperatures in rare earth ions can, in principle, lead to extremely narrow holes limited ultimately by the decay time of metastable levels, i.e., ~100 Hz.

Hole burning in these materials gave linewidths that were substantially broader (i.e., 1-2 MHz) than the homogeneous widths. This was due to both laser frequency jitter during hole burning and probing, and the slowly varying local fields from nearby  $^{19}\text{F}$  nuclei whose mutual flip rate had been slowed down by the detuning effect of the  $\text{Pr}^{3+}$  moment.

## Hole Burning and Dephasing in Stoichiometric and Concentrated Systems — The Role of Energy Transfer

### A) Stoichiometric Materials: Europium Pentaphosphate

To complement our hole burning measurements in  $\text{EuP}_5\text{O}_{14}$ , we have extended photon echo studies of optical dephasing to this material.<sup>10</sup> This is the first measurement of coherent transients in a stoichiometric material. It is well known that rare-earth pentaphosphates exhibit high-yield intrinsic fluorescence and minimal trapping of the excitation, making them attractive materials for miniature solid-state lasers. These properties imply that they have very narrow exciton bands and weakly delocalized excited states. Using the recently developed delayed heterodyne photon-echo technique,<sup>18</sup> we find surprisingly long dephasing times of  $\sim 20 \mu\text{sec}$ , which supports this picture. In addition, we find interesting and novel behavior in that the dephasing time varies in a systematic way as a function of position in the inhomogeneous line, indicating a corresponding variation in the nature of the excited state. This behavior is interpreted in terms of delocalization of the excitation and is qualitatively different from that observed previously in dilute impurity systems. For example, in  $\text{YAlO}_3:(0.25\% \text{Eu}^{3+})$ , dephasing is due principally to  $\text{Eu}^{3+}-^{27}\text{Al}$  magnetic dipole-dipole interactions and  $T_2$  is not frequency dependent. These measurements indicate that observation of optical coherence in excitonic systems may not be as difficult as previously thought and can provide a very useful probe of the dynamics in such systems.

At the peak of the inhomogeneous line of the  $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$  transition of  $\text{EuP}_5\text{O}_{14}$  at 5785Å the photon-echo decay yielded a dephasing time of  $T_2 = 10 \mu\text{sec}$ , corresponding to a linewidth (full width at half maximum) of  $\Gamma = 32 \text{ kHz}$ . This is surprisingly narrow, and in fact comparable to that of dilute impurity systems, e.g.,  $\text{LaF}_3:\text{Pr}^{3+}$ .<sup>18</sup> However, in contrast to such systems, the photon-echo decay in  $\text{EuP}_5\text{O}_{14}$  showed a strong and systematic

dependence on laser frequency, being shorter at the center of the inhomogeneous line and longer in the wings [ Fig. 8(a) ]. No dependence of  $T_2$  on external magnetic fields up to 400G was found ( Fig. 9 ) and it is independent of temperature in the region of 2K. To confirm our suspicion that these characteristics were associated with delocalization of the optical excitation we measured photon-echo decays on the same  ${}^5D_0 \leftrightarrow {}^5F_0$  transition in the dilute system  $YAlO_3:(0.25\% Eu^{3+})$ . In that case, considerably longer dephasing times ( $T_2 \sim 60 \mu\text{sec}$ ) were measured, which are almost certainly due to the fluctuating field from  ${}^{27}\text{Al}$  nuclei interacting with  ${}^{151}\text{Eu}$  and  ${}^{153}\text{Eu}$  nuclear magnetic moments. Since the ground-state nuclear moment of  $Eu^{3+}$  is anomalously small,<sup>9,22</sup> most of the width can be attributed to excited state interactions. The role of hyperfine dephasing is supported by the observation of a characteristic lengthening of  $T_2$  (see Fig. 2) in the presence of an external dc magnetic field as observed in  $Pr^{3+}$  systems<sup>18,19</sup> and in ruby.<sup>23</sup> For  $YAlO_3:Eu^{3+}$  we observed a narrowing from 5.5 to 3.1 kHz (full width at half maximum) in a 400G field.<sup>10</sup> These linewidths did not vary across the inhomogeneous line [ Fig. 1(b) ], since the magnetic response of the localized  $Eu^{3+}$  ions is not sensitive to the strain fields responsible for the inhomogeneous broadening.

We propose that the frequency dependent dephasing in  $EuP_5O_{14}$  reflects the stronger  $Eu^{3+} - Eu^{3+}$  resonant transfer interactions in the center of the inhomogeneous line due to the larger effective concentration of resonant ions.<sup>24</sup> In view of the weak delocalization in  $EuP_5O_{14}$  it is appropriate to characterize the excitation as a wave packet extending over several lattice sites. Dephasing then occurs when this wave packet is distorted by scattering from a defect potential. In this picture, the energy of interaction with the defect provides the frequency shifting needed to produce dephasing and the continuum states to scatter into are provided by the energy of interaction between the  $Eu^{3+}$  ions themselves. It therefore

appears that we have observed a novel effect: The greater delocalization of the  $\text{Eu}^{3+}$  excitation in the center of the inhomogeneous line corresponding to the stronger resonant interactions leads to more rapid scattering and a short  $T_2$ . A completely localized or hopping model cannot easily account for this frequency dependence since such a model requires that the dephasing (e.g., due to phonons or hyperfine interactions) be fast compared to  $\text{Eu}^{3+}-\text{Eu}^{3+}$  resonant energy transfer and hence would be independent of position in the inhomogeneous line.

The observation of temperature independent dephasing in  $\text{EuP}_5\text{O}_{14}$  at low temperatures apparently rules out phonon scattering as a dephasing mechanism. At higher temperatures, however, the role of phonons must be accounted for. We note for example, that a frequency dependence of the homogeneous linewidth has been observed in a very different physical system, i.e., Eu doped silicate glass at high temperatures ( $\sim 300\text{K}$ ).<sup>25</sup> These results differ from ours in that the homogeneous linewidth exhibits the  $T^2$  temperature dependence characteristic of dephasing by "two-level systems"<sup>26</sup> or tunneling states present in amorphous materials, or by a high-temperature Raman process. The monotonic frequency dependence was accounted for in this case in terms of a variation in photon coupling across the very broad ( $\sim 150\text{ cm}^{-1}$ ) inhomogeneous line. The lack of temperature dependence in  $\text{EuP}_5\text{O}_{14}$  also allows phonon-assisted energy transfer to be ruled out as a dephasing mechanism, although a two-phonon process similar to that observed in  $\text{LaF}_3:\text{Pr}^{3+}$ <sup>27</sup> may appear at higher temperatures. Since this is essentially independent of energy mismatch it would not lead to a frequency dependent  $T_2$ .

B) Concentrated Disordered Impurity System:  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$

We have also used photon echoes to study optical dephasing due to energy delocalization in a system where the energy transfer is between disordered impurity ions i.e.,  $\text{Eu}^{3+}$  ions at 2% and 5% concentration in  $\text{Y}_2\text{O}_3$ .<sup>28</sup> The measurement of the transfer rates was made possible by the choice of a host matrix in which nuclear hyperfine fields are very small since hyperfine dephasing could otherwise mask dephasing due to energy transfer.

Two pulse photon echo measurements were made on the  $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$  transition of  $\text{Eu}^{3+}$  in the  $\text{C}_2$  sites of  $\text{Y}_2\text{O}_3$ . The absorption peaked at 5808Å and had an inhomogeneous width of 10 GHz. Laser pulse lengths of from 1 to 4.5  $\mu\text{sec}$  were chosen to excite a frequency packet broad compared to the laser frequency jitter ( $\sim 30$  kHz). No dependence of the optical dephasing time on pulse width was observed. Measurements of photon echo decay were made as a function of frequency across the inhomogeneous line. The result is shown in Fig. 10. The homogeneous linewidth varies from 2.5 kHz ( $T_2 = 130 \mu\text{sec}$ ) at line center to 760 Hz ( $T_2 = 420 \mu\text{sec}$ ) 20 GHz off resonance. The echo decays were approximately exponential over the one decade of amplitude which we measured. The application of magnetic fields of up to 400G, i.e., large compared to Y-Eu and Y-Y magnetic dipolar interactions, produces less than 100 Hz change in the linewidth which is consistent with our estimate of the broadening due to the  $^{89}\text{Y}$  nuclear spins. We attribute the major part of the linewidth observed to quasi-resonant energy transfer. This is supported by the frequency dependence of  $T_2$  (see Fig. 10) which reflects the higher effective concentration of resonant  $\text{Eu}^{3+}$  ions in the center of the optical absorption line as compared with the wings.<sup>20</sup> In addition, we made measurements on a crystal with a nominal concentration of 5%  $\text{Eu}^{3+}$ , and at the center of the absorption line  $\Gamma_h = 26$  kHz, i.e., the homogeneous linewidth increases rapidly with concentration in this range. The dephasing time measured at the peak of the

inhomogeneous line was the same for path lengths of 3.4 mm and 9.4 mm showing that reabsorption of the echo was not responsible for the observed frequency dependence of  $T_2$ . We note that the quasi-resonant energy transfer invoked here as the mechanism for dephasing occurs on a time scale of hundreds of microseconds. This is faster than the intersite ( $C_{3i}$  site  $\rightarrow$   $C_2$  site) transfer which was observed to occur on the millisecond timescale for  $\text{Eu}^{3+}$  concentrations in the 1-5% range.<sup>29</sup> The measured linewidth is more than an order of magnitude smaller than the laser frequency jitter, and we cannot unequivocally rule out the possibility of a small jitter contribution to the decay. However, we have shown previously<sup>18</sup> that an increase in the jitter from a level comparable to the homogeneous linewidth to one over 100 times greater did not affect the observed echo decay time in  $\text{YAlO}_3:\text{Pr}^{3+}$ .

#### Hole Broadening by Spectral Diffusion

We have recently made an interesting observation of the hole width in  $\text{Pr}^{3+}:\text{CaF}_2$  where hole burning occurs because of optically induced spin flips of the  $^{19}\text{F}$  nuclei.<sup>5</sup> The hole width was found to be 9 MHz (Fig. 3), substantially larger than either the laser jitter (1 MHz) or the homogeneous linewidth measured by optical free decay (430 kHz). What appears to be happening is that spectral diffusion occurs due to slow spin flips of neighboring  $^{19}\text{F}$  nuclei. These occur on a time scale much longer than the homogeneous dephasing, but shorter than the hole burning and measuring times. This is a direct consequence of the existence of a "frozen core" of perturbed nuclear spins surrounding the hole burning center. At the boundary of this core (roughly determined by when the  $\text{Pr}-^{19}\text{F}$  interaction equals the  $^{19}\text{F}-^{19}\text{F}$  interaction) the  $^{19}\text{F}$  spin-flip time is determined by  $^{19}\text{F}-^{19}\text{F}$  flip-flop processes and is  $\sim 100$   $\mu\text{sec}$ . This determines the homogeneous linewidth measured by optical free decay. For spins inside the core the flip rate is much slower due to the strong  $\text{Pr}^{3+}$  local

field which makes these flip-flop processes non-energy-conserving. But these frozen core spins, of course, have a stronger coupling and their flips produce slower but larger frequency excursions. Thus the dynamics of the frozen core spins can be of crucial importance in determining hole widths.

In earlier measurements we have observed the effects of spectral diffusion due to optical energy transfer in a system  $Y_2O_3:Eu^{3+}$  where the hole burning center, in this case  $Eu^{3+}$  is disordered and in sufficient concentration (2-5%) that quasi-resonant energy transfer occurs during the excited state lifetime. Evidence for this was found by burning a hole in a time comparable to the optical dephasing time of 20  $\mu$ sec, and then probing at later times by a pulsed readout of the hole width by optical free decay. Immediately after hole burning, the free decay corresponds to a hole width limited by the optical dephasing time. At longer delays, the hole broadened by about a factor of two suggesting a time dependent spectral diffusion. This is reasonable since the optical dephasing at these concentrations is due to  $Eu^{3+}-Eu^{3+}$  interactions.

#### **Hole Widths in Inorganic Glasses**

Homogeneous linewidths of rare earth ions in inorganic glasses have been investigated by several groups using fluorescence like narrowing techniques.<sup>12,13</sup> These experiments show that the optical linewidth has an unusual  $T^2$  temperature dependence over an extremely wide temperature range. Measurements on  $Eu^{3+}$  doped silicate glass,<sup>13</sup> showed that the linewidth is given by  $\Gamma \approx 5T^2$  MHz between 10K and 200K. These measurements were not extended to lower temperature due to the resolution limitations of fluorescence line narrowing.

In  $\text{Eu}^{3+}$ -silicate glass we have observed a hole width of 50 MHz at 2K using nuclear quadrupole optical hole burning. This point falls on the line extrapolated from the high temperature data showing that the same  $T^2$  law is obeyed from below 2K to over 200K. It is expected that the holes would continue to narrow as  $T$  is decreased down to  $\sim 30$  mK when the hyperfine dephasing mechanism would set in.

This is an interesting result in light of the current theory describing dephasing in glasses in terms of impurity-ion "two-level system" interactions.<sup>30</sup> These theories predict a crossover from a quadratic to linear temperature dependence at these low temperatures<sup>31</sup> which is not observed.

### III. HOLE BURNING SPECTROSCOPY

Hole burning techniques offer the ability to make spectroscopic observations in solids which are nearly free of inhomogeneous broadening. This increased resolution makes possible the measurement of hyperfine structure, small Zeeman splittings, etc., which could not be observable with conventional methods. Hole burning by nuclear optical pumping also allows a sensitive optical-radio frequency double resonance experiment to be performed which can yield magnetic resonance spectra of dilute nuclei with good signal to noise ratio.

#### Optical Zeeman Spectroscopy by Hole Burning

As discussed above, magnetic interactions between surrounding nuclei and the optically active species often limit the linewidths at low temperatures. It is therefore of interest to measure the magnetic response of the levels involved in hole burning. We found that two types of hole burning experiments can be done, which produce complementary information. Experiments were carried out on the 5925A transition of  $\text{Pr}^{3+}:\text{LaF}_3$ .<sup>32</sup>

Hole burning in the presence of a magnetic field produces a pattern of holes which gives directly the excited state linear nuclear Zeeman effect, i.e., measures the nuclear magnetic moment in the electronically excited state (Fig. 11a). The electronic excitation is important because there is a sizeable contribution from the electronic states to the g-tensor. By measuring the hole splittings as a function of the direction of the applied magnetic field it was possible to determine the complete g-tensor and its orientation  $\varphi$  with respect to the  $C_3$  axis of the crystal. We found  $g_x=2.2$ ,  $g_y=1.9$  and  $g_z=3.6$  kHz/G and  $\varphi=20^\circ$  (Fig. 11b).

This g-tensor is smaller in overall magnitude and differs in orientation from that in the ground state. Since the two tensors are oriented differently, the energy fluctuations of ground and excited state hyperfine levels need not be correlated, i.e., they may respond independently to the three components of the local field. These measurements emphasize the need to consider the full anisotropic g-tensor in analyzing the optical dephasing. This analysis is currently in progress.

In addition to the linear high field splitting of nuclear levels observed in these experiments, one expects a quadratic shift of the levels due to a second order electronic Zeeman effect. Since this shift is small, the high resolution provided by hole burning spectroscopy is necessary to measure it. This can be accomplished in the present case because the holes, initially burned in zero magnetic field, live long enough to apply a field and observe their shift. Since the quadratic nuclear Zeeman effect and the enhanced nuclear splitting are proportional to each other, but only the latter depends on the hyperfine coupling constant  $A_J$ , these measurements can be used to derive a value of  $A_J=600$  MHz for  $^1D_2$ .

### Optical Coherent Transient Measurement of Electronic Spin-Lattice Relaxation $\text{LaF}_3:\text{Er}^{3+}$

Coherent transient measurements have been made on a number of rare earth systems - notably those containing  $\text{Pr}^{3+}$  and  $\text{Eu}^{3+}$  ions. In these cases, there is an even number of f-electrons and the electronic magnetic moment is quenched by crystal field interactions. We have studied the odd electron system  $\text{LaF}_3:\text{Er}^{3+}$  where there is a large magnetic moment and found that this leads to strongly magnetic field dependent optical dephasing.

The optical transition at 5388Å is between the lowest Kramers doublets of the  $^4S_{3/2}$  and  $^4I_{15/2}$  multiplets. In zero magnetic field, dephasing due to hyperfine interactions was found to be very fast ( $T_2=12$  nsec). These measurements were made using the technique of optical phase switching. The application of magnetic fields,  $H_0$ , greater than the  $\text{Er}^{3+}-^{19}\text{F}$  interaction strength (i.e.,  $\geq 10$  kG) results in a lengthening of  $T_2$  by about three orders of magnitude. We have particularly studied this high field region. Since only the lowest Zeeman component of the ground state is appreciably populated, there are two important transitions to consider. These are labelled  $g_{e-}$  and  $g_{e+}$  in Fig. 12. The dephasing of  $g_{e-}$  at low concentrations of  $\text{Er}^{3+}$  (below 0.03%) is independent of magnetic field. This is in contrast to  $g_{e+}$  where the dephasing becomes much faster (i.e., the linewidth  $\Gamma=(\pi T_2)^{-1}$  increases) above  $\sim 30$  kG and is proportional to  $H_0^5$ . It is in fact given quantitatively by the excited state spin lattice relaxation rate determined by optical fluorescence.<sup>33</sup> At the low temperatures of these experiments only the relaxation of the upper Zeeman level of  $4S_{3/2}$  is important. Very interesting behavior is observed at higher  $\text{Er}^{3+}$  concentrations, i.e., both the  $g_{e-}$  and  $g_{e+}$  transitions now broaden at lower fields where before they were independent of  $H_0$  (Fig. 14). Our interpretation of this is that mutual electronic spin flips among  $\text{Er}^{3+}$  ions produces a fluctuating local field at the site of other  $\text{Er}^{3+}$  ions and causes

dephasing. As  $H_0$  decreases, the population of the upper Zeeman component of the ground state increases, allowing these mutual spin flips to occur. To test this hypothesis, we measured the temperature dependence of the linewidth of  $g_{e_}$  at 23 kG where the ground state electronic splitting was  $9 \text{ cm}^{-1}$ , and found an activation energy corresponding to this, i.e.,  $10.5 \pm 2 \text{ cm}^{-1}$  (Fig. 15).

### Isotope Structure of $\text{YAlO}_3:\text{Eu}^{3+}$

We have shown that laser hole burning spectroscopy can be used to resolve isotope structure in optical transitions, by studies of the  $\text{Eu}^{3+}$  ion in several matrices notably  $\text{EuP}_5\text{O}_{14}$ <sup>7</sup> and  $\text{YAlO}_3$ .<sup>22</sup> Since holes or reduced absorption occur for transitions from a given ground level to all excited levels, the  $^5\text{D}_0$  excited state splittings can be obtained directly from the hole spectrum (Fig. 16). In this way we measured the excited state quadrupole splittings of  $^{151}\text{Eu}^{3+}$  (89 and 61 MHz) and  $^{153}\text{Eu}^{3+}$  (226 and 156 MHz) in  $\text{YAlO}_3$ . This provides a method of measuring the ratio of the nuclear quadrupole moments of these isotopes.

The  $^7\text{F}_0$  ground state quadrupole splittings were obtained by optically detected NQR. In these experiments, holes were filled by application of rf at the ground state splitting frequencies and the resulting change in sample fluorescence monitored. Although not required by symmetry, the  $^7\text{F}_0$  quadrupole tensor is very close to axial, the splittings for each isotope being almost in the ratio 2:1  $^{151}\text{Eu}$  (45.99 and 23.03 MHz) and  $^{153}\text{Eu}$  (119.20 and 59.65 MHz).

The large difference in magnitude and anisotropy of the quadrupole tensor between  $^5\text{D}_0$  and  $^7\text{F}_0$  states is attributed to the contribution to the electric field gradient of two

important mechanisms, as discussed by Judd, et al.<sup>34</sup> and by Edmonds.<sup>35</sup> Since no quadrupole coupling exists for a pure  $J=0$  level, the observed field gradients are due to admixture of excited states into the  ${}^7F_0$  or  ${}^5D_0$  wave function by the crystal field. The two contributions are of opposite sign<sup>34,35</sup> and are from the excited states of the  $4f^6$  configuration, and from configurations involving excitation of a 5p electron. Elliott<sup>9</sup> estimated the former for europium ethyl sulfate where the crystal field is weaker than in  $YAlO_3$  and found  $P({}^{153}\text{Eu}) \sim 10$  MHz. This contribution is essentially absent for  ${}^5D_0$  which has no nearby  $J=2$  level. The 5p contribution should be quite similar for both states. Therefore, it is reasonable to attribute the smaller quadrupole coupling for  ${}^7F_0$  to partial cancellation of the 5p contribution by the  ${}^7F_2$  admixture.

#### Measurement of the Anomalous Nuclear Magnetic Moment of $\text{Eu}^{3+}$

Our work on the optical detection of nuclear resonance in  $\text{Eu}^{3+}$  systems suggested the possibility of measuring the anomalously small ground state magnetic moment of trivalent Europium predicted over twenty years ago by Elliott.<sup>9</sup> The origin of this effect is that the electronic contribution to the moment due to second order hyperfine coupling with the  ${}^7F_1$  levels  $\sim 400$   $\text{cm}^{-1}$  higher in energy is of opposite sign to, and almost cancels, the intrinsic moment of the Eu nucleus. Since the  ${}^7F_0$ - ${}^7F_1$  splitting is spin-orbit in origin and does not vary greatly from host to host, this cancellation is expected to be a general phenomenon with small modifications depending on the crystalline environment. As Elliott pointed out, this effect makes conventional NMR or NQR observations of trivalent europium very difficult and no such experiments have yet been reported. For this reason Elliott's prediction of the small  $\text{Eu}^{3+}$  moment has, until now, remained unconfirmed.

In  $\text{YAlO}_3:\text{Eu}^{3+}$  we have used hole burning and optically detected NQR (Fig. 17) in an external magnetic field parallel to the b axis to measure the effective nuclear moment of  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$  in both the ground  $^7\text{F}_0$  and the excited  $^5\text{D}_0$  states. In the  $^7\text{F}_0$  state we obtain values of  $0.743 \mu_{\text{N}}$  for  $^{151}\text{Eu}$  and  $0.314 \mu_{\text{N}}$  for  $^{153}\text{Eu}$  corresponding to 21% of the intrinsic moment. These values are used to derive a radial hyperfine parameter  $\langle r^{-3} \rangle = 49.6 \pm 1 \text{A}^{-3}$  which compares well with the best available theoretical value of  $49 \text{A}^{-3}$ . The  $^5\text{D}_0$  state on the other hand, shows splittings corresponding to the bare Eu nuclear moment. This is expected since the  $J=1$  level in this case is much further away ( $\sim 2000 \text{ cm}^{-1}$ ).

#### Hole Burning in Organometallics: Eu Chelate

Hole burning has been demonstrated in a number of inorganic rare earth doped crystals and glasses, particularly those containing  $\text{Pr}^{3+}$  and  $\text{Eu}^{3+}$  ions. We were interested in finding out how the incorporation of the rare earth ion in an organometallic complex affected the hole burning process and the width of the holes. For this reason we have studied  $\text{Eu}^{3+}$  in a chelate complex.

Before presenting the results obtained, we briefly recall the hole burning properties of the trivalent europium ion in inorganic systems. In crystals, hole burning occurs due to population transfer among the nuclear quadrupole levels by an optical pumping cycle. Hole recovery due to relaxation between the quadrupole levels takes place in about 60 mins. The width of the holes is less than 1 MHz and of course, in order to burn holes this must be less than the quadrupole splittings which are typically 10-100 MHz. In glasses, rather different behavior is observed (see elsewhere in this report) i.e., broader holes ( $\sim 50 \text{ MHz}$ ) and fast hole recovery due to enhanced relaxation between the quadrupole levels brought about by

coupling to very low frequency motion associated with the characteristic "two-level system" structural modes of the glass. Furthermore, extensive inhomogeneous broadening of optical and nuclear quadrupole levels occur due to the distribution of local environments.

The europium chelate studied was Eu-thenoyltrifluoroacetate and was in the form of a polycrystalline powder. The emission spectrum showed a line at 5800A with a width of  $\sim 10 \text{ cm}^{-1}$  which coincided with a peak in the excitation spectrum and was therefore assigned to the  ${}^5D_0 \leftrightarrow {}^7F_0$  transition. Hole burning was observed at 2K with a 1 MHz bandwidth cw dye laser. The properties of the holes observed were more similar to those of inorganic glasses than crystals, i.e., a hole width of 30 MHz and a hole lifetime of  $\sim 3$  secs. This suggests that very low frequency motions are present in the chelate complex and further experiments, including temperature dependence, are planned to test this. We have shown that the mechanism for hole burning in the chelate is again optical pumping of the nuclear quadrupole levels, since we observed holes and antiholes shifted by typical quadrupole splittings from the hole burned at the laser frequency.

The preliminary experiments show that hole burning has great promise as a technique for studying organometallic compounds using the hole burning properties of the metal ion to probe the dynamics of the organic chelating agent.

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**FIGURE CAPTIONS**

Figure 1. Schematic diagram of (a) an inhomogeneously broadened optical absorption line, and (b) a hole burned by selective laser irradiation.

Figure 2. The temperature-dependent part of the spin-lattice relaxation rates of 0.05%  $\text{Pr}^{3+}:\text{LaF}_3$ . The exponential temperature dependence confirms the presence of a resonant two-phonon (Orbach) relaxation process involving the first excited electronic state at  $57 \text{ cm}^{-1}$ .

Figure 3. Spectrum of a hole burned into one of the hyperfine lines of 0.01%  $\text{CaF}_2:\text{Pr}^{3+}$ . Anti-holes due to optically induced spin-flips of near neighbor  $^{19}\text{F}$  nuclei are clearly visible, separated by  $\sim 10 \text{ MHz}$  from the hole. The solid line represents the unperturbed inhomogeneous profile.

Figure 4. ODNMR lines detected on the 5941A transition of  $\text{Pr}^{3+}:\text{CaF}_2$  at 2K and their behavior in a small applied magnetic field. (a) Stick diagram showing the resonant frequencies and indicating the relative intensities of the six ODNMR lines with no applied external field. The assignments of the lines as nearest neighbors (nn), next nearest neighbors (nnn) and the interstitial fluorine (i) are indicated. (b) Splittings of the two nn lines near 10 MHz in an applied field. (c) Splitting of the interstitial ODNMR line near 20 MHz in a field.

Figure 5. Two deep exposure-broadened holes in the 6070A zero phonon line of the  $N_1$  center in NaF, detected in polarization and transmission spectroscopy. In the polarization-spectroscopy trace (a) the zero level has been suppressed but the increase in detected intensity at peak is roughly 100%. In trace (b) — obtained in transmission without polarization selection — the zero level has been greatly suppressed, and the holes result in only a 2% increase in the intensity at the detector.

Figure 6. Effect of  $^{19}\text{F}$  nuclear spin decoupling on the homogeneous linewidth of the 5925.2A  $^1\text{D}_2 \leftrightarrow ^3\text{H}_4$  transition of 0.05%  $\text{Pr}^{3+}:\text{LaF}_3$  at 2K. (a) Zero field: dc magnetic field  $H_0=0$ ; rf magnetic field  $H_1=0$ . (b) In external dc field only:  $H_0=375\text{G}$ ,  $H_1=0$ . (c) On resonance decoupling:  $H_0=375\text{G}$ ,  $H_1=36\text{G}$  at the  $^{19}\text{F}$  resonance frequency of 1.5 MHz. (d) With magic-angle irradiation:  $H_0=375\text{G}$ ,  $H_1=45\text{G}$  applied 120 kHz above the  $^{19}\text{F}$  resonance frequency.

Figure 7. Photon echo measurement of the optical dephasing time (or homogeneous linewidth) of  $\text{Pr}^{3+}:\text{YAlO}_3$ . (a) The pulse sequence, with the heterodyne detected echo at 40  $\mu\text{sec}$ . (b) The echo decay curves.

Figure 8. Inhomogeneous line profile and homogeneous linewidth of the  $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$  transition as a function of laser frequency for (a)  $\text{EuP}_5\text{O}_{14}$  and (b)  $\text{YAlO}_3:(0.25\% \text{Eu}^{3+})$ .

Figure 9. Magnetic field dependence of dephasing in  $\text{EuP}_5\text{O}_{14}$  and  $\text{YAlO}_3:(0.25\% \text{Eu}^{3+})$ . Photon-echo amplitude is plotted versus  $2\tau$ , where  $\tau$  is the separation between the excitation pulses.

Figure 10. Frequency dependence of the homogeneous linewidth of the  ${}^7\text{F}_0 \leftrightarrow {}^5\text{D}_0$  transition of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}(2\%)$  at 1.6K.

Figure 11. (a) Holes burned in the 5925A transition of  $\text{Pr}^{3+}:\text{LaF}_3$  in the presence of an external magnetic field ( $H_0 \perp C_2, C_3$ ). The splittings between holes are linear with magnetic field and directly give the excited state nuclear level splittings, leading to a  $g$ -value of 2.2 kHz/G. (b) Pattern of Zeeman splittings for rotations about  $C_2$  and  $C_3$ , i.e.,  $\phi=90^\circ$ ,  $\theta=90^\circ$ , respectively. The triangles denote the set of ions whose  $C_2$  axes are parallel to the rotation axis and for this set the maxima and minima correspond to the  $z$  and  $y$  principal  $g$  values. The circles correspond to ions whose  $C_2$  axes are at  $60^\circ$  to the rotation axis.

Figure 12. Energy levels of  $\text{Er}^{3+}:\text{LaF}_3$  as a function of applied magnetic field. SLR denotes spin lattice relaxation in the excited state.

Figure 13. Homogeneous linewidth of the 5388A transition of  $0.03\% \text{Er}^{3+}:\text{LaF}_3$  as a function of external magnetic field.

Figure 14. Homogeneous linewidth of the 5388A transition of more concentrated (nominal 0.1%)  $\text{Er}^{3+}:\text{LaF}_3$  showing the effect of  $\text{Er}^{3+}-\text{Er}^{3+}$  interactions at low external magnetic fields.

Figure 15. Activation energy of the low field linewidth showing that the slope corresponds to the ground state splitting of  $9 \text{ cm}^{-1}$ .

Figure 16. Hole burning spectrum of  $\text{YAlO}_3:\text{Eu}^{3+}$  at 1.5K. The solid colored peaks are assigned to  $^{153}\text{Eu}$  and the cross hatched peaks to  $^{151}\text{Eu}$ . The lower part of the figure shows the positions of holes and anti-holes predicted from the quadrupole splittings given in the text. The inset shows hole splittings for  $^{153}\text{Eu}$  produced by an external magnetic field.

Figure 17. (a) ODNQR spectrum in the  $^7F_0$  level of  $^{153}\text{Eu}$ . (b) Splitting in 2.2 kG external field.

**PUBLICATIONS APPEARING OR SUBMITTED DURING THE CONTRACT PERIOD**

**Ultra-High Resolution Spectroscopy: Photon Echoes in  $\text{YAlO}_3:\text{Pr}^{3+}$  and  $\text{LaF}_3:\text{Pr}^{3+}$**

R. M. Macfarlane, R. M. Shelby and R. L. Shoemaker, Phys. Rev. Lett. 43, 1726 (1979).

**Optical Line Narrowing by Nuclear-Spin Decoupling in  $\text{Pr}^{3+}:\text{LaF}_3$**

R. M. Macfarlane, C. S. Yannoni and R. M. Shelby, Opt. Comm. 32, 101 (1980).

**Optical Measurement of Spin-Lattice Relaxation in Dilute Nuclei —  $\text{Pr}^{3+}:\text{LaF}_3$**

R. M. Shelby, R. M. Macfarlane and C. S. Yannoni, Phys. Rev. B21, 5004 (1980).

**Laser Hole Burning Spectroscopy of Solids**

R. M. Macfarlane and R. M. Shelby, J. Opt. Soc. Am. 70, 583 (1980).

**Observation of Very Narrow Optical Resonances in Solids Using Photon Echoes**

R. M. Shelby and R. M. Macfarlane, J. Opt. Soc. Am. 70, 613 (1980).

**Coherent Transients by Optical Phase Switching: Dephasing in  $\text{Pr}^{3+}:\text{LaCl}_3$**

A. Z. Genack, D. A. Weitz, R. M. Macfarlane, R. M. Shelby and A. Schenzle, Phys. Rev. Letters 45, 438 (1980).

**Polarization Spectroscopy Measurement of the Homogeneous Linewidth of an Inhomogeneously Broadened Color Center Band**

M. D. Levenson, R. M. Macfarlane and R. M. Shelby, Phys. Rev. B22, 4915 (1980).

**Measurement of Nuclear and Electronic Zeeman Effects Using Optical Hole Burning Spectroscopy**

R. M. Macfarlane and R. M. Shelby, Opt. Lett. 6, 96 (1980).

**Frequency Dependent Optical Dephasing in the Stoichiometric Material  $\text{EuP}_5\text{O}_{14}$**

R. M. Shelby and R. M. Macfarlane, Phys. Rev. Letters 45, 1098 (1980).

**Nuclear Quadrupole Optical Hole Burning in the Stoichiometric Material  $\text{EuP}_5\text{O}_{14}$**

R. M. Macfarlane, R. M. Shelby, A. Z. Genack and D. A. Weitz, Opt. Lett. 5, 462 (1980).

**Thin-Film Aggregate Color Centers as Media for Frequency Domain Optical Storage**

C. Ortiz, R. M. Macfarlane, R. M. Shelby, W. Lenth and G. C. Bjorklund, Appl. Phys. 25, 87 (1981).

**Sub-kilohertz Optical Linewidths of the  ${}^7\text{F}_0 \leftrightarrow {}^5\text{D}_0$  Transition in  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$**

R. M. Macfarlane and R. M. Shelby, Opt. Comm. (to be published).

**Optical Hole Burning by Superhyperfine Interactions in  $\text{CaF}_2:\text{Pr}^{3+}$ .**

R. M. Macfarlane, R. M. Shelby and D. P. Burum, Opt. Lett. (to be published).

**Measurement of the Anomalous Nuclear Magnetic Moment of Trivalent Europium**

R. M. Shelby and R. M. Macfarlane, Phys. Rev. Lett., October 19, 1981.

**Hole Burning ODNMR in  $\text{Pr}^{3+}:\text{CaF}_2$**

D. P. Burum, R. M. Shelby and R. M. Macfarlane, Phys. Rev. B (submitted).

## CONFERENCE PRESENTATIONS

The following presentations were made at the Second Conference on Dynamical Processes of Ions and Molecules in Solids, Madison, Wisconsin, June 18-20, 1979.

**Optical Detection of Coherent Nuclear Spin Resonance Transients**

(Invited talk), R. M. Shelby, C. W. Yannoni and R. M. Macfarlane, *Bul. Am. Phys. Soc.* 24, 896 (1979).

**Measurement of Nuclear Spin Lattice Relaxation in  $\text{Pr}^{3+}:\text{LaF}_3$  Using Optical Population Hole Burning**

R. M. Macfarlane, C. S. Yannoni and R. M. Shelby, *Bul. Am. Phys. Soc.* 24, 857 (1979).

The following presentations were made at the Eleventh International Quantum Electronics Conference, Boston, Massachusetts, June 23-26, 1980.

**Laser Hole Burning Spectroscopy of Solids**

R. M. Macfarlane and R. M. Shelby.

**Observation of Very Narrow Optical Resonances in Solids Using Photon Echoes,**

R. M. Shelby and R. M. Macfarlane

**Coherent Transients by Optical Phase Switching: Dephasing in  $\text{Pr}^{3+}:\text{LaCl}_3$**

A. Schenzle, R. M. Macfarlane, R. M. Shelby, D. A. Weitz and A. Z. Genack.

### Other Conference Presentations

**Hole-Burning Spectroscopy in Solids**

(Invited) R. M. Shelby, U.S.-Japan Seminar on Nonlinear Laser Spectroscopy, Kanai, Hawaii, September 8-12, 1980.

**Submegahertz Optical Spectroscopy of Solids**

(Invited talk) R. M. Macfarlane and R. M. Shelby, Optical Society of America Annual Meeting, Chicago, October 14, 1980.

**High Resolution Laser Spectroscopy in Solids**

(Invited) R. M. Shelby, Gordon Research Conference on Magnetic Resonance, Wolfeboro, New Hampshire, June 15-19, 1981.

**Photon Echo Measurements of Optical Dephasing**

(Invited) R. M. Macfarlane, US-France Seminar on Molecular Dynamics in the Condensed State, Talloires, France, June 23-26, 1981.

**Magnetic Field Dependent Dephasing in  $\text{LaF}_3:\text{Er}^{3+}$**

R. M. Macfarlane and R. M. Shelby, Conference on Dynamical Processes in Solids, Regensburg, West Germany, July 27-29, 1981.

**PATENT DISCLOSURES****Rare Earth Pentaphosphates - A New Class of Photoreactive Hole Burning Materials**

R. M. Macfarlane and R. M. Shelby, IBM Tech. Discl. Bull. 23, 1632 (1980).

**The F<sub>3</sub> Center in CaF<sub>2</sub> - A Material for Hole Burning Storage Using Semiconductor Lasers**

M. D. Levenson, R. M. Macfarlane and R. M. Shelby, IBM Tech. Discl. Bull. 23, 2953 (1980).

**Method for Producing Controlled Spatial Distributions of Color Centers for Photochemical Hole Burning Memories**

G. C. Bjorklund, R. M. Macfarlane, C. Ortiz and R. M. Shelby, IBM Tech. Discl. Bull. 23, 3356 (1980).

**Narrow Band Optical Filters Produced by Photochemical Bleaching**

R. M. Macfarlane and R. M. Shelby, IBM Tech. Discl. Bull. 23, 3859 (1981).

**Inorganic Glasses as Materials for Photochemical Hole Burning Storage**

R. M. Macfarlane, R. M. Shelby and A. Sievers, SA8810386.

**Professional Personnel Associated with the Research Effort**

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Some of the work carried out under this contract was in collaboration with the following people:

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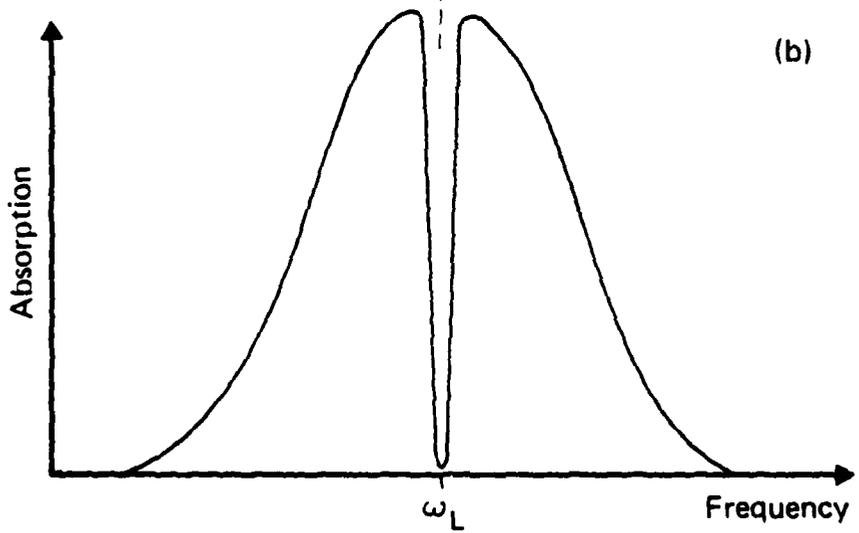
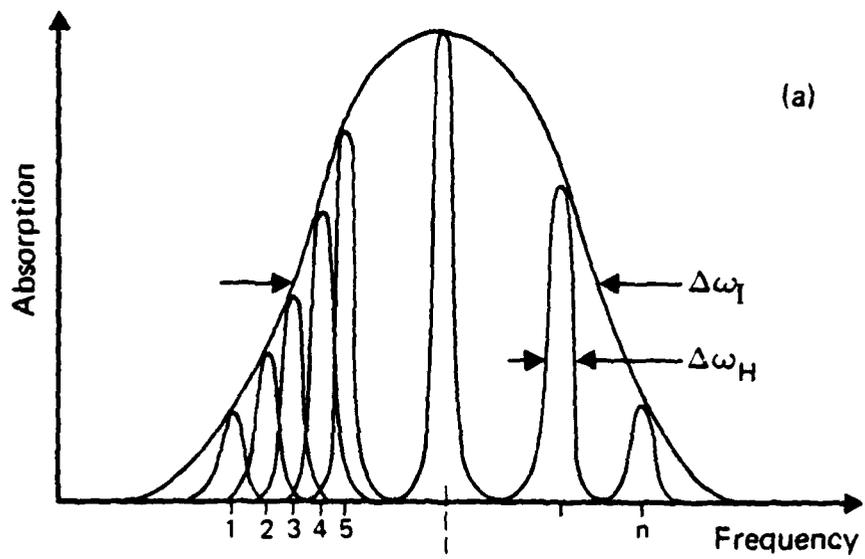
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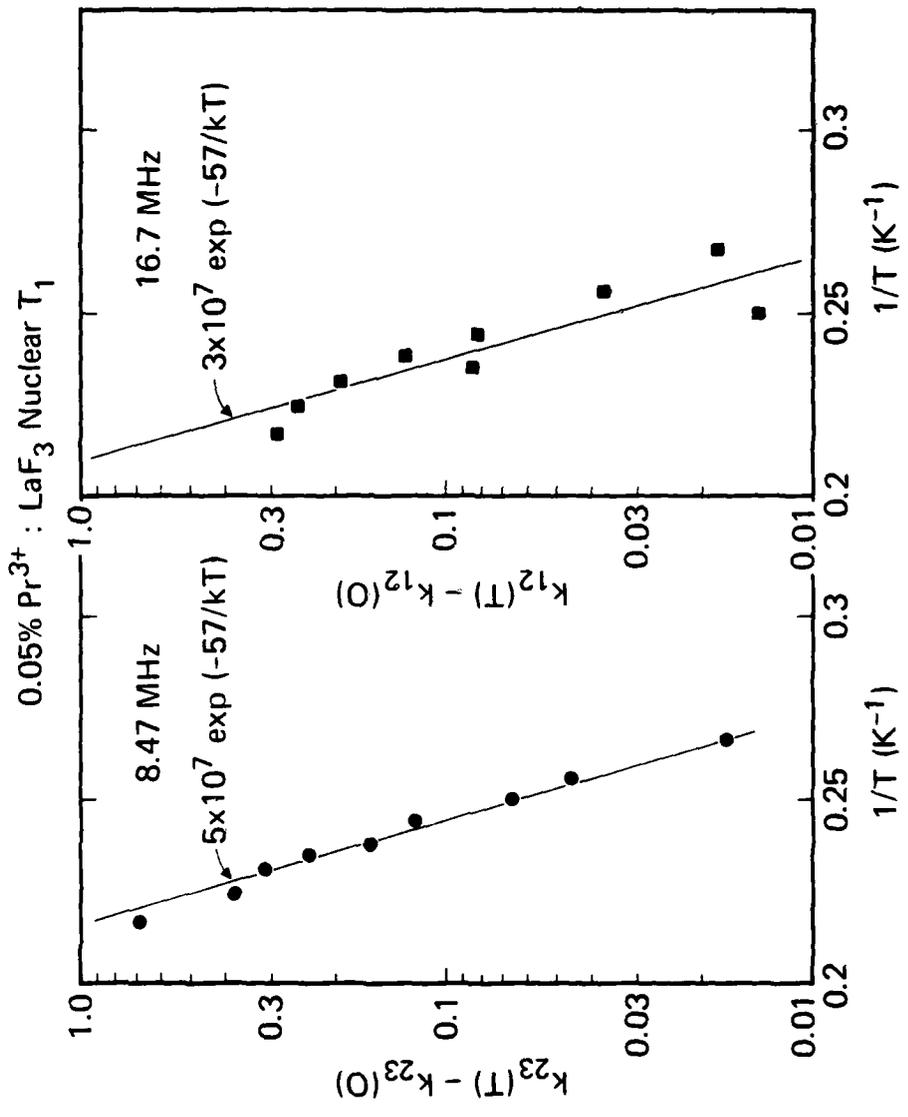
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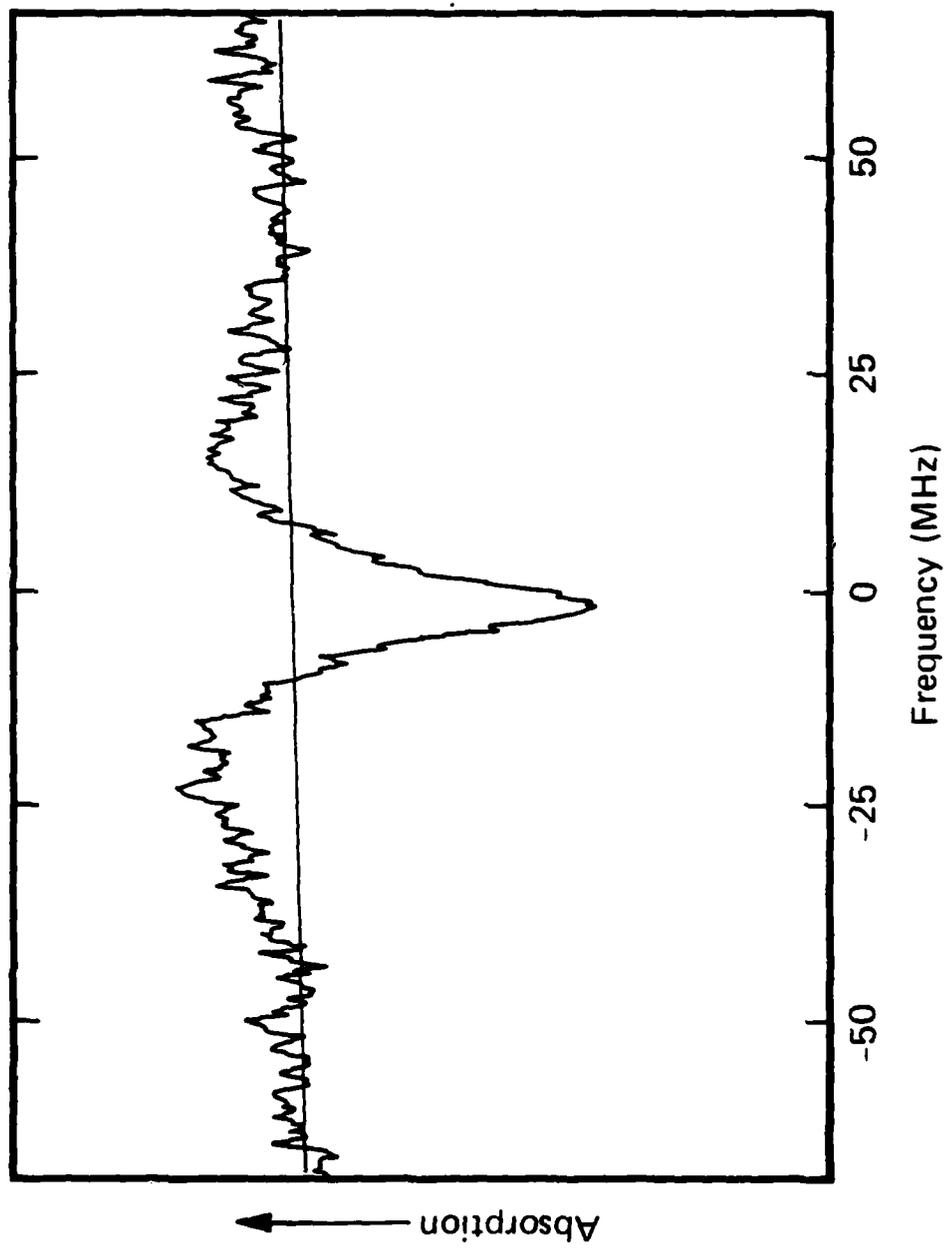
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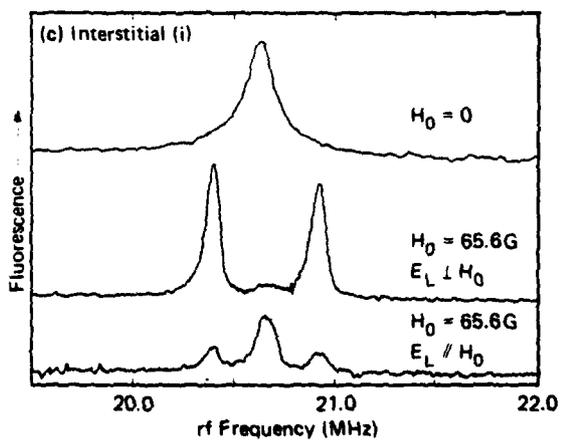
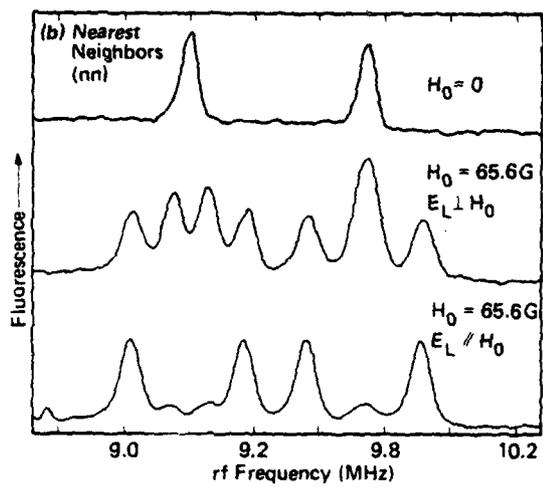
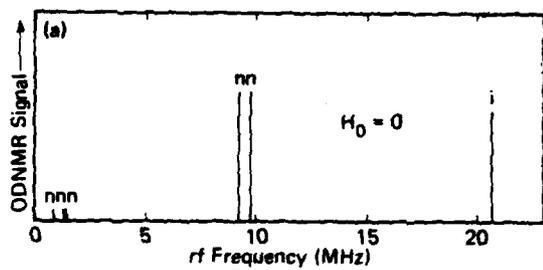
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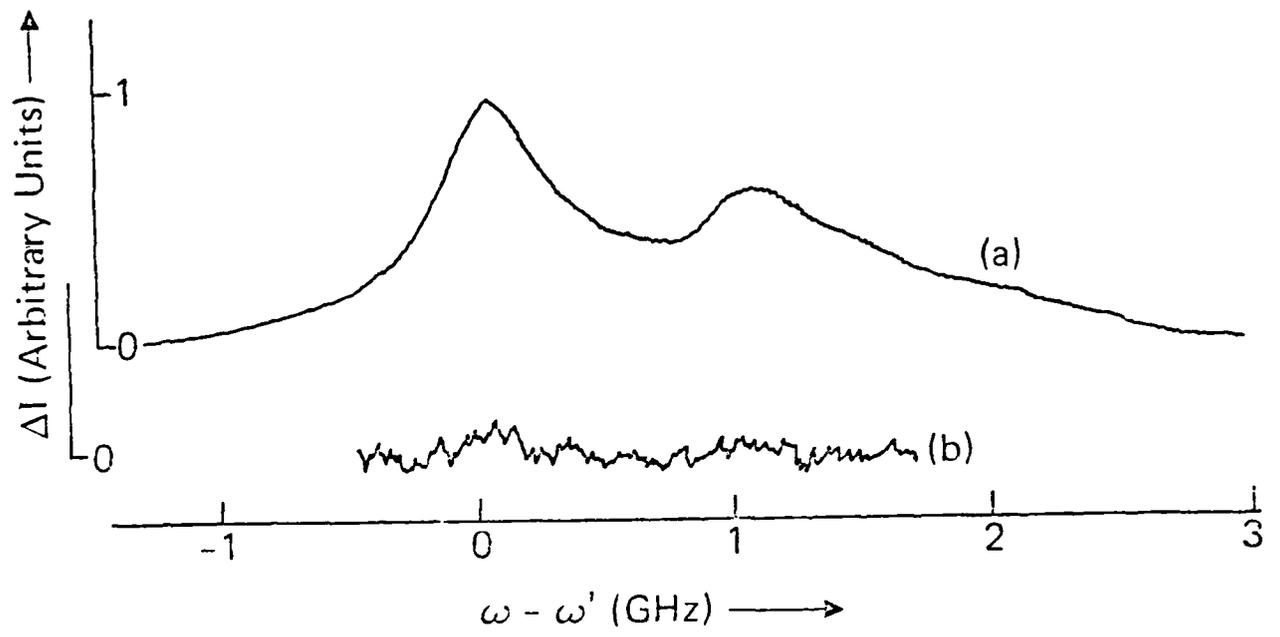
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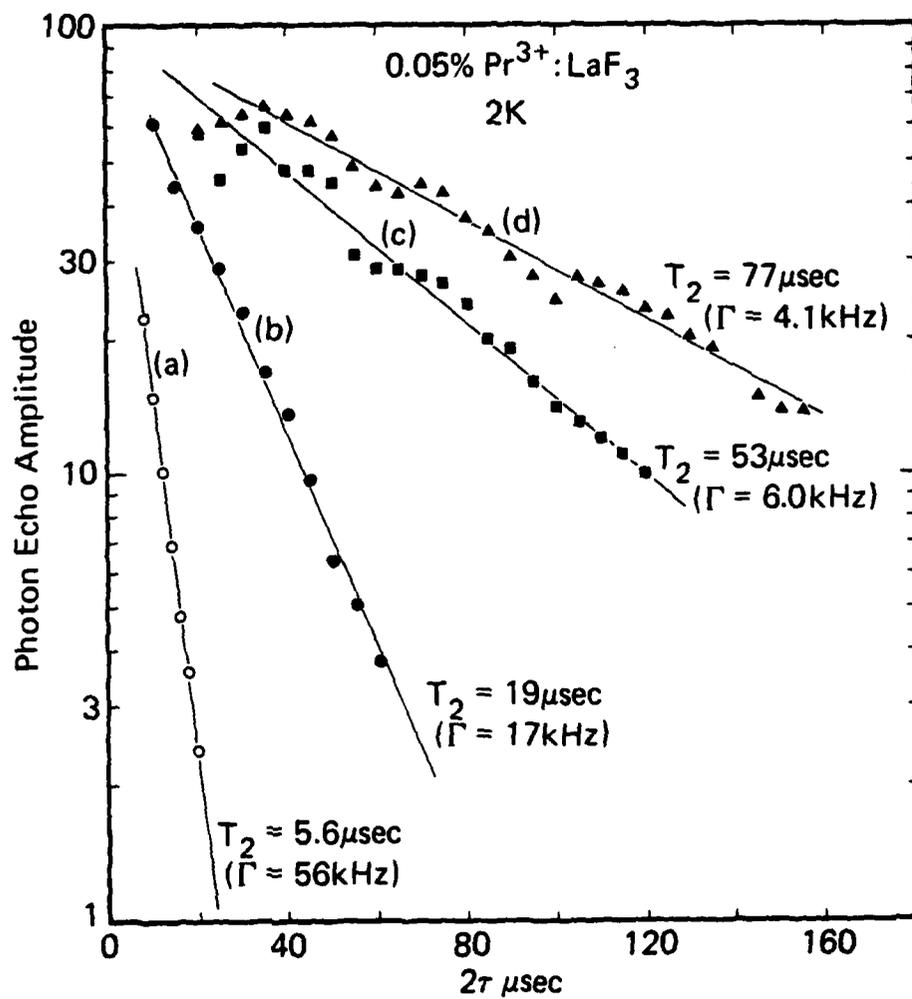


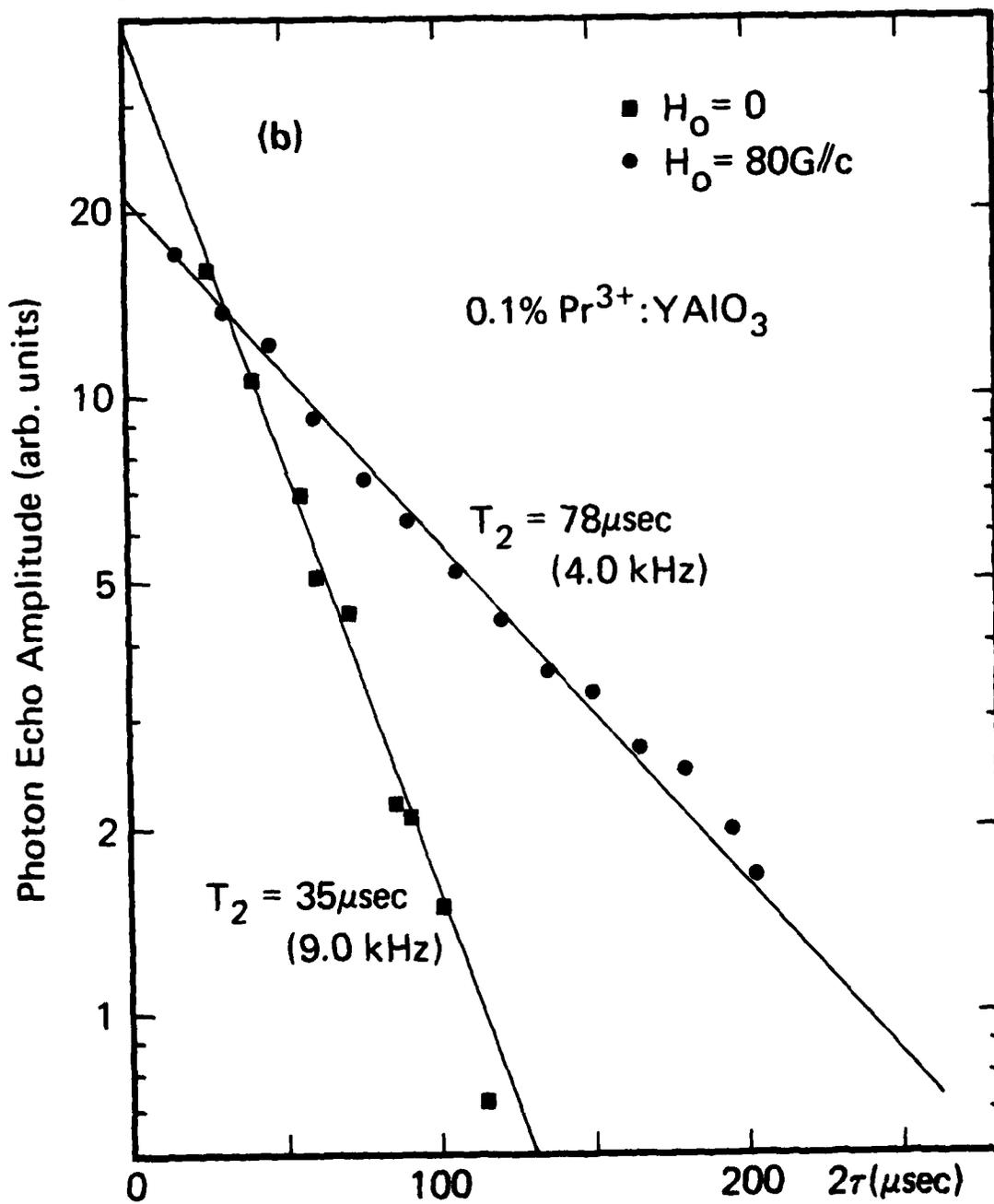
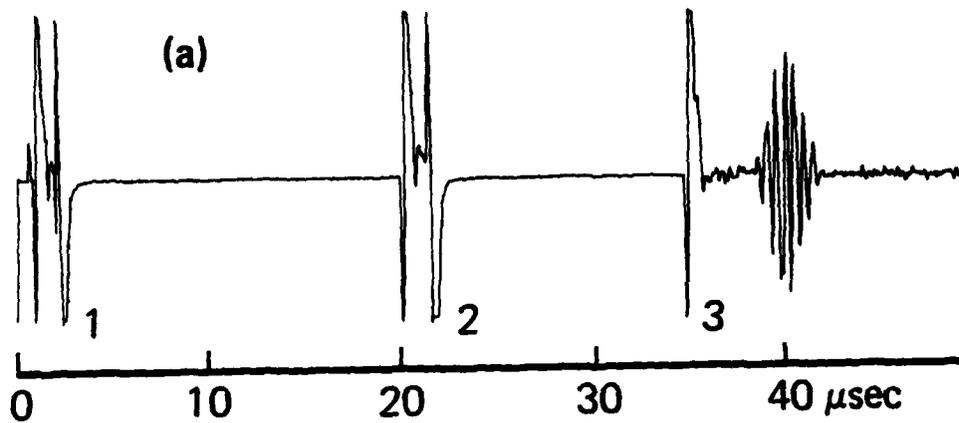


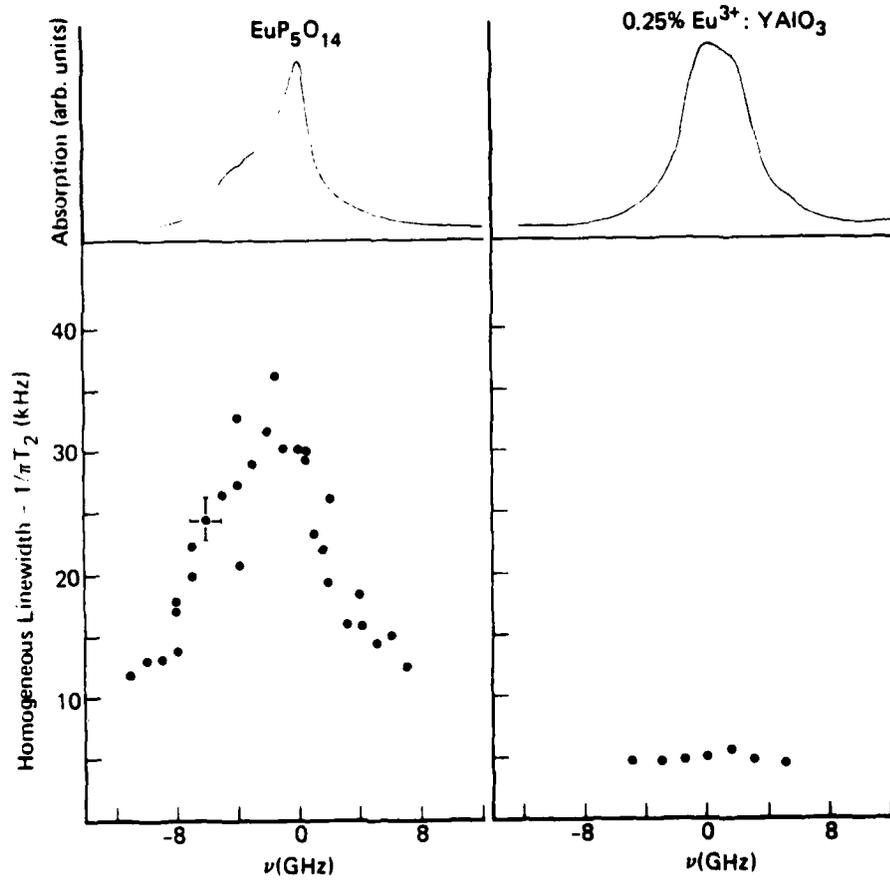


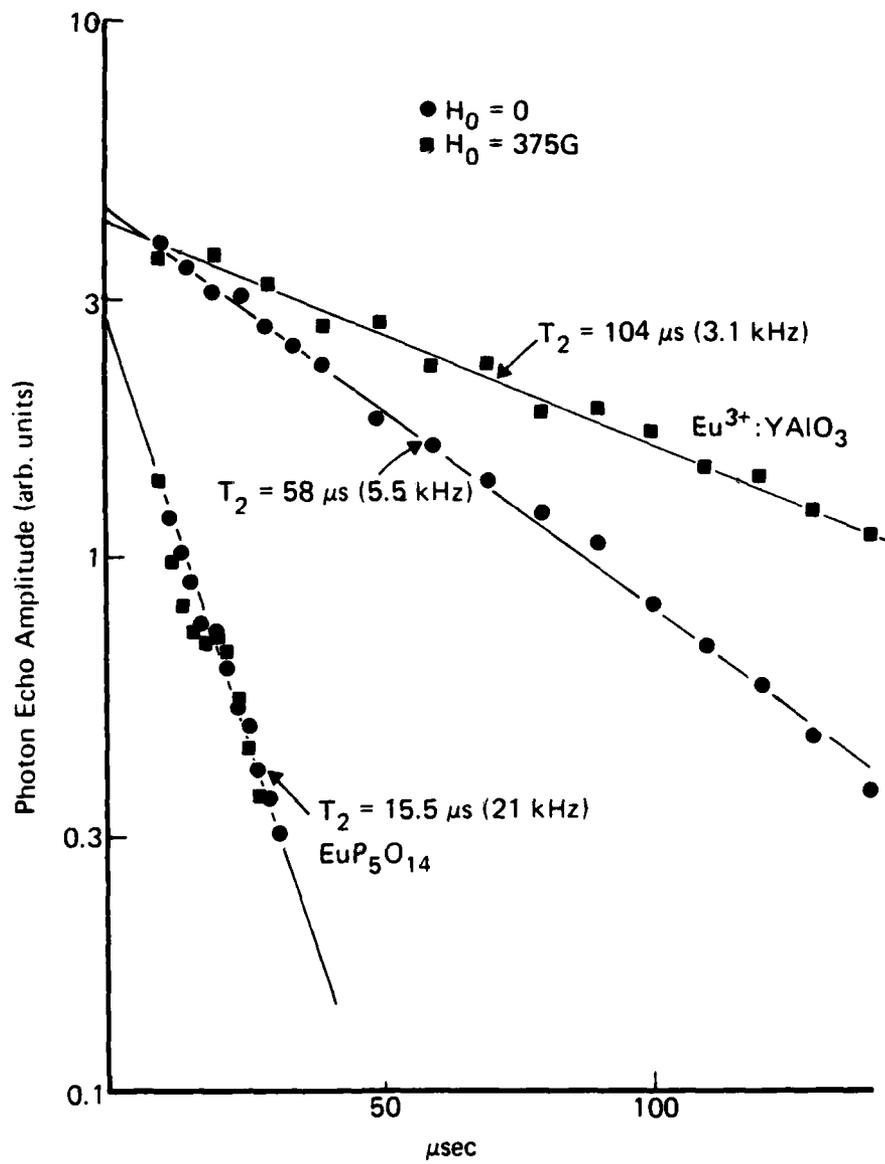


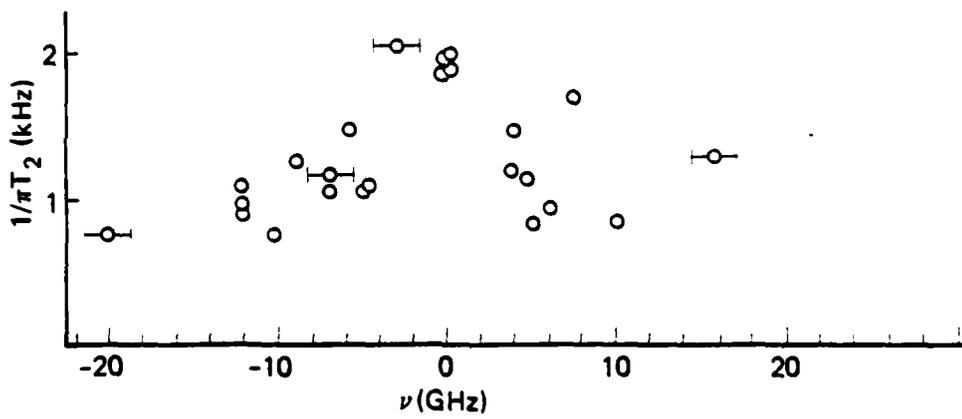
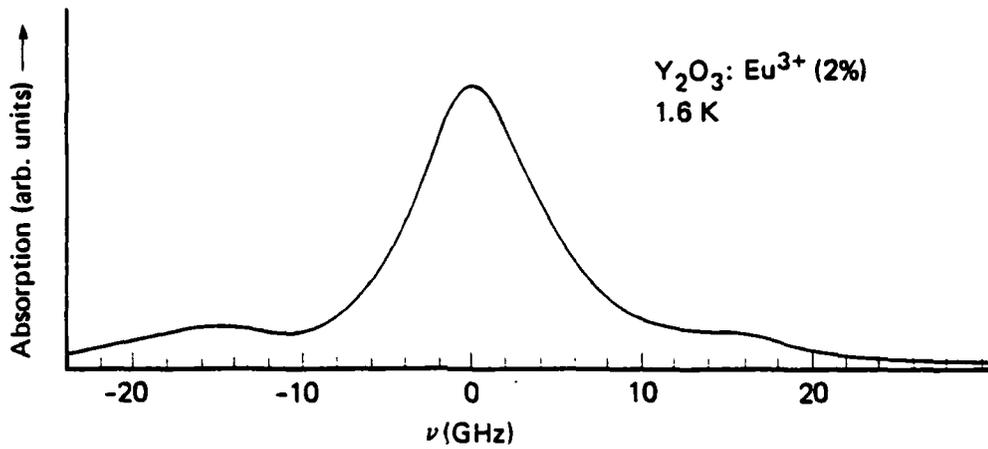


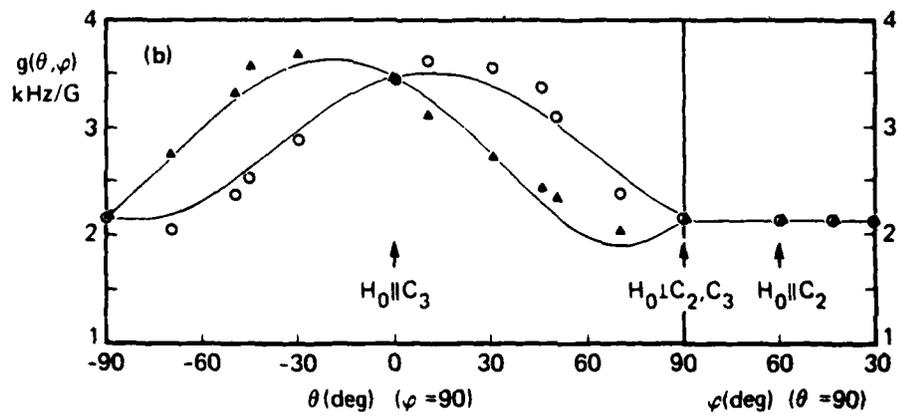
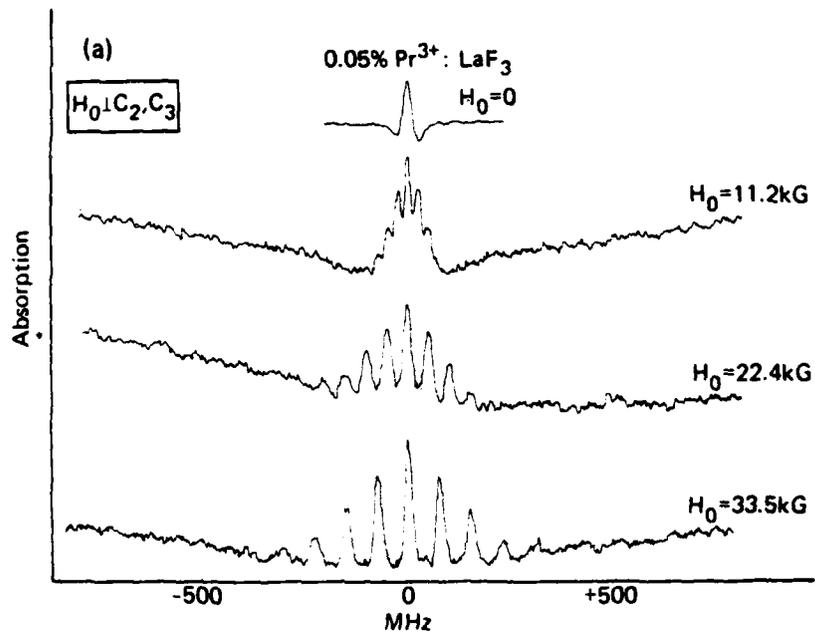




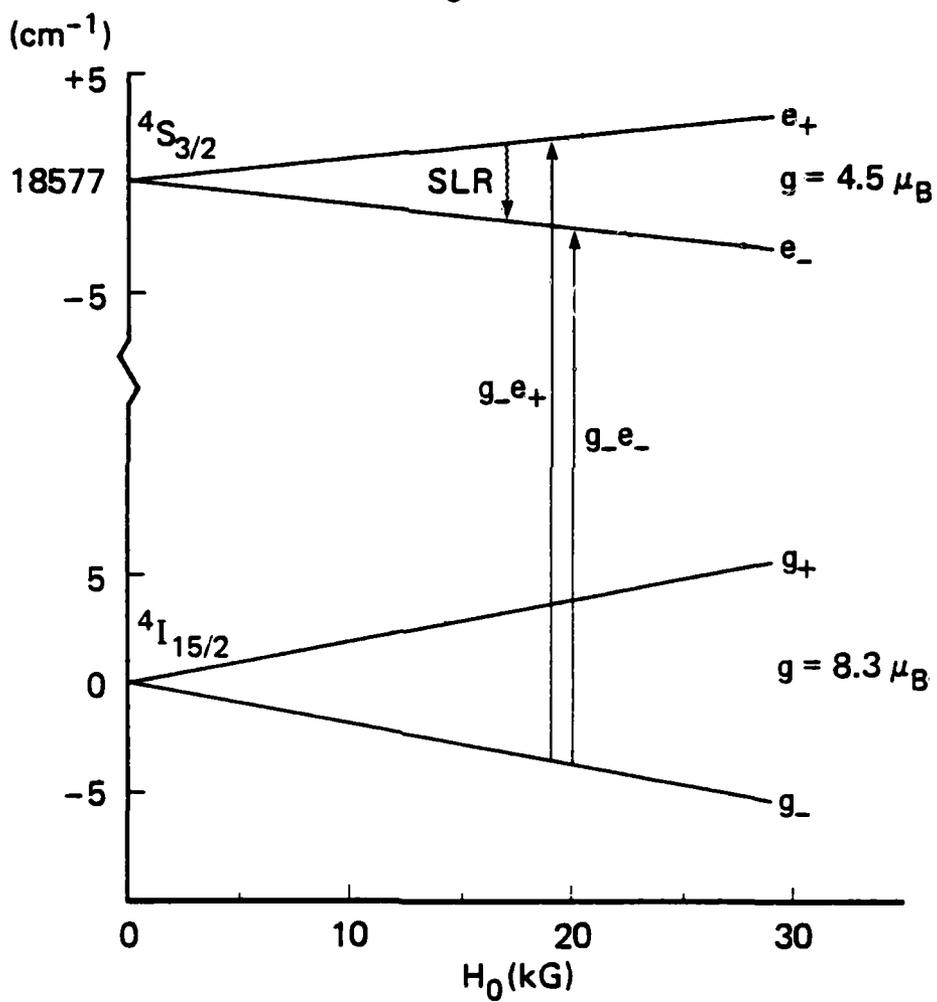


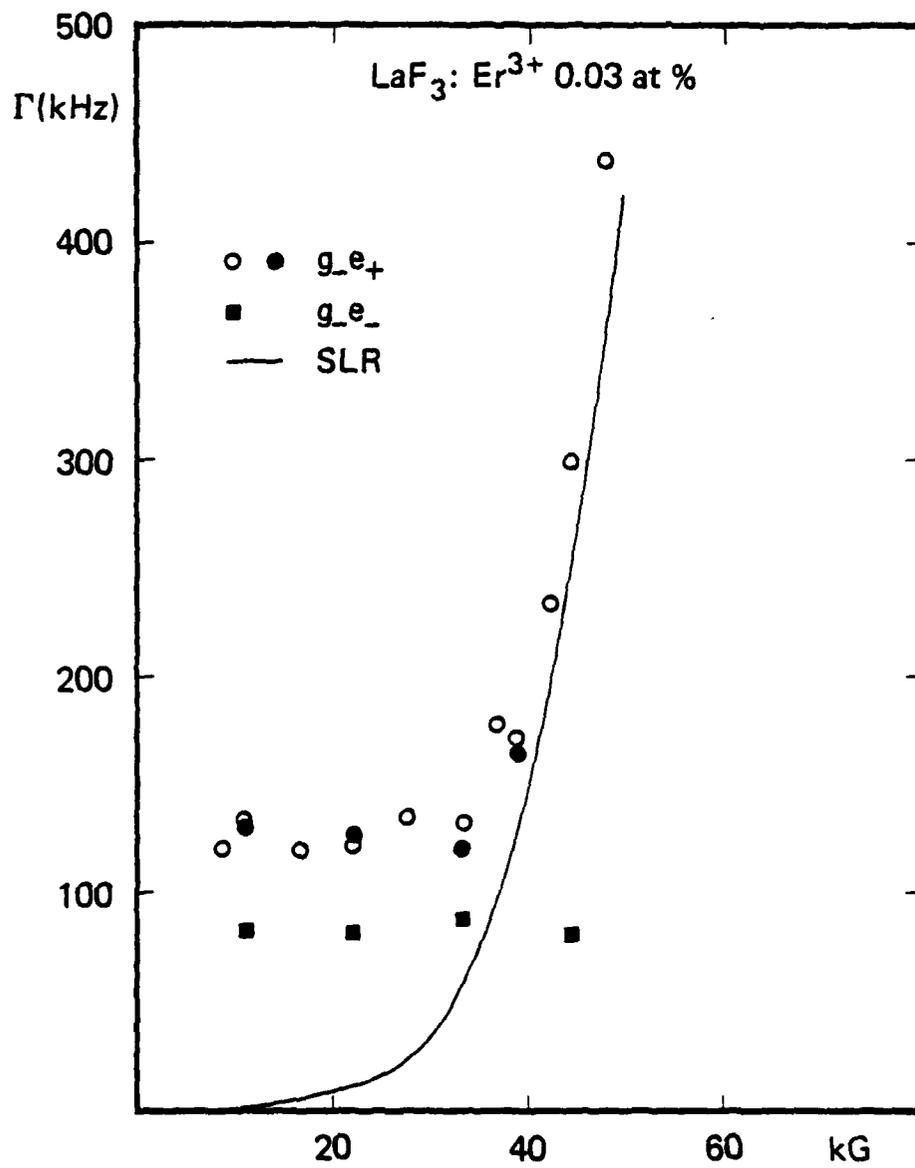


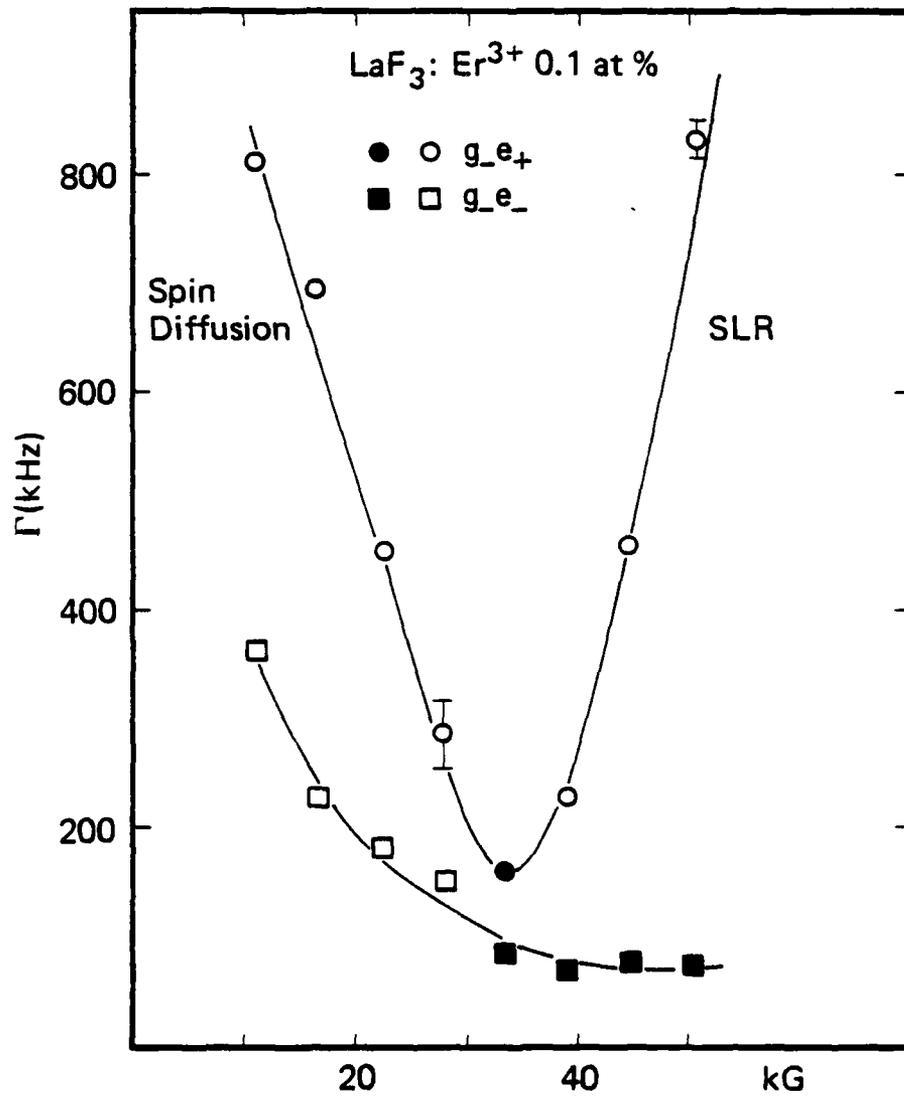


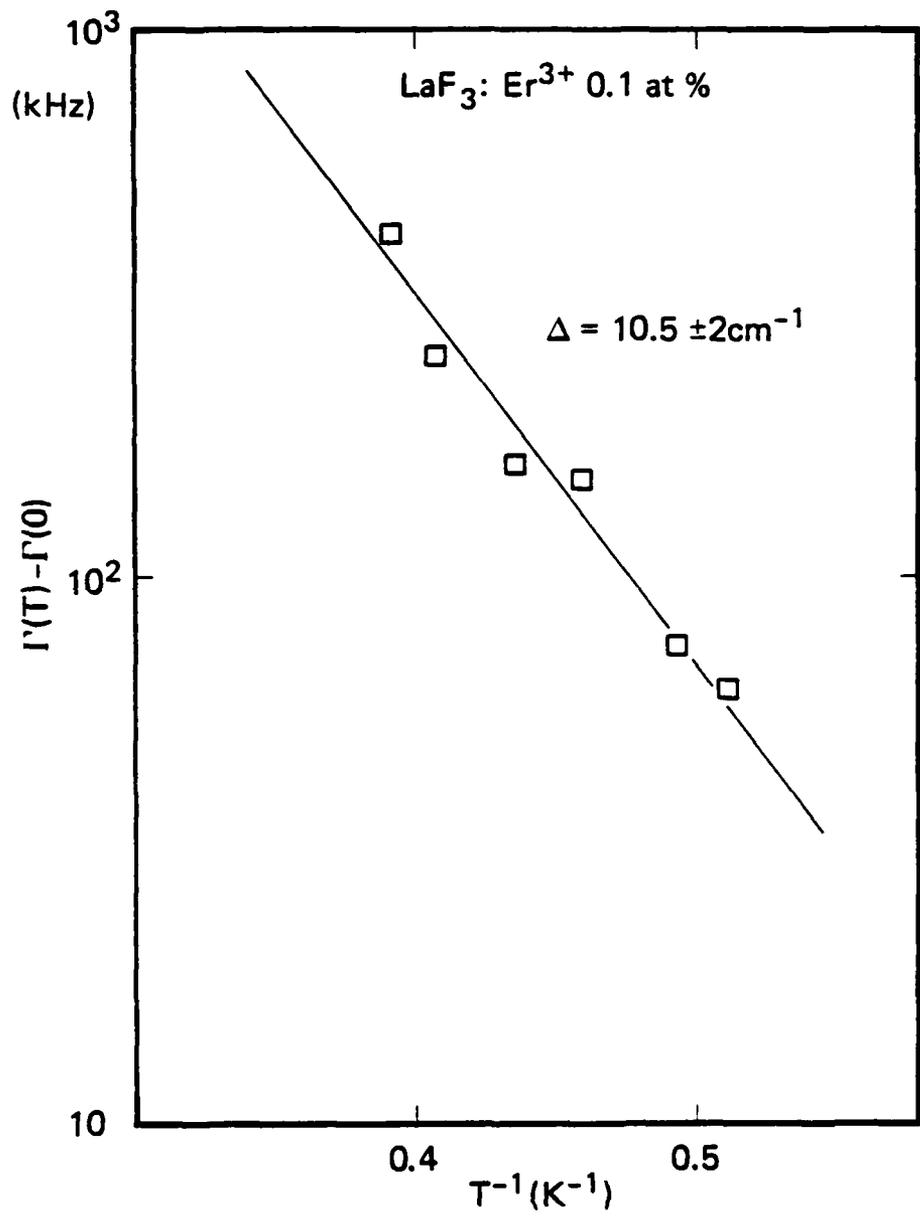


LaF<sub>3</sub>: Er<sup>3+</sup>









YAlO<sub>3</sub>: Eu<sup>3+</sup>  
7F<sub>0</sub> → 5D<sub>0</sub>

H<sub>0</sub> = 46 kG || x'



Absorption →

