



Spectroscopic evaluation and fluorescence dynamics of several erbium doped laser materials
by Bruce Farris

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of
Philosophy in Chemistry
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Abstract:

Spectroscopic analysis and kinetic modeling of relaxation processes have been completed for 2.1% and 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG at room temperature. Simultaneously time and frequency resolved emission spectra were obtained using step scan Fourier transform spectroscopy. Experimental emission lifetimes of the $4I_{13/2}$, $4I_{11/2}$, and $4S_{3/2}$ levels were obtained directly from these spectra. The $4I_{13/2}$ lifetimes were found to be 6.6, 6.5, 8.6, and 5.7 msec for 2.1% and 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG, respectively. Lifetimes of 67.3, 10.5, and 67.7 μ sec were observed for 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG, respectively for the $4I_{11/2}$ state. Experimental lifetimes of 10.7, 3.5, and 12.3 μ sec were observed for the $4S_{3/2}$ state in 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG.

Quantum-mechanical calculations using Morrison's code were performed and theoretical radiative rates were generated. Comparison of these values with experimental emission lifetimes allowed determination of non-radiative relaxation rates and branching ratios.

Additionally, an experimentally based new method of determining non-radiative rates was developed that utilizes the intensity "volume" under the three-dimensional emission bands. The two methods provided good agreement.

Finally, the rate constants obtained by these methods were plugged into a set of coupled differential equations and numerically solved using the fifth order Runge-Kutta method in Mathematica. Good agreement with the experimental temporal behavior was obtained (including emission rises as well as decays) indicating the validity of the results. Non-radiative vs. radiative branching ratios were approximately equal for the first excited state $4I_{13/2}$, but higher electronic states typically showed > 99% of the population relaxing via the non-radiative channel.

SPECTROSCOPIC EVALUATION AND FLUORESCENCE DYNAMICS
OF SEVERAL ERBIUM DOPED LASER MATERIALS

by

Bruce Farris

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This dissertation has been read by each member of the dissertation 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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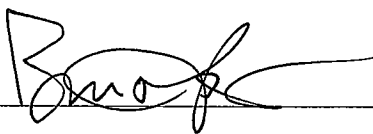
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ABSTRACT

Spectroscopic analysis and kinetic modeling of relaxation processes have been completed for 2.1% and 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG at room temperature. Simultaneously time and frequency resolved emission spectra were obtained using step scan Fourier transform spectroscopy. Experimental emission lifetimes of the $^4I_{13/2}$, $^4I_{11/2}$, and $^4S_{3/2}$ levels were obtained directly from these spectra. The $^4I_{13/2}$ lifetimes were found to be 6.6, 6.5, 8.6, and 5.7 msec for 2.1% and 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG, respectively. Lifetimes of 67.3, 10.5, and 67.7 μ sec were observed for 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG, respectively for the $^4I_{11/2}$ state. Experimental lifetimes of 10.7, 3.5, and 12.3 μ sec were observed for the $^4S_{3/2}$ state in 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG.

Quantum-mechanical calculations using Morrison's code were performed and theoretical radiative rates were generated. Comparison of these values with experimental emission lifetimes allowed determination of non-radiative relaxation rates and branching ratios.

Additionally, an experimentally based new method of determining non-radiative rates was developed that utilizes the intensity "volume" under the three-dimensional emission bands. The two methods provided good agreement.

Finally, the rate constants obtained by these methods were plugged into a set of coupled differential equations and numerically solved using the fifth order Runge-Kutta method in Mathematica. Good agreement with the experimental temporal behavior was obtained (including emission *rises* as well as decays) indicating the validity of the results. Non-radiative vs. radiative branching ratios were approximately equal for the first excited state $^4I_{13/2}$, but higher electronic states typically showed > 99% of the population relaxing via the non-radiative channel.

CHAPTER 1

INTRODUCTION

Erbium has been found to be a useful and versatile active atom for a variety of laser applications. It is capable of lasing near $3\text{ }\mu\text{m}$, a desirable wavelength for laser surgery, and around $1.7\text{ }\mu\text{m}$ in the eyesafe region (1,2). Lasing has also been achieved at several IR and visible wavelengths via upconversion processes (2-8). Erbium is often doped into solid-state crystalline hosts, which offer the benefits of durability, reliability, and convenience. For these reasons, there has been considerable interest in solid-state lasers using erbium as the active ion. Since the optical properties such as absorption and emission influence laser performance, spectroscopic investigation has been carried out on erbium in a wide variety of crystalline hosts (9-56). Additionally, lasing has been achieved in many solid state laser materials using erbium as the active lasing species. (2-11, 36, 45, 54-76).

Energy Levels in Erbium Laser Materials

Erbium, like all rare earth elements typically used as active lasing species, is most commonly incorporated into crystalline hosts in the trivalent

state. The resulting ground electron configuration of the Er^{3+} ion is a xenon-like electron structure with 11 additional electrons in the partially filled 4f orbitals ($[\text{Xe}] 4f^{11}$). The energy level structure of the erbium ion in crystalline hosts results from the Coulombic interaction of the 4f electrons with the nucleus and with each other, spin orbit coupling, and the host crystal field (77). The energy levels of the free Er^{3+} ion result from the electrostatic interaction and spin orbit coupling. The Coulombic interaction yields $2s+1L$ terms, which are further split into J states by the spin-orbit interaction. The resulting free ion energy level diagram with the $2s+1L_J$ states is shown in Figure 1, which includes the ground $^4I_{15/2}$ state through the seventh excited state ($^4F_{7/2}$). In actuality, the levels shown in Figure 1 are not pure $2s+1L_J$ states, due to mixing of the levels. Each of the levels referred to by the $2s+1L_J$ term symbol has other states mixed in. As can be seen by examination of the diagram, the free ion level separation is typically thousands of wavenumbers and transitions between the free ion levels are in the visible and infrared regions of the spectrum.

The host crystal field further splits each $2s+1L_J$ term into a manifold of Stark levels. The degeneracy of the $2s+1L_J$ states is $2J+1$, and this degeneracy is reduced by the crystal field splitting (77). The splitting is relatively small, with an overall manifold width of typically several hundred cm^{-1} , and a splitting between adjacent Stark levels of normally 50 - 100 cm^{-1} , due to the shielding of the 4f electrons from the host crystal field by the outer 5s and 5p

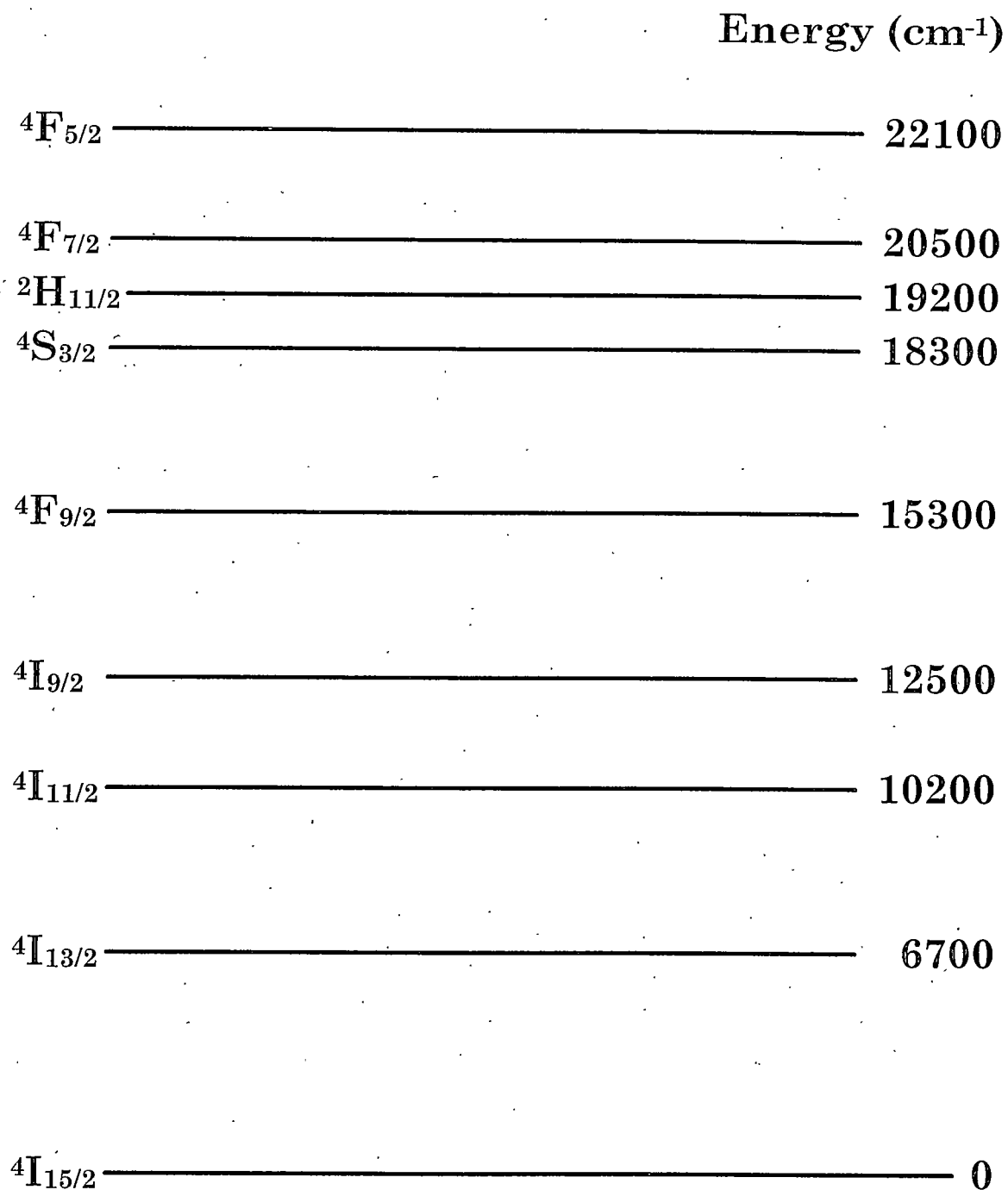


Figure 1. Free Ion Energy Levels for the Er³⁺ Ion.

electrons. The Stark level splitting can be exploited when a laser operating at a specific wavelength is desired. Coarse wavelength selection can be accomplished by choice of a specific rare earth ion, and fine "tuning" can be accomplished by selection of a host crystal that shifts the Stark levels such that the material is suited for the desired application. For that reason, Stark level assignment for different rare earth ions (including Er^{3+}) in crystalline hosts has historically been of interest, and a significant amount of work has been performed in this area for erbium(1,2,4,6,13,14,16,19-21,23,26,33,36,38-41,46,52,54,65).

Characterization of Laser Materials

The potential performance and operating characteristics of laser materials are to a large extent due to their spectroscopic properties. The absorption spectrum will determine potential pump wavelengths and influence pump efficiency, since pumping will be more efficient at strong absorption frequencies. After excitation has taken place, relaxation can occur via spontaneous radiative emission, nonradiative decay processes such as multiphonon relaxation, and/or ion-ion energy transfer processes. Radiative emissions can potentially be used as lasing transitions, and nonradiative

processes including energy transfer and multiphonon decay can enhance or detract from laser performance, depending upon the desired operating characteristics and pumping mechanism.

To ascertain the effect of the aforementioned properties on a particular lasing medium, it is useful to answer the following questions:

- What is the Stark level structure of the material?
- After excitation to a given manifold of Stark levels, what levels are involved in the relaxation process? Are these levels populated radiatively or nonradiatively? What levels are bypassed?
- Once populated, how is an excited state manifold depopulated? Is the manifold depopulated by radiative processes, nonradiative processes, or both? How quickly is it depopulated?
- What is the relative distribution (branching ratio) of the terminal levels of transitions originating from a particular manifold? What are the branching ratios of nonradiative relaxation processes?
- Do changes in dopant ion concentration (Er^{3+} in this study) or host crystal affect these population and/or depopulation processes?
- What, if any effects, are introduced by external factors such as temperature or excitation beam power?

Experimental methods or strategies that can answer some or all of these questions are of interest. Characterization of a material involves

absorption spectra, emission spectra resulting from continuous excitation to various manifolds, and temporally resolved emission spectra following modulated or pulsed excitation to the same manifolds. The absorption spectra are useful for determination of Stark level structure and identification of both excitation frequencies for emission experiments and pump frequencies for laser operation. The emission spectra provide information about the relaxation mechanisms from particular manifolds and identify promising laser transitions. The temporally resolved emission spectra provide information about the dynamics of both the radiative and nonradiative relaxation processes, which is of interest since the relative rates of population and depopulation of energy levels can affect whether and how well a material can function as a laser. For these reasons, these three experimental methods are all used in this study.

While spectroscopic study is useful in providing the previously mentioned information, combining it with complementary tools such as quantum-mechanical models and kinetic modeling using rate equations can increase its effectiveness. Emission spectra alone allow for direct observation of radiative emission transitions and provide some indirect information about nonradiative relaxation transitions. However, nonradiative relaxation rates and branching ratios can be gained by comparing experimentally determined lifetimes (which result from both radiative and nonradiative means of depopulation) with either low temperature or theoretically determined

radiative manifold lifetimes (which assume radiative processes are entirely responsible for depopulation). In this study, theoretical lifetimes are obtained from the quantum-mechanical model discussed in the next section. Alternatively, the rate and the relative contribution of the nonradiative relaxation processes can be determined by a newly developed method (presented in Chapter 4) that utilizes the intensity "volume" under the three dimensional emission bands of the temporally resolved spectra.

The kinetics of relaxation can be investigated by using the rate constants for the various relaxation processes (obtained by the experimental and/or theoretical methods discussed in the previous paragraph) following excitation to a particular level by solving sets of simultaneous rate equations for the involved energy levels. The combination of experimental methods, quantum-mechanical modeling, and kinetic modeling using rate equations can provide information that none of the three methods can provide alone, including information about processes that cannot be observed spectroscopically.

Quantum-Mechanical Model

A quantum-mechanical model developed by Morrison *et al* was used to calculate theoretical radiative lifetimes. The model is described in detail in Refs. 78-80 and is described briefly in this section.

Free ion wavefunctions are determined using a Hamiltonian that contains electrostatic, spin-orbit, and L^2 interactions (81). The host crystal field splits the free ion energy levels into Stark levels. Calculations of the Stark effects use a crystal field Hamiltonian of the form:

$$H_{CF} = \sum_i B_{nm} C_{nm}(i) \quad (1)$$

where the B_{nm} are crystal field parameters which describe the effect of the host crystal field on the free ion energy levels, the C_{nm} are spherical tensor operator components, nm covers the values of n and m allowed by the symmetry of the site of the rare earth in the host crystal, and the i summation is over all of the 4f electrons of the rare earth ion. The crystal field parameters are related to the crystal field components A_{nm} , which are spherical tensor components of the host crystal field at the ion site, calculated by a point charge lattice summation. The A_{nm} and B_{nm} are related by the radial factor ρ_n , which are primarily functions of the rare earth ion, though they can be influenced slightly by the host crystal, and the relationships:

$$B_{nm} = \rho_n A_{nm} \quad (2)$$

$$\rho_n = \frac{(B_{n0}^2 + 2B_{n2}^2 + 2B_{n4}^2 + \dots)^{1/2}}{(A_{n0}^2 + 2A_{n2}^2 + 2A_{n4}^2 + \dots)^{1/2}} \quad (3)$$

Stark levels for a rare earth ion in a particular host crystal can be calculated entirely from the theoretical model. To do so, host x-ray data can be used to determine A_{nm} and Equation 2 can be used with the newly

determined A_{nm} to calculate the crystal field parameters B_{nm} . The calculated B_{nm} can then be used with Equation 1 used to determine the crystal field Hamiltonian. Alternatively, if experimental energy levels are known, a set of B_{nm} can be fit to the experimental data. The B_{nm} from the fit can then be used along with the A_{nm} for the host and Equation 3 to calculate ρ_n , which are then used with A_{nm} for a similar host and Equation 2 to calculate B_{nm} for the similar host. By the second method, experimentally determined Stark levels for a rare earth ion in one host can be fit and used to calculate Stark levels for the same ion in the other hosts from the same "family" (i.e. the garnets) providing better results than purely theoretical calculations (1). The Morrison model is limited to low dopant concentrations, as it does not include the effect of the rare earth dopant ion on the host crystal (which would change the point charge lattice summation and the A_{nm} values).

The model can also be used to calculate theoretical emission transition probabilities, which means that theoretical radiative lifetimes of a particular energy level can be obtained as well, using the Judd - Ofelt treatment (82,83). In this treatment, the Judd-Ofelt parameters Ω_k (which contain the host dependent part of the electric dipole line strengths) can be calculated (39,79) and used to calculate the theoretical electric dipole line strength $S_{ed}(J \rightarrow J')$. The magnetic dipole line strength $S_{md}(J \rightarrow J')$, which is entirely dependent on the rare earth ion within the theory, is calculated from the theoretical magnetic dipole oscillator strength. The line strengths for each transition of

interest can then be related to the Einstein A coefficients for the respective transitions.

CHAPTER 2

EXPERIMENTAL PROCEDURE

In this chapter, the overall approach to analysis of the materials, including types of spectra collected and justification for collecting them, will be explained. Next, the discussion includes a description of the analyzed samples and the equipment and techniques utilized in obtaining the various spectra. The chapter concludes with a brief discussion of the temporally resolved Fourier Transform spectroscopic technique used to gather most of the data.

Overall Method of Analysis

We are interested in the various population and depopulation processes (both radiative and nonradiative) of the energy levels in erbium-doped laser materials. The project goal was to use several spectroscopic techniques to gain relevant information about these processes. First, absorption spectra were collected for each sample. Although absorption spectra of laser materials are of fundamental interest since they provide information on potential pump wavelengths for laser use, the more

immediate and practical use for the purposes of this project was to provide appropriate excitation frequencies of the samples for collection of emission spectra. While absorption spectra for Er:YAG (4,6,26,34,35,37,38,46), Er:LuAG (9), and Er:YSO (34,36,39,40), are well documented in the literature; it was still beneficial to run absorption on the specific samples analyzed to account for any impurities or anomalies.

Two different emission techniques were employed in this project: standard emission and temporally resolved emission. The standard emission spectra were obtained using a continuous excitation source, but source modulation was necessary to obtain the temporally resolved spectra. The standard emission spectra were obtained much more rapidly and conveniently than the temporally resolved spectra and provided sufficient information to make them worthwhile, even though the spectral information was reproduced in the temporally resolved emission spectra. First, the continuously pumped emission spectra were useful for initial identification and assignment of emission bands and their relative contribution toward depopulating higher energy levels after excitation. Secondly, they provided information useful in the setting up of the temporally resolved spectra. The longer-lived emission bands typically appeared stronger in the continuous spectra, so some very rough qualitative information on emission band lifetime could be extracted. However, this information is by no means conclusive since actual emission transition intensity must also be considered.

Finally, identification of emission bands by continuous spectra facilitated the setting up of appropriate wavelength ranges for temporally resolved spectroscopy.

In addition to providing the above-mentioned information, the temporally resolved emission spectra provided emission decay rates and allowed the deconvolution of multiple overlapping bands which were difficult to distinguish in the spectral dimension. Second, since emission bands with the same decay profiles likely originate from the same manifold, it provided more convincing evidence for the assignment of emission transitions. Third, comparing emission spectra excited at different frequencies yielded information about the nonradiative processes involved in deexcitation. Finally, the ability to pump several excited states of the sample and observe the "turning on and off" of emission bands helped identify the originating manifold of the emission transitions. These capabilities will be demonstrated in Chapters 3 and 4.

Samples

Scientific Materials Corporation provided the erbium-doped YSO, YAG, and LuAG samples analyzed in this project. The samples were discs cut from crystals grown by Scientific Materials and polished on the edges and faces. They are approximately one-eighth inch thick and range from 0.5 to 1.5

inches in diameter. Erbium ions occupy yttrium sites in both the YAG and YSO crystal lattices, while they occupy lutetium sites in LuAG. There are two inequivalent sites occupied by erbium in Er:YSO, and the YSO host has three principal axes of polarization (39). While both orientationally resolved and unoriented absorption spectra were obtained for Er:YSO, orientationally resolved emission spectra were not obtained since it has been determined that the contribution of the two erbium centers to emission (on the time scales studied in this work) does not depend on which one is pumped more efficiently. (39) Moncorge *et al* found that the fluorescence bandshapes were identical for all the pump wavelengths studied (it is expected that for a particular wavelength one site would be excited more efficiently than the other), indicating that energy transfer occurs on a sufficiently faster time scale than the emission transitions studied, which occur on the microsecond and millisecond time scales.

Equipment and Techniques

The need to conduct the various experiments discussed earlier in this chapter makes a versatile spectroscopic facility necessary. The equipment and experiment setups used in this project are nearly identical to those described by Richard Martoglio (a previous member of the Lee Spangler research group at Montana State University) in his thesis (84) detailing his

similar work with thulium-doped materials. These procedures will be briefly outlined in this section, and all differences from the equipment setups described by Martoglio will be discussed in detail. A general equipment layout is shown in Figure 2.

Absorption

Absorption experiments were carried out using the Bruker IFS66 Fourier Transform Spectrometer. The instrument, which was described in detail by Martoglio (84), utilizes a Michelson interferometer as its basic design. The source was a broadband tungsten lamp included in the spectrometer. Two different beamsplitters were used depending on the spectral range desired for the specific experiment: a calcium fluoride beamsplitter was generally used for lower frequency measurements and a quartz beamsplitter was utilized for higher frequency spectra. A liquid nitrogen cooled indium antimonide detector was utilized in the infrared, while visible detection was accomplished using a silicon diode. Figure 3 shows response curves for all four possible detector/beamsplitter combinations. The detector/beamsplitter combinations for all absorption and emission experiments were chosen to get the best signal response for the desired spectral region.

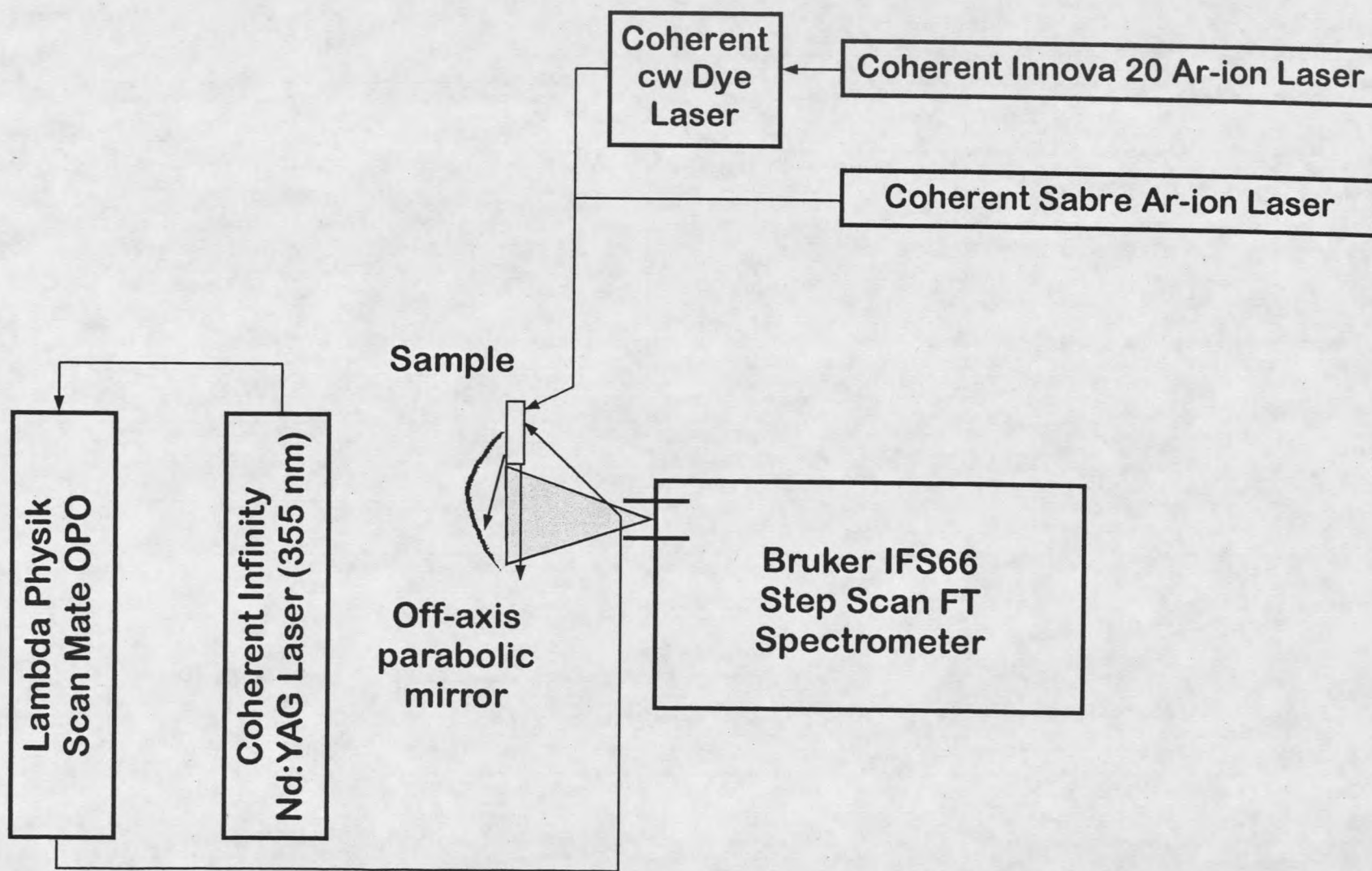


Figure 2. Experimental Set-up for Absorption and Emission.

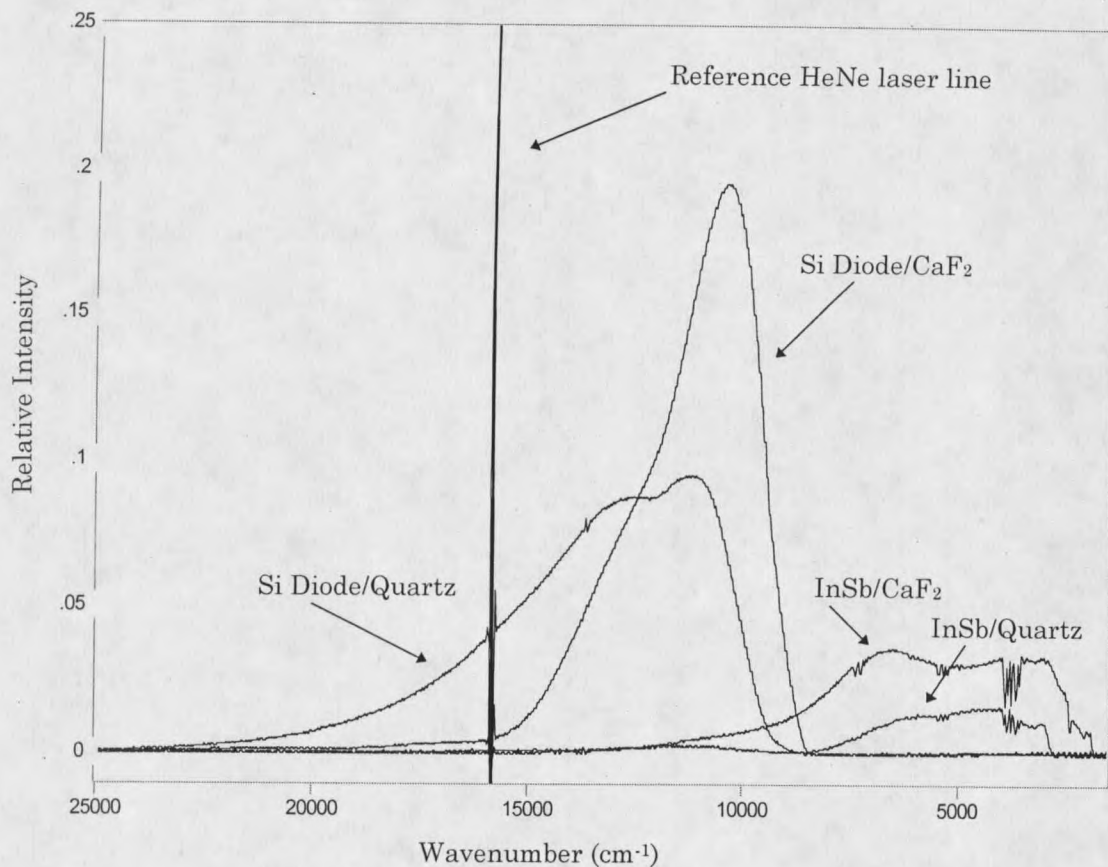


Figure 3: Response Curves for Detector/Beamsplitter Combinations.

Emission

An argon-ion laser provided a convenient excitation source for emission experiments since all the samples studied absorb the 488 nm line. Two different Ar-ion lasers were used as sources during the project. In addition to functioning directly as an excitation source, one of the Ar-ion lasers was also used to pump a Coherent continuous dye laser, allowing access to other erbium absorption bands.

The general emission setup is illustrated in Figure 2. After excitation by the Ar-ion laser, sample emission was collected by an off-axis parabolic mirror. The parabolic mirror was obtained from Bruker and was originally designed for light collection before entering the IFS66 spectrometer, thereby ensuring f-matching ($f/4.5$) to the IFS66. The sample was placed at the appropriate distance outside the interferometer to allow f-matching. Collecting the emission in the off-axis parabolic mirror improved emission signal-to-noise by a factor of approximately 40 over simply placing the sample in front of the IFS66 emission port, due to collection of a larger solid angle of the emitted radiation. Additionally, an aperture was sometimes placed at the IFS66 emission port to eliminate unwanted scattered laser light. The same beamsplitters and detectors used for absorption were used for the emission measurements, and optical filters were sometimes placed in the IFS66 absorption sample chamber to prevent unwanted emission signal and/or scattered source light from reaching the detector.

Temporally Resolved Emission

In this section, the equipment and setup for the temporally resolved emission experiments are discussed. The temporally resolved spectroscopic method is discussed in more detail in the next section.

Since source modulation was necessary to conduct the time-resolved experiments, the Ar-ion source (or Ar-ion pumped continuous dye laser) was

modulated using either a chopper (for millisecond pulses) or an acousto-optic modulator (for microsecond pulses) for the earlier experiments during the initial stages of the project.

A shorter excitation pulse was necessary to study the relaxation processes in these materials, many of which occur on the microsecond time scale or faster, thus nanosecond pulses were used for most of the temporally resolved work. The 1064 nm output from a Coherent Infinity Nd:YAG laser was tripled to 355 nm and used to pump a Lambda-Physik ScanMate OPO. The OPO could provide tunable output from 400 nm to nearly 2.5 microns, and output powers used were typically 2-5 mJ/pulse. With system repetition rates adjustable from 0.1 to 100 Hz, the Infinity/ScanMate combination provided the necessary flexibility to excite each different sample to a number of different electronic states. Additionally, the repetition rate could be set to allow for complete relaxation of the material before the next pulse was delivered.

The general experiment layout for the temporally resolved emission work was identical to the continuous emission setup (see Figure 2). When the Infinity/OPO excitation source was used, the beam was focused from approximately one cm to 2 mm in diameter using a $f/12$ lens (based on lens diameter) placed between the OPO outlet and the sample. The sample was placed at the focal point to maximize pump power density. Additionally, the sample placement was such that the excitation beam struck the sample near

the edge to minimize self absorption. The moving mirror in the Bruker interferometer was operated in step scan mode rather than rapid scan mode (this will be discussed further in the next section). Since the mirror was designed to be at a complete stop while gathering data, the system was susceptible to mechanical vibration. There are two major differences in the equipment setup used for gathering most of the time resolved data in this study with the setup employed by Martoglio. (84) First, the Infinity/OPO source was mounted on a larger optical table along with the interferometer. The optical table in use when Martoglio gathered his data was too small to accommodate the entire system. Tying the entire system together on one table greatly diminished the effect of building vibrations on the system, enhancing the signal-to-noise ratio. Additionally, the setup was moved to the Spangler group's temporary laboratory facility at Scientific Materials Corporation, which was located on the ground floor as opposed to the second floor laboratory in Gaines Hall at MSU. The overall building vibrations were less on the ground floor location, again providing improved mechanical stability and signal-to-noise ratio.

Temporally Resolved FT Spectroscopy

In this section, the temporally resolved Fourier Transform technique is briefly discussed. The technique is discussed in detail by Martoglio. (84)

In a standard Fourier Transform experiment using a Michelson interferometer, the moving mirror is scanned continuously on the order of 40 kHz, known as "rapid scan" mode. Temporal resolution at a given wavelength cannot be obtained in rapid scan mode because the mirror position changes during the course of the temporal event. However, operation of the IFS66 in step scan mode allows the user to obtain temporal information. In step scan mode, the moving mirror is stopped at each location and data is obtained. The method of obtaining data is illustrated on Figure 4. At each mirror position, the desired number of data points are obtained at a time interval corresponding to the desired temporal resolution. This process can be completed as many times as desired for signal averaging. Data corresponding to a particular mirror position is shown as a horizontal column in the first part of the figure. An interferogram is constructed using the data from each of the different mirror positions at one moment in time, known as a "time slice" (illustrated in the second part of Figure 4). This process is repeated for each of the time slices, resulting in a separate interferogram for each moment in time. The data needed for each of these interferograms is a vertical column in the first part of Figure 4. Each interferogram is then Fourier transformed to yield a spectrum for each time slice (last part of Figure 4), resulting in a temporally resolved emission spectrum.

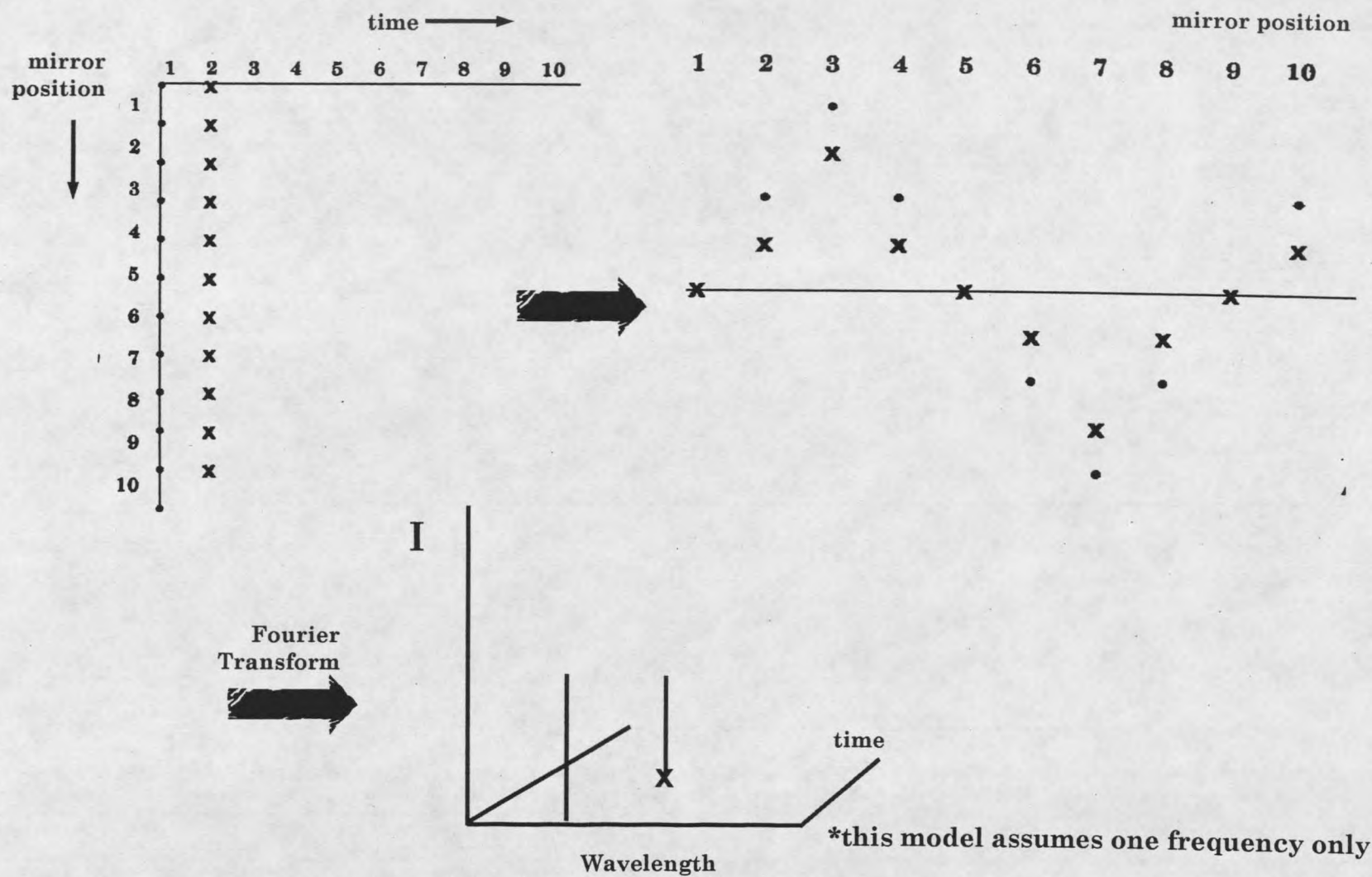


Figure 4. Formation of the Interferogram in Step-Scan Mode.

Intensity fluctuations in the Infinity/OPO source coupled with the time resolved FT method led to broadband baseline noise which decayed proportionately with the signal over time (see Figure 5). The way in which these fluctuations manifested themselves as broadband noise can most easily be seen by looking at the example of a single emission frequency (see Figure 6). If the emission intensity is the same for each mirror position, the interferogram will be a sine wave, which is Fourier transformed into a single frequency. Fluctuations in emission intensity lead to an interferogram that is not quite sinusoidal (see Figure 6). This nonsinusoidal interferogram is Fourier transformed into multiple frequencies, corresponding to the actual emission frequency and noise. This effect is of course compounded in emission from the erbium doped laser crystals, which have multiple emission bands as opposed to a single emission frequency. This effect can actually sometimes be beneficial since the noise from intensity fluctuations is spread over the whole spectral region rather than being concentrated over the emission band. However, it can be detrimental in the case where an emission spectrum contains both strong and weak bands, since noise from intensity fluctuations in the strong bands can obscure the weak bands.

Two actions were taken to address these noise issues. Increased signal averaging was the simplest solution, although it meant longer experiment times, leaving the experiment more susceptible to long-term fluctuations. Also, when it was desirable to examine a weaker emission band, stronger

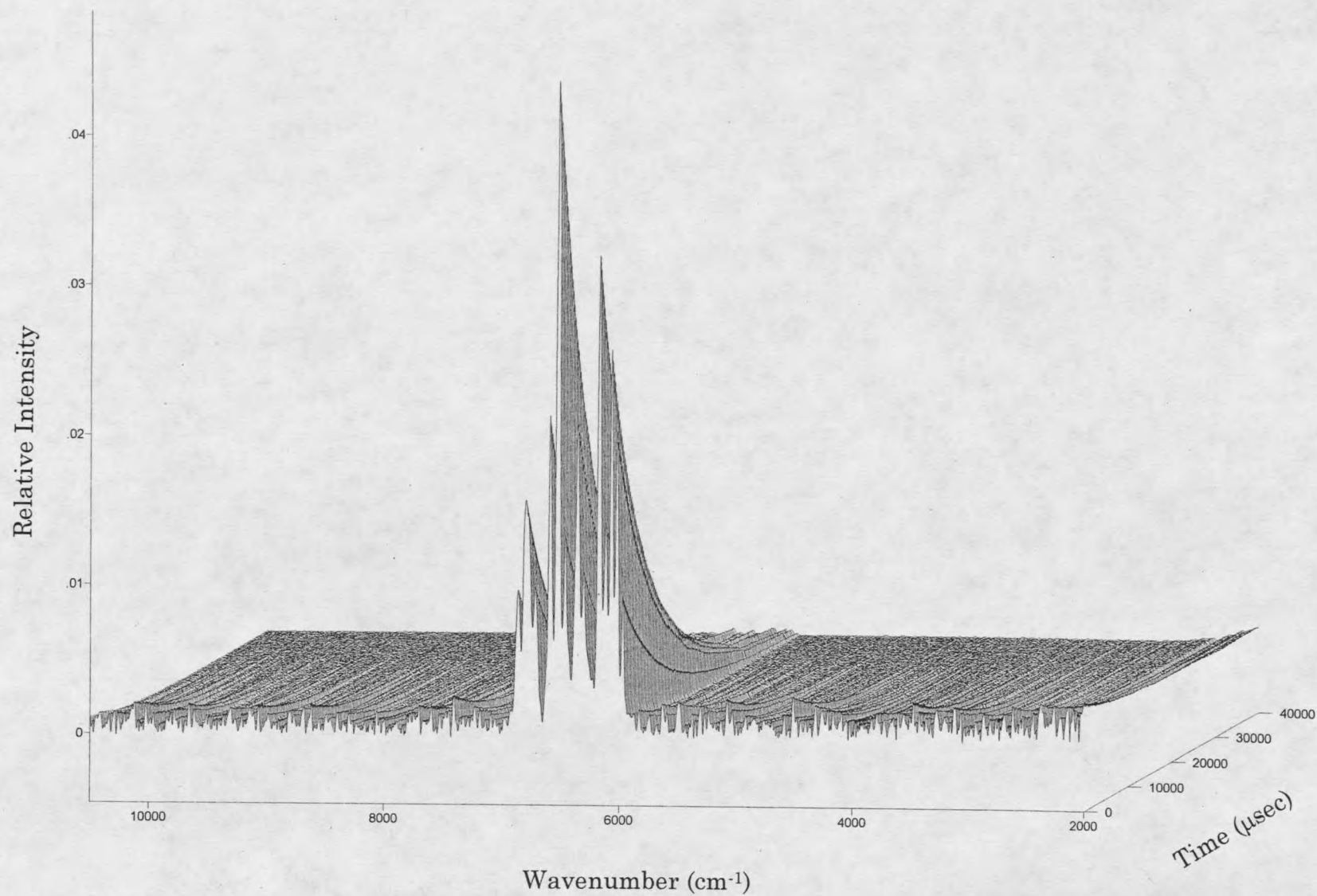
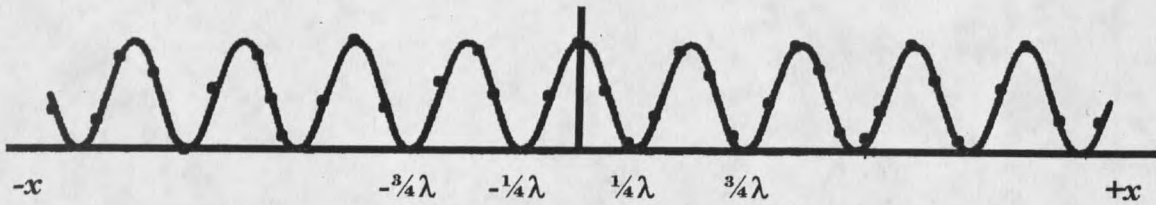
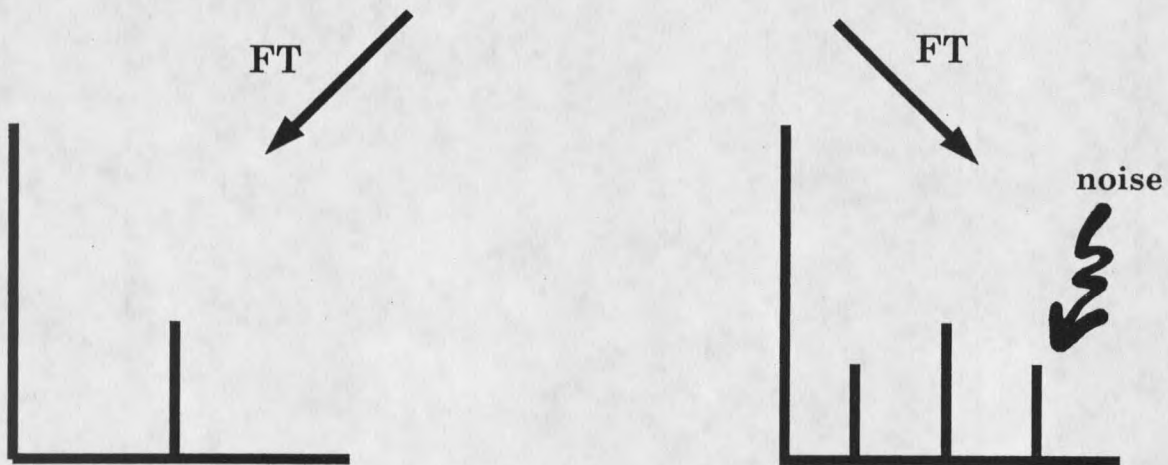


Figure 5. Time Resolved Spectrum Exhibiting Broadband Systematic Noise.

For a pulsed monochromatic source, if the intensity of all pulses is equal, the interferogram will be a sine wave consisting of discrete points.



What happens if one pulse is more intense than the next?



When the signal is an entire emission band or bands, this effect is compounded greatly, leading to broadband noise.

Figure 6. Illustration of systematic noise introduced by source pulse instability

bands which contributed noise to the weaker band were filtered out optically, either by the use of filters or strategic selecting of detector/beamsplitter combination.

In extreme cases including very low signal, large source intensity fluctuations, and/or significant scattering of laser light into the detector, a mirror position other than the position corresponding to the zero path difference has had the highest intensity in the interferogram. The position corresponding to zero path difference should be the most intense in the interferogram since it is the only position where there is complete constructive interference of all wavelengths and is the centerburst in a typical interferogram. (85) It was necessary to fix the proper zero path difference position, as opposed to the most intense, as the centerburst, or Fourier transform errors resulted.

CHAPTER 3

EXPERIMENTAL RESULTS

This chapter contains results from absorption and emission spectra obtained from the Er:YAG, Er:LuAG, and Er:YSO samples, and a brief interpretation of the results. A more thorough discussion and examination of the data will follow in Chapter 4.

Absorption

Absorption spectra of Er:YAG (4,6,26,34,35,37,38,46), Er:LuAG (9), and Er:YSO (34,36,39,40) are well documented in the literature. These include spectra collected at both room temperature (~ 300 K) and at low (liquid helium or nitrogen) temperatures. While low temperature spectra are necessary to make individual Stark level assignments, all absorption spectra in this study were obtained at room temperature (~ 300 K), which was sufficient to identify pump frequencies for emission study and to check for any impurities or anomalies in the specific samples.

The Bruker IFS66 Spectrometer was used for all absorption measurements. Measurements were taken over two spectral regions:

"visible" (9000-25000 cm^{-1}), which utilized a quartz beamsplitter and a Si diode detector, and IR (2000-15780 cm^{-1}), which used a calcium fluoride beamsplitter and indium antimonide detector (see Figure 3). Some IR absorption spectra were also taken over the 2000-10500 cm^{-1} range. A tungsten lamp was used as the light source for all measurements. The number of scans for signal averaging ranged from 32 to 2000, and spectral resolution was typically 2 cm^{-1} .

Figure 7 contains Er:YAG absorption spectra. Although measurements were taken on several concentrations of erbium in YAG only the 2.1% concentration data is shown, since varying the concentration in a given crystal host was found by experiment to not affect the absorption bandshapes. Er:LuAG absorption spectra are shown in Figure 8. Absorption spectra for Er:YSO are shown in Figures 9-11. There are two inequivalent sites occupied by erbium in Er:YSO, and the YSO host has three principal axes of polarization (39). Unoriented absorption spectra are shown in Figure 9. Figures 10 and 11 are infrared and visible absorption spectra for light polarized parallel to the three polarization axes. All the transitions seen in Figures 7 through 11 have the ground state $^4I_{15/2}$ manifold as their initial level and terminate in the levels as indicated on the spectra. Figure 12 shows the energy level diagram containing the manifolds involved in the absorption bands in Figures 7-11. The same bands are present in Figures 10

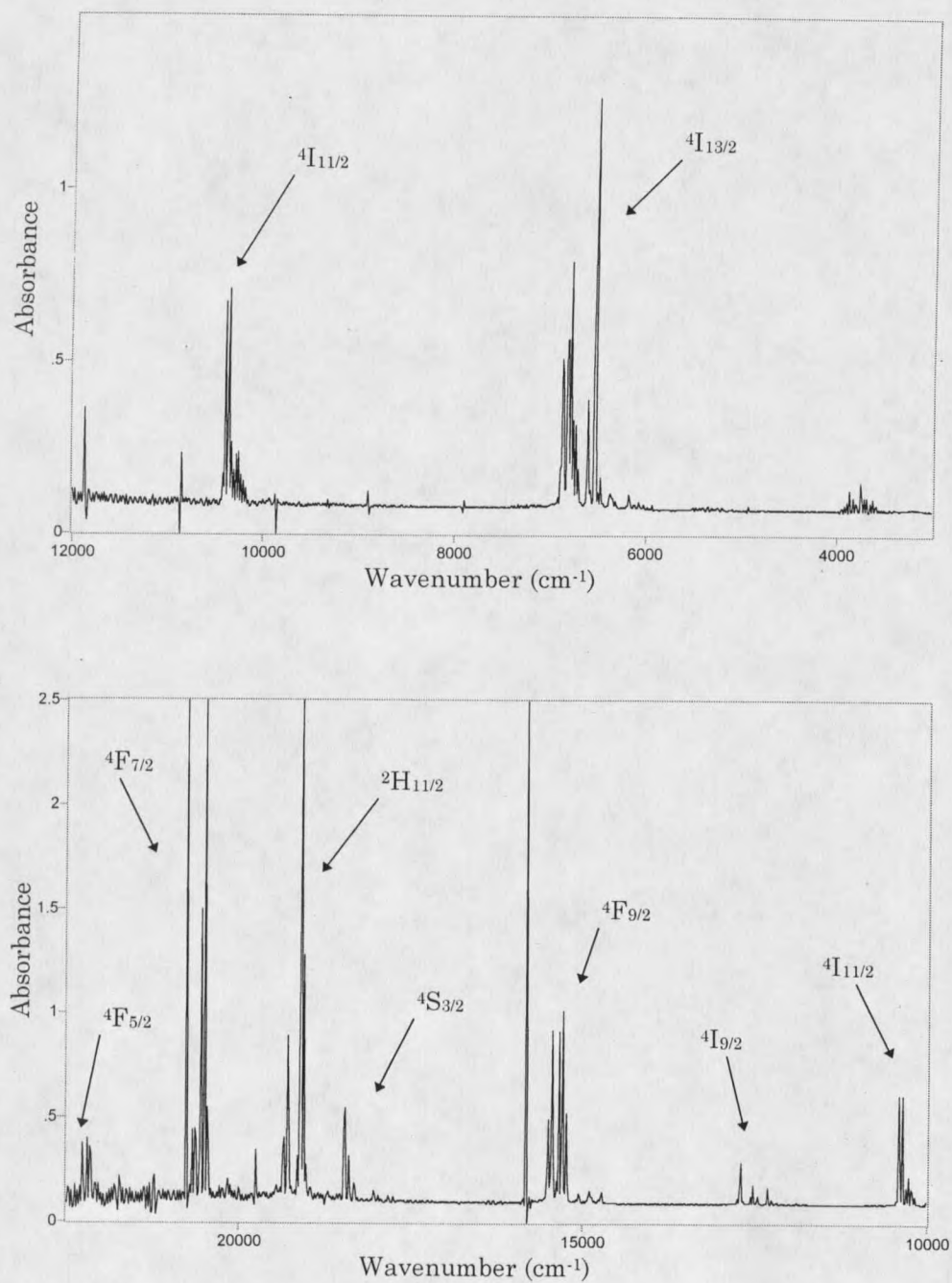


Figure 7. IR (top) and Visible Absorption Spectra of Er:YAG.

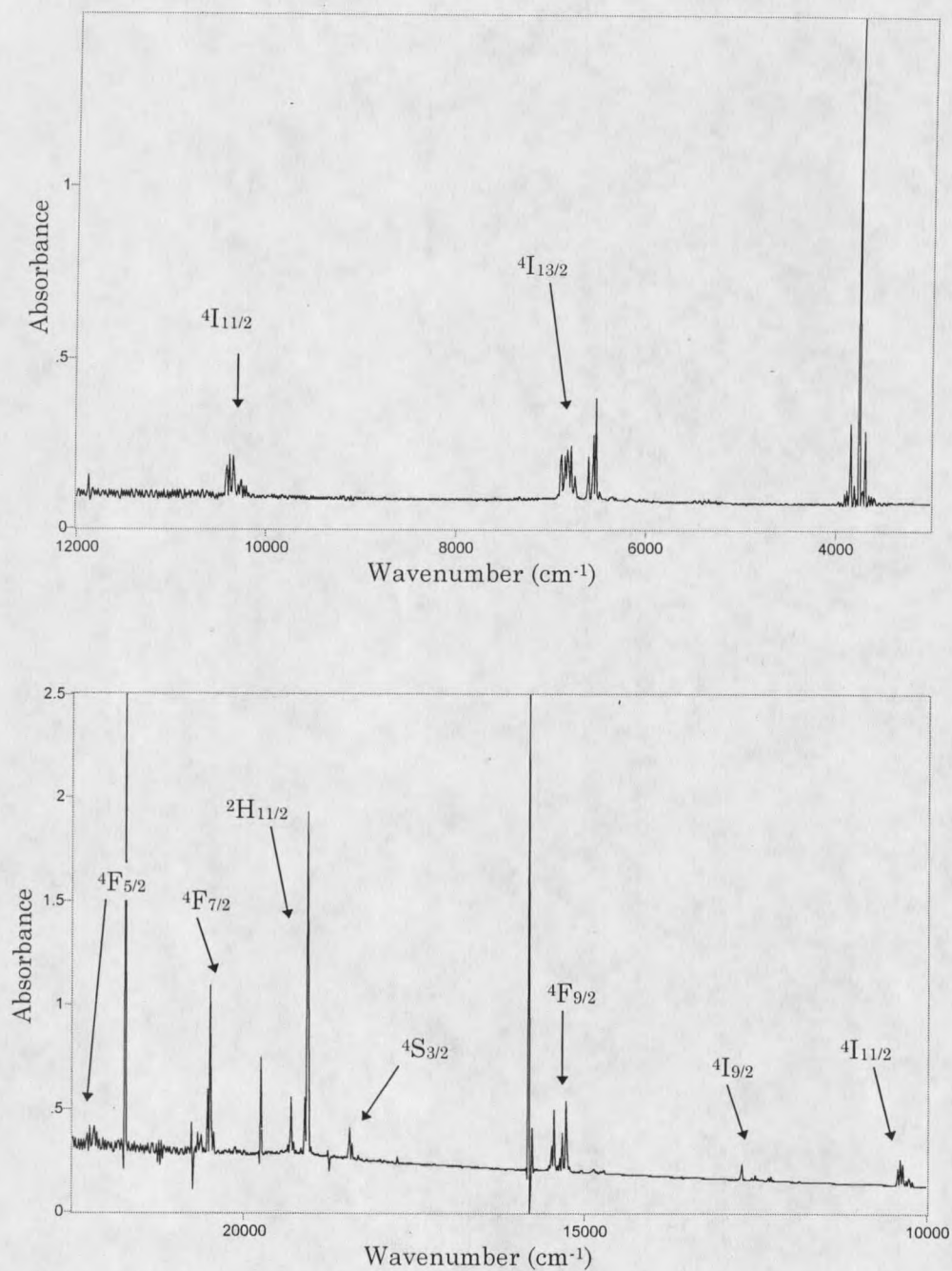


Figure 8. IR (top) and Visible Absorption Spectra of Er:LuAG.

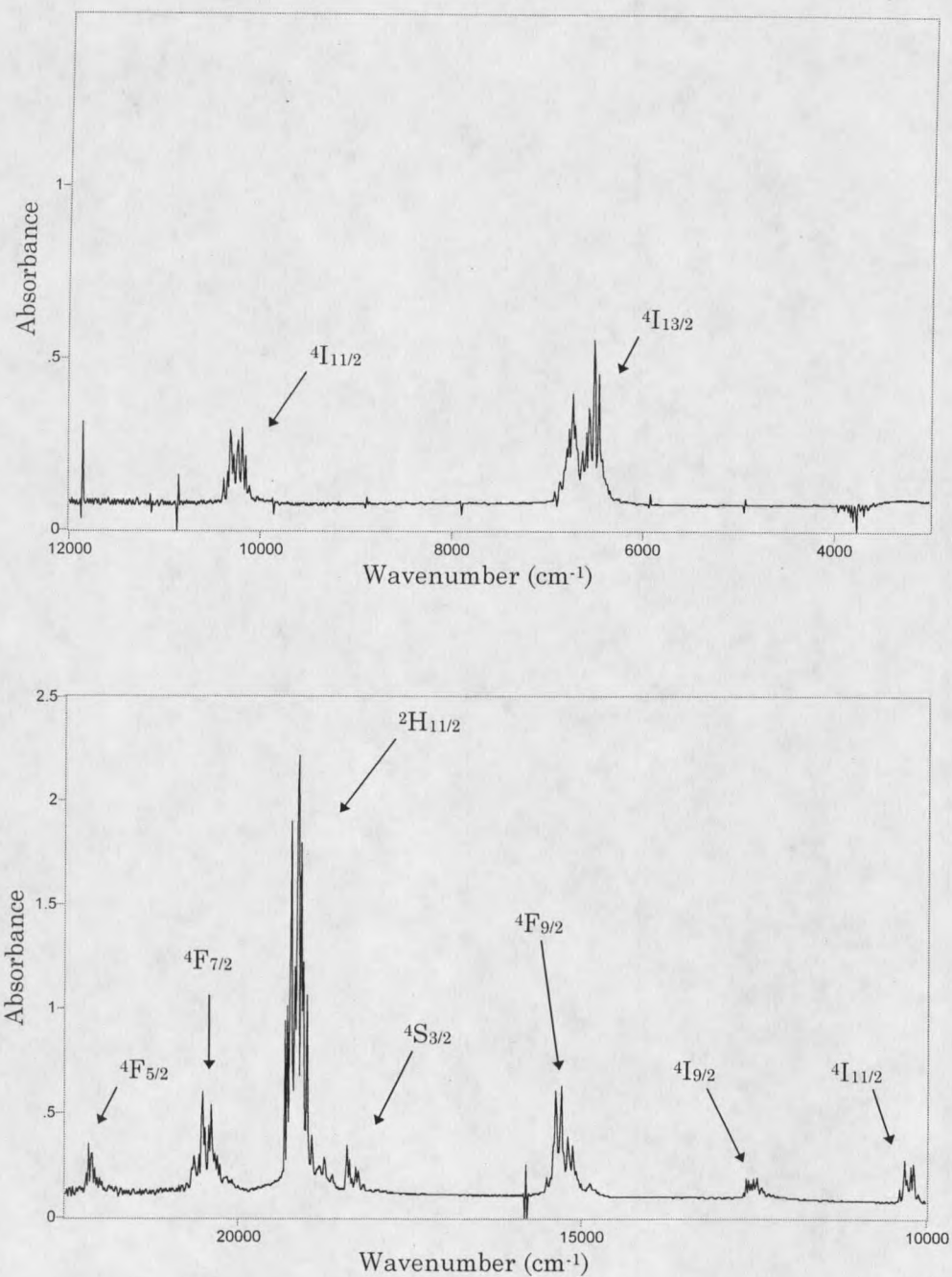


Figure 9. Unoriented IR (top) and Visible Absorption Spectra of Er:YSO.

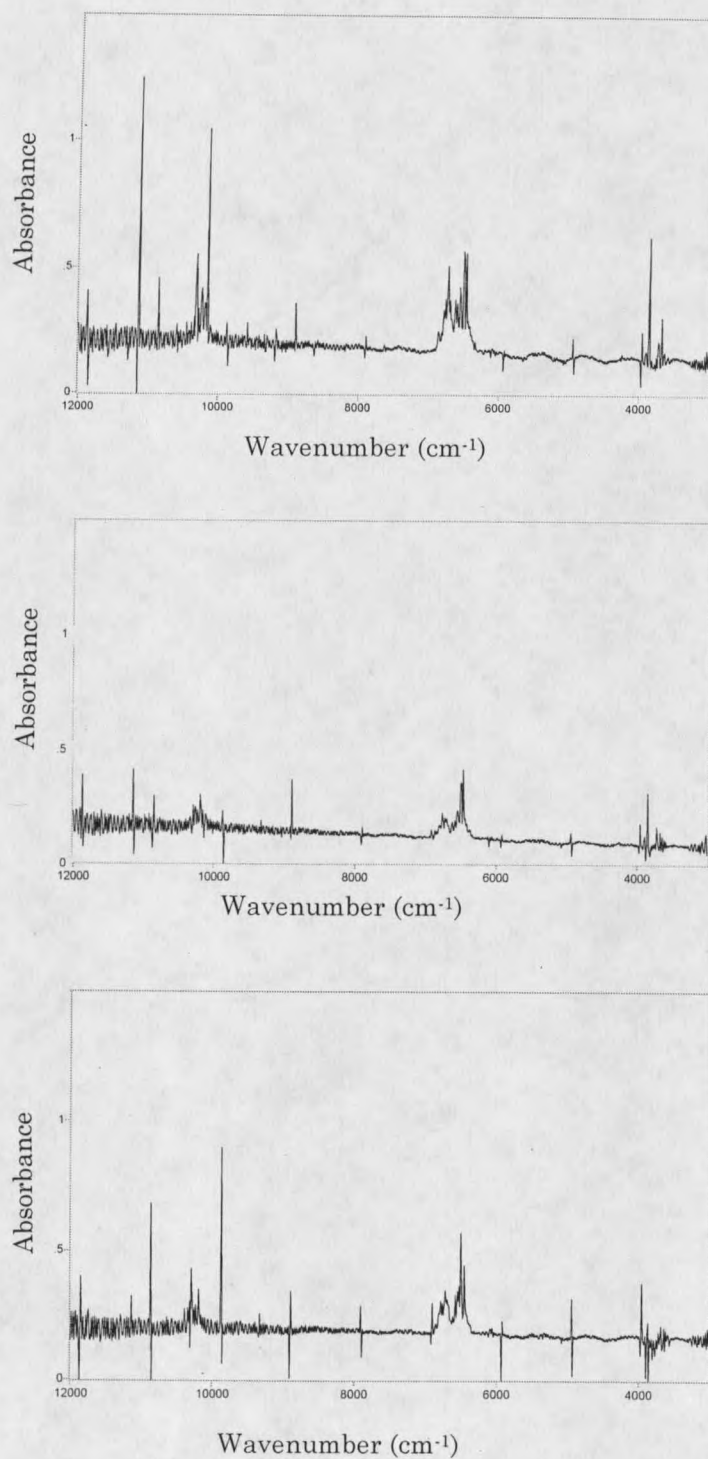


Figure 10. IR Absorption Spectra of Er:YSO for Light Polarized Parallel to the $\langle 010 \rangle$, D_1 , and D_2 Directions.

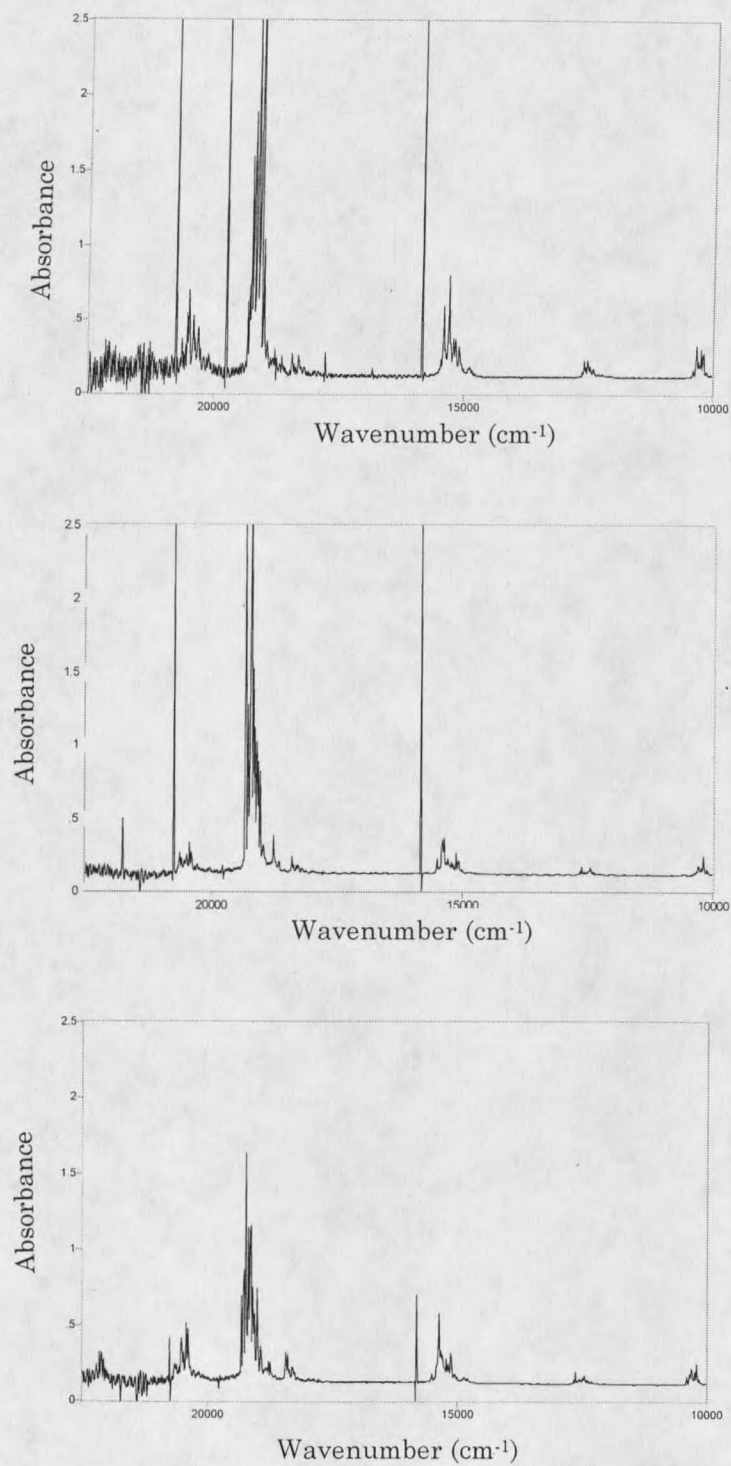


Figure 11. Visible Absorption Spectra of Er:YSO for Light Polarized Parallel to the $\langle 010 \rangle$, D_1 , and D_2 Directions.

and 11 as in Figure 9. The band just under 4000 cm^{-1} in the IR spectra is a water absorption band resulting from imperfect background correction. The sharp spikes occurring at regular wavenumber intervals (especially noticeable in Figure 10) are noise caused by interference from AC power supplies in the laboratory.

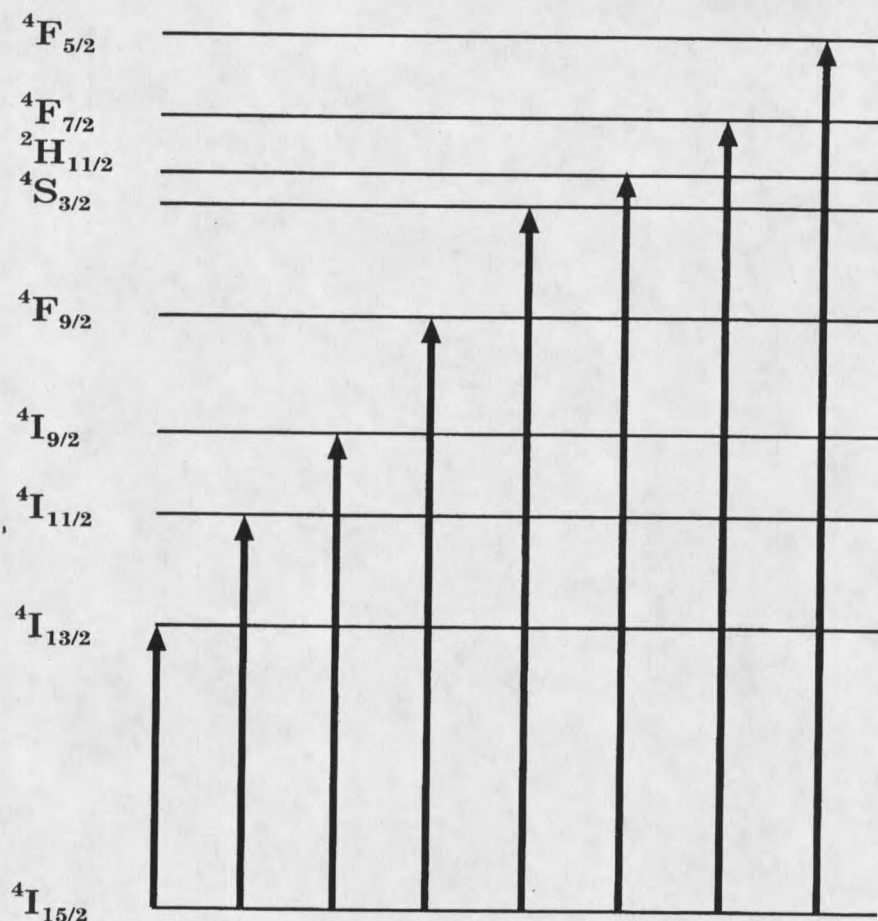


Figure 12. Absorption Transitions Observed in Figures 7-11.

Comparison of Figures 7, 8 and 9 (IR spectra of Er:YAG, Er:LuAG, and Er:YSO respectively) shows the effect of the host crystal field on the erbium

energy level structure. Examination of the spectra shows that, in general, the Er:YSO bands are about 100 cm^{-1} lower in energy than the corresponding bands in the Er:YAG and Er:LuAG spectra. More notably, for any of the transitions labeled 1 through 8 on Figure 12, the absorption bandshapes for Er:YSO are quite different than those of the erbium doped garnets. These differences are due to the crystal fields of the hosts splitting the erbium free ion levels differently, yielding a different Stark level structure in the three host materials. Since the crystal fields of the two garnet hosts are much more similar to each other than they are to YSO, the differences in the absorption spectra of Er:YAG and Er:LuAG are much more subtle.

Absorption spectra (4,6,26,34,35,37,38,46) and studies in which individual Stark levels are identified (26,37) have been performed previously in Er:YAG. Good overall agreement was seen between the measurements taken in this study and room temperature measurements in the literature (4,6,35,38). Both bandshapes and absorption band frequencies were in good general agreement. Similarly, good overall agreement was noted between the Er:LuAG absorption spectra from this study and literature data (9). Comparison of the Er:YAG and Er:LuAG spectra with data obtained in the individual energy level cold temperature studies (4,9,26,37) shows some deviations which are expected between spectra taken at room temperature and liquid helium or nitrogen temperature. First, the room temperature spectra were more congested with features. Secondly, each manifold in my

room temperature data is broadened 60 - 100 cm^{-1} over the corresponding band in the 4K data. In each case, the broadening was toward the low frequency side of the bands. This was expected since population of the upper Stark levels of the ground state $^4I_{15/2}$ manifold leads to more absorption pathways to each upper state manifold, broadening the absorption bands. The resulting new absorption pathways are lower in frequency, since they are initiated from upper Stark levels of the ground state manifold.

Analogously, good agreement was seen the orientationally resolved absorption spectra of Er:YSO (Figures 10 and 11) in this study and the room temperature data in the literature (34,36,39,40). Similar broadening of the room temperature Er:YSO spectra relative to cold temperature spectra in the literature (39) was observed. Table 3 at the end of this chapter lists individual absorption peak frequencies for the three materials studied. The peak frequencies correspond to absorptions between individual Stark levels and show reasonable agreement with those encountered in the literature. (1,4,9,26,37,39,46).

Continuous Emission

Fluorescence spectra have been obtained for Er:YSO (39), Er:YAG (4,16,37,38,46), and Er:LuAG (9) at a variety of erbium concentrations. The spectra obtained in this study were consistent with the literature

measurements. The Er:YSO emission spectra obtained in this study were not orientationally resolved along the three polarization directions. As would be expected, comparison of the polarized emission spectra of Er:YSO in the literature (39) with data obtained in this study shows features resulting from all three polarizations are present in my data.

In this study, the 488 nm line from one of two Ar-ion lasers (see Chapter 2) provided continuous excitation of erbium in both YAG and YSO to the $^4F_{7/2}$ manifold. Additionally, the Ar-ion was used to pump a cw dye laser, which, when using the laser dye DCM, provided cw excitation to the $^4F_{9/2}$ manifold. Figure 13 contains energy level diagrams illustrating the emission transitions observed after $^4F_{9/2}$ and $^4F_{7/2}$ excitation, respectively. Nonradiative relaxations are not indicated in the energy level diagrams. Continuous emission data was not obtained for Er:LuAG, though numerous temporally resolved emission spectra were obtained for this material (discussed in the next section). Visible and IR emission spectra were obtained at the same spectral ranges and using the same beamsplitters and detectors as the absorption spectra. The number of scans used for signal averaging ranged from 64 to 2000, and resolutions of either 8 or 16 cm^{-1} were obtained at room temperature. In order to compare the strength of different emission transitions in the same spectrum, it was necessary to correct for instrument response. This was accomplished by recording a response curve

using a tungsten lamp, then eliminating the lamp contribution by dividing a calculated intensity versus frequency curve for a blackbody at 3500 K.

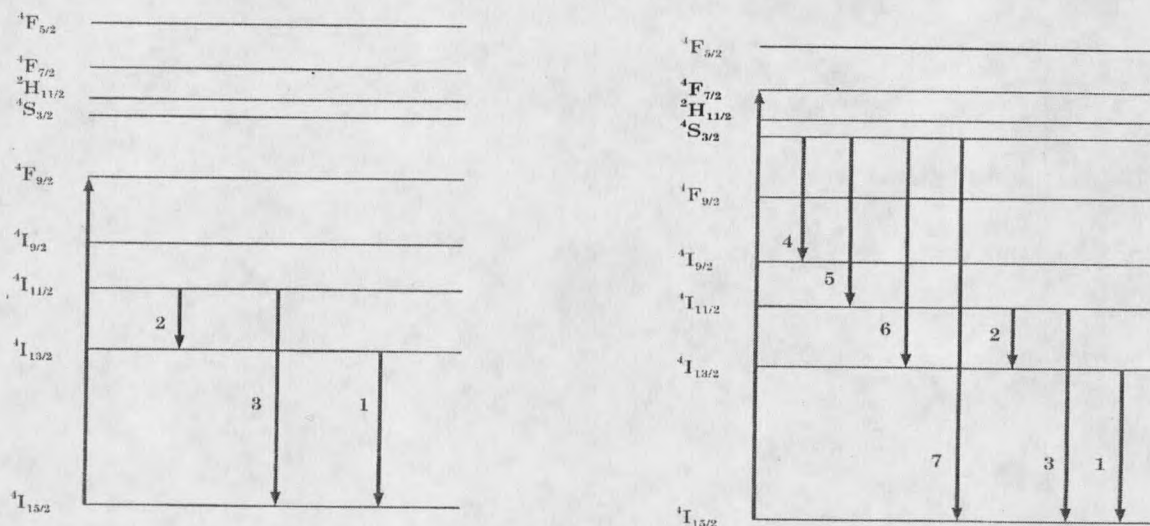


Figure 13. Radiative Emission Transitions Observed for $4F_{9/2}$ and $4F_{7/2}$ Excitation.

IR Emission

Figure 14 is a fluorescence spectrum of 4% Er:YAG, pumped to the $4F_{9/2}$ manifold by 15446 cm^{-1} dye laser output. Assignments of the emission bands are shown on the spectra. In the bottom view, the y-axis (intensity) is scaled to enable a closer look at the two weaker transitions. The same transitions were observed in the emission spectrum of 2.1% Er:YAG. Figure 15 contains a similar spectrum of 2% Er:YSO, which was excited at a slightly lower frequency (15376 cm^{-1}) due to the different Stark level splitting of the YSO host. The transitions initiated from the $4I_{11/2}$ manifold are not seen due

to the lower signal to noise ratio in this experiment. The different host

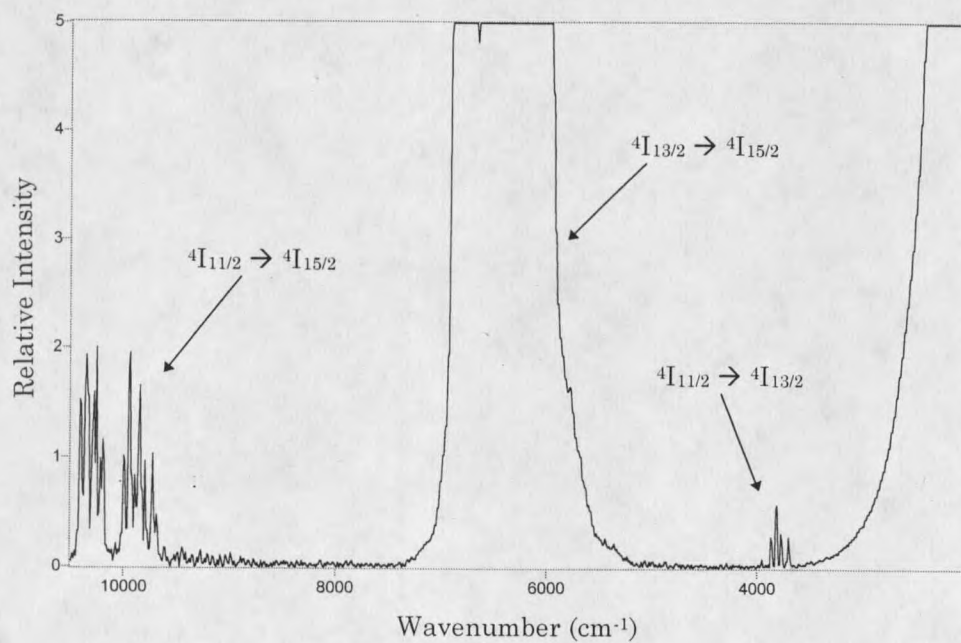
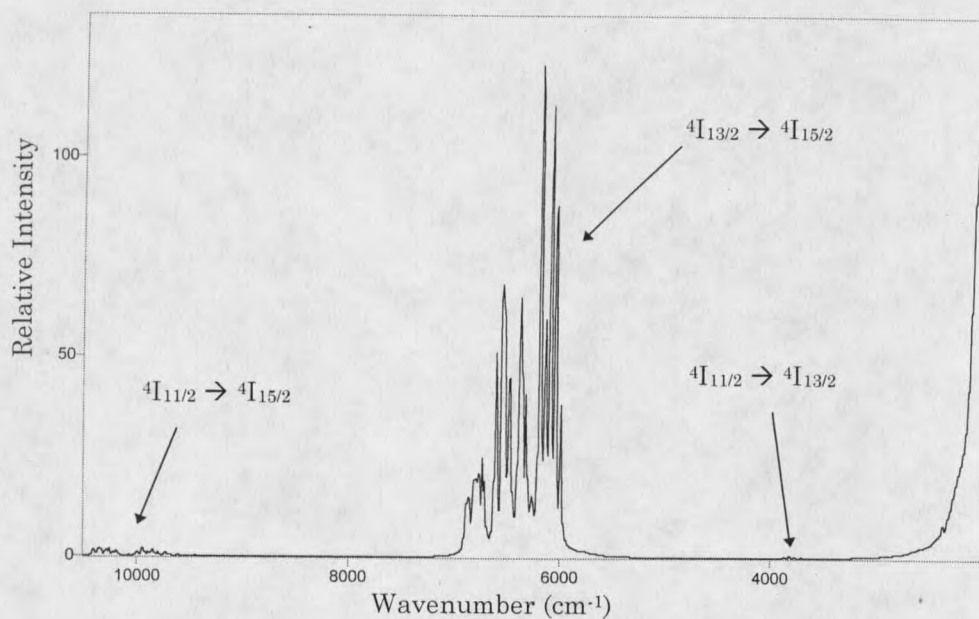


Figure 14. IR Emission Spectrum of Er:YAG Pumped to the $4F_{9/2}$ Manifold.

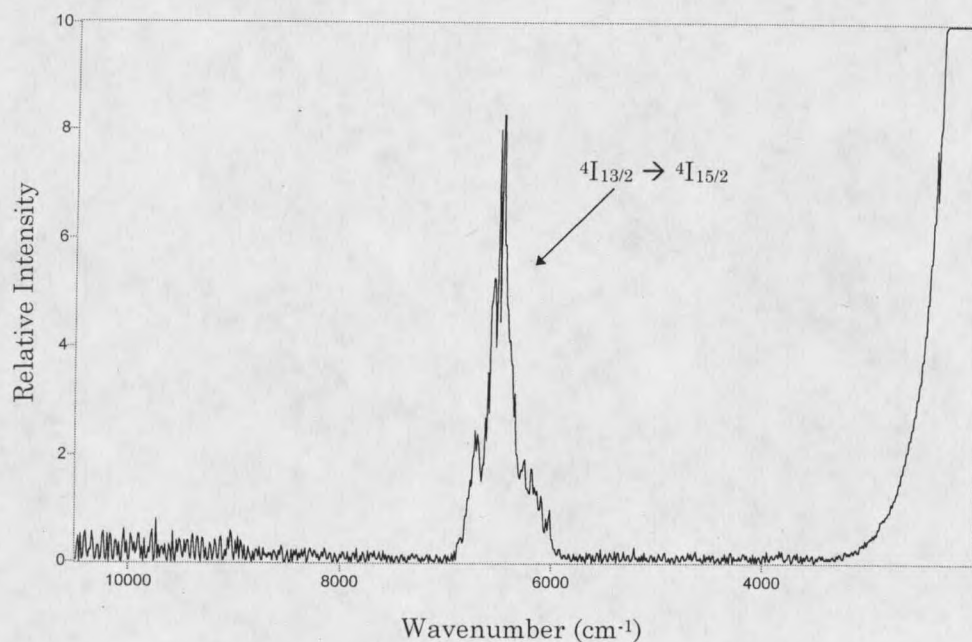


Figure 15. IR Emission Spectrum of Er:YSO pumped to the ${}^4F_{9/2}$ Manifold.

effects also exhibit themselves in the emission spectra. The Er:YSO ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission band does not exhibit the sharp lines seen in the Er:YAG samples. This trend generally holds for the other emission bands throughout the infrared and visible regions examined in this study. The apparent sharp rise in intensity below about 2800 cm^{-1} is not real emission, but results from imperfect correction for the instrument response curve, thereby representing the lower useful frequency limit for the emission spectra.

Figure 16 contains an emission spectrum of 4% Er:YAG excited to the ${}^4F_{7/2}$ manifold using the 488 nm Ar-ion line. The top and bottom parts of the figure are simply the same spectrum, with the y-axis scaled differently to

allow examination of all the emission bands. Figure 17 features a similar treatment of 2% Er:YSO. Examination of Figures 14 and 16 reveals that $^4F_{7/2}$ excitation results in an emission transition that is not there under $^4F_{9/2}$ excitation. This transition, from the $^4S_{3/2}$ to the $^4I_{11/2}$ manifold, occurs at around 8000 cm^{-1} . The analogous emission transitions take place in Er:YSO, and are seen in Figure 17.

Visible Emission

Figure 18 shows visible emission spectra of 4% Er:YAG and 2% Er:YSO, respectively. The transition around 10000 cm^{-1} is the same $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition seen in the IR emission spectra. The strong green emission at approximately 18000 cm^{-1} is the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition, and the very weak band at 15000 cm^{-1} is the $^4F_{9/2} \rightarrow ^4I_{15/2}$ emission. The large spike seen just above 20000 cm^{-1} in both spectra is scattered 488 Ar-ion laser light. The lower signal-to-noise ratio above 22000 cm^{-1} is due to decreased instrument response (see Figure 2).

Temporally Resolved Emission

The temporally resolved emission measurements presented in this section were obtained using the experimental setup described in Chapter 2. The Infinity/OPO system provided nanosecond excitation pulses for all the

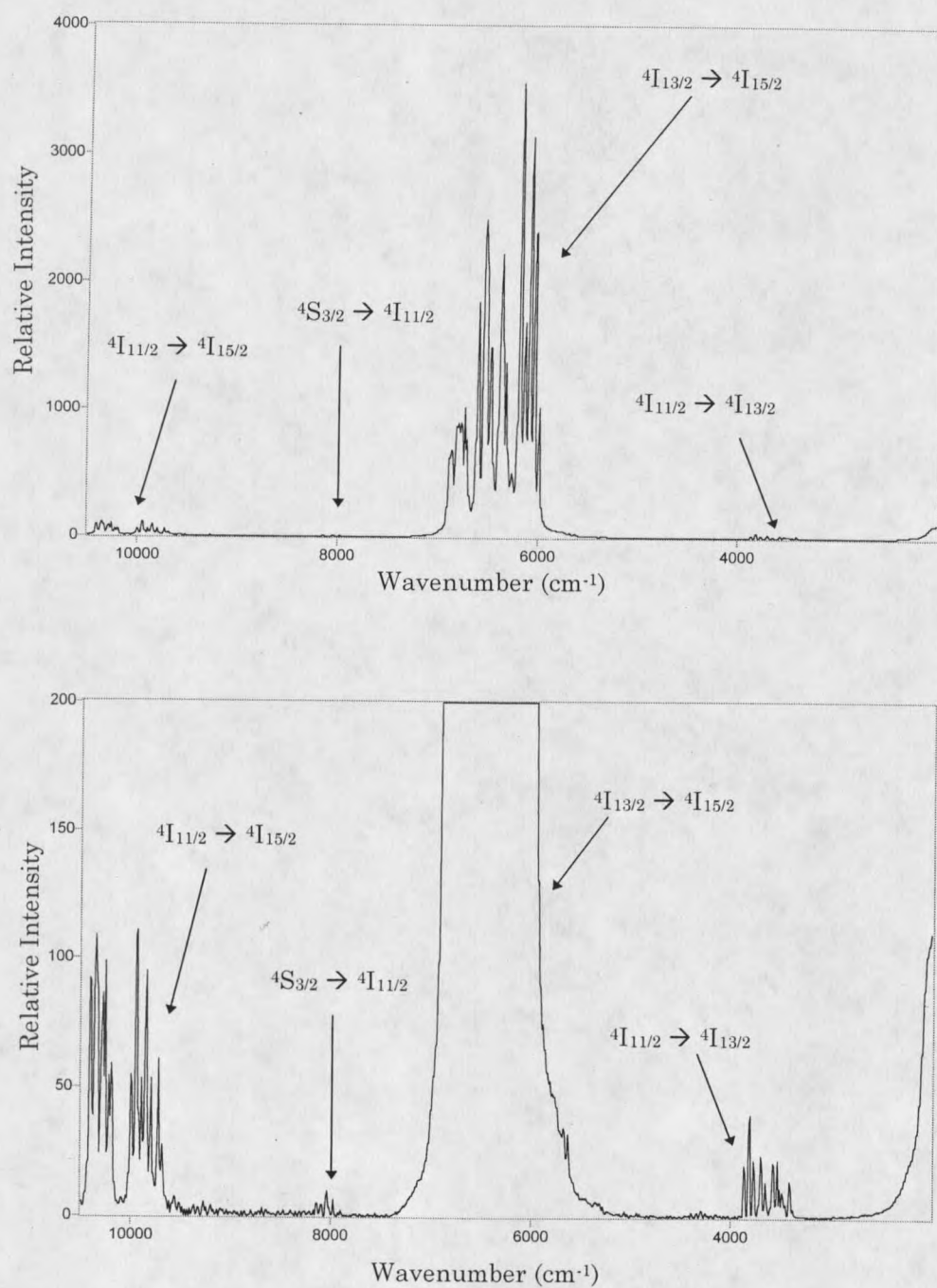


Figure 16. IR Emission Spectrum of Er:YAG Pumped to the $4F_{7/2}$ Manifold.

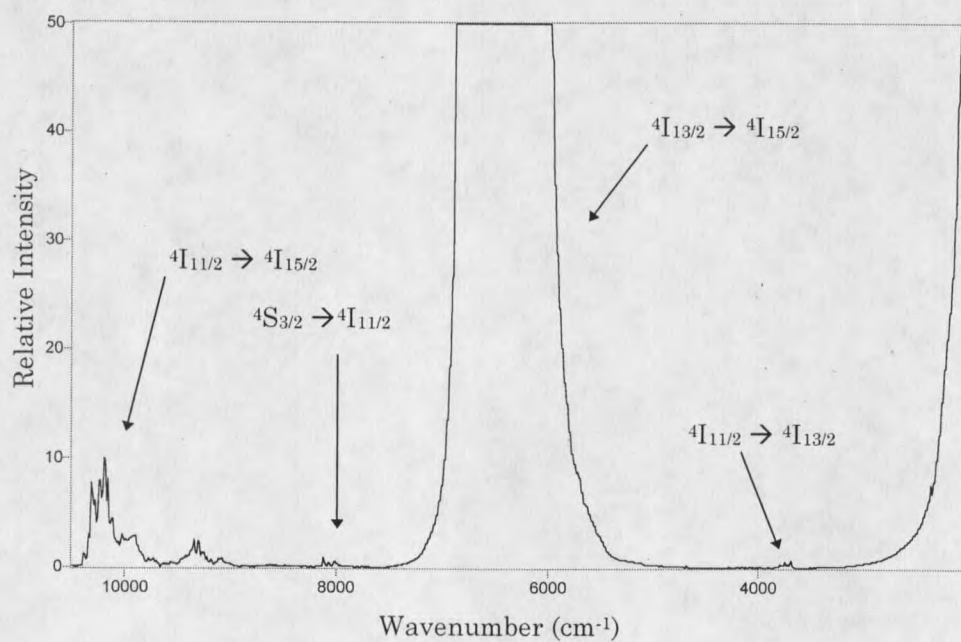
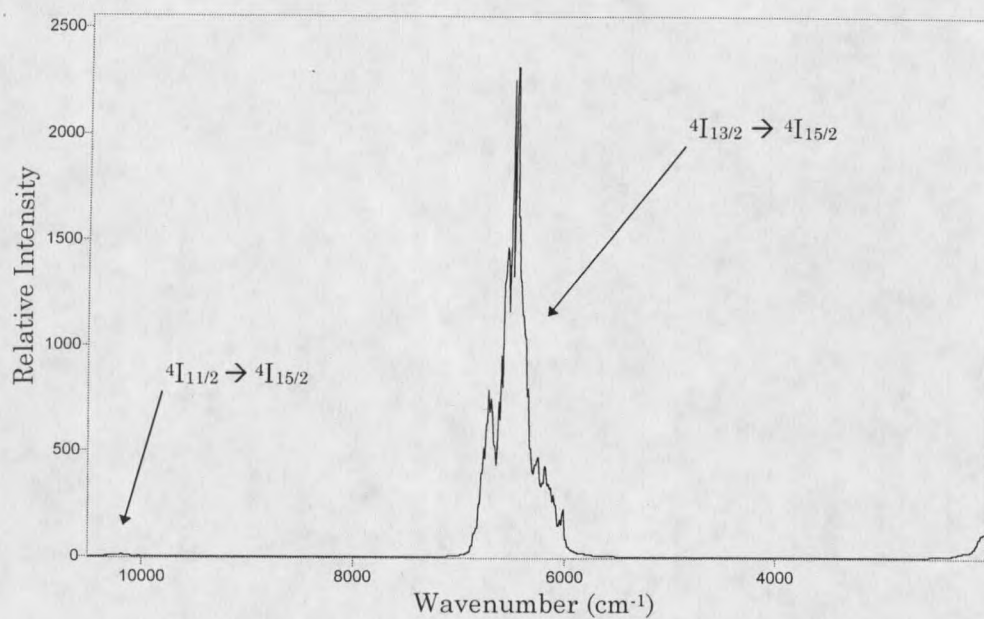


Figure 17. IR Emission Spectrum of Er:YSO Pumped to the $4F_{7/2}$ Manifold.

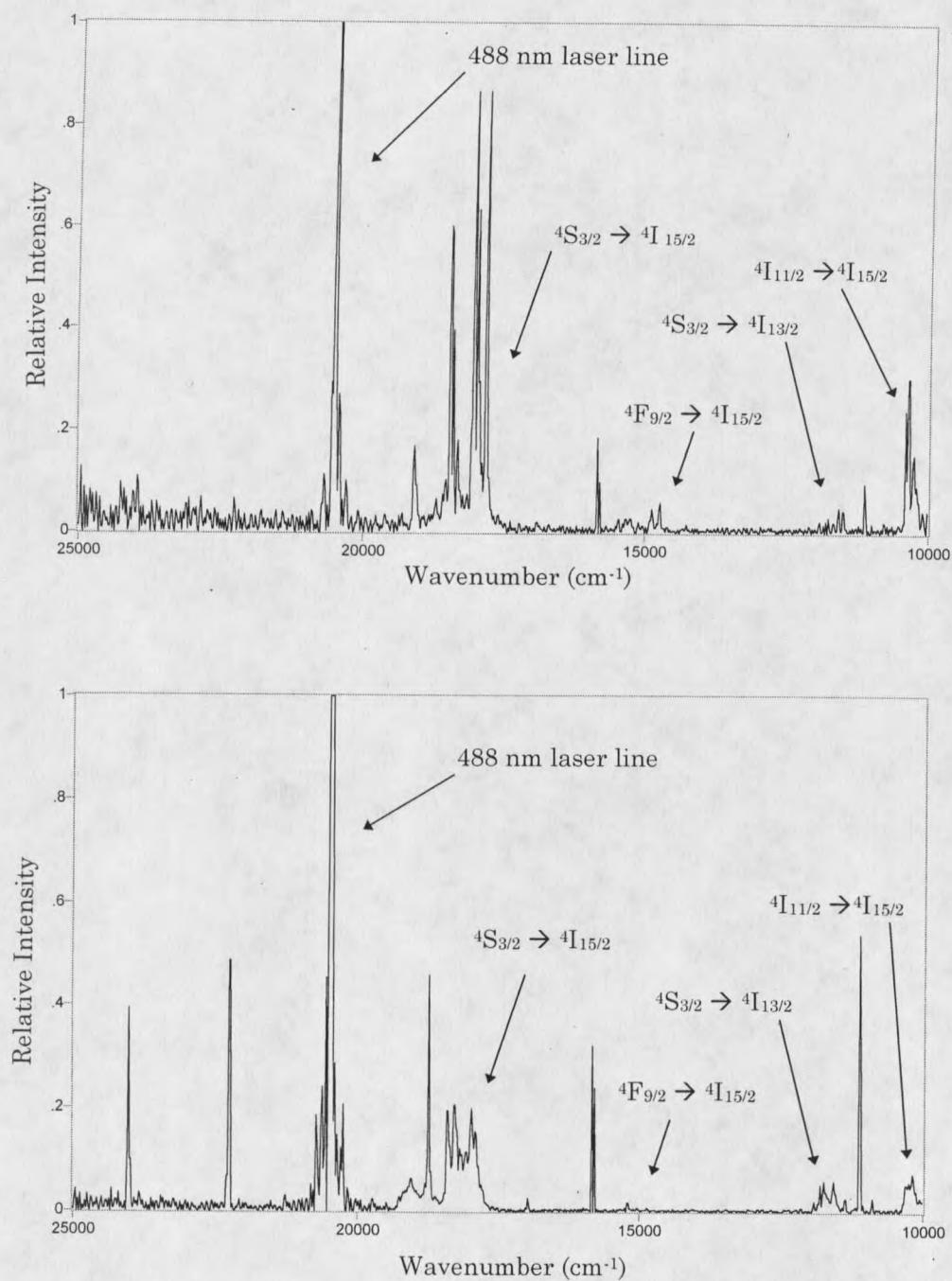


Figure 18. Visible Emission Spectra of Er:YAG (top) and Er:YSO Pumped to the $^4F_{7/2}$ Manifold.

measurements presented in this section. The spectral resolution was 16 cm^{-1} for most experiments. Unless otherwise noted, the excitation repetition rate was set at 15 Hz, which provided an interval of 66.67 ms between pulses. This repetition rate was used to allow nearly complete relaxation and corresponds to at least five exponential lifetimes for the slowest emission ($^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$) decay. Infrared time-resolved emission was collected after excitation to each of the first eight excited state manifolds of erbium ($^4\text{I}_{13/2}$ through $^4\text{F}_{5/2}$). These excitation manifolds can be seen in Figure 12.

In the following paragraphs, results which are common to all the erbium materials studied will be presented. Where applicable, examples to illustrate these results will be provided using Er:YSO emission spectra since the time resolved spectra collected for this material showed the best overall signal-to-noise. The spectra shown in this section have not been corrected for instrument response.

Selective excitation at different pump wavelengths allowed observation of the "turning on and off" of emission bands, helping to confirm the originating manifold of the emission transitions. When pumped to the $^4\text{I}_{13/2}$ manifold, the resulting emission spectrum (Figure 19) contains only one transition, from the $^4\text{I}_{13/2}$ directly back to the ground state manifold. The emission occurs on the millisecond time scale at around 6500 cm^{-1} . Each spectral "time slice" shown in Figure 19 is at a 250 microsecond interval.

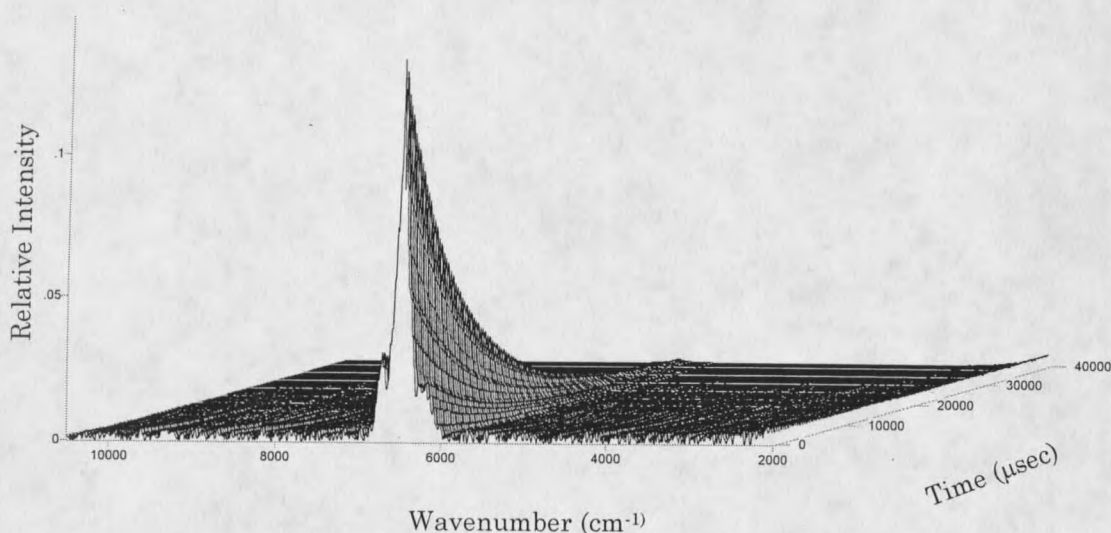


Figure 19. Temporally Resolved Emission of Er:YSO Following Excitation to the $^4I_{13/2}$ Manifold.

Excitation to any of the next three higher manifolds ($^4I_{11/2}$, $^4I_{9/2}$, or $^4F_{9/2}$) yields two additional emission transitions, originating from the $^4I_{11/2}$ manifold and terminating in the $^4I_{13/2}$ and $^4I_{15/2}$ manifolds, resulting in an emission spectrum as seen in Figure 20. These two new emissions decay on a considerably faster time scale than the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition shown in the previous spectrum. The $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition is still present at 6500 cm^{-1} , but is still rising in intensity on the faster time scale of Figure 20, where each time slice is five microseconds. The fact that the two new emissions decay on the same time scale indicates that their emitting levels are depopulated on the same time scale, so they almost certainly originate from the same manifold. This illustrates one benefit of the temporally resolved method, that it helps in assignment of the emission transitions.

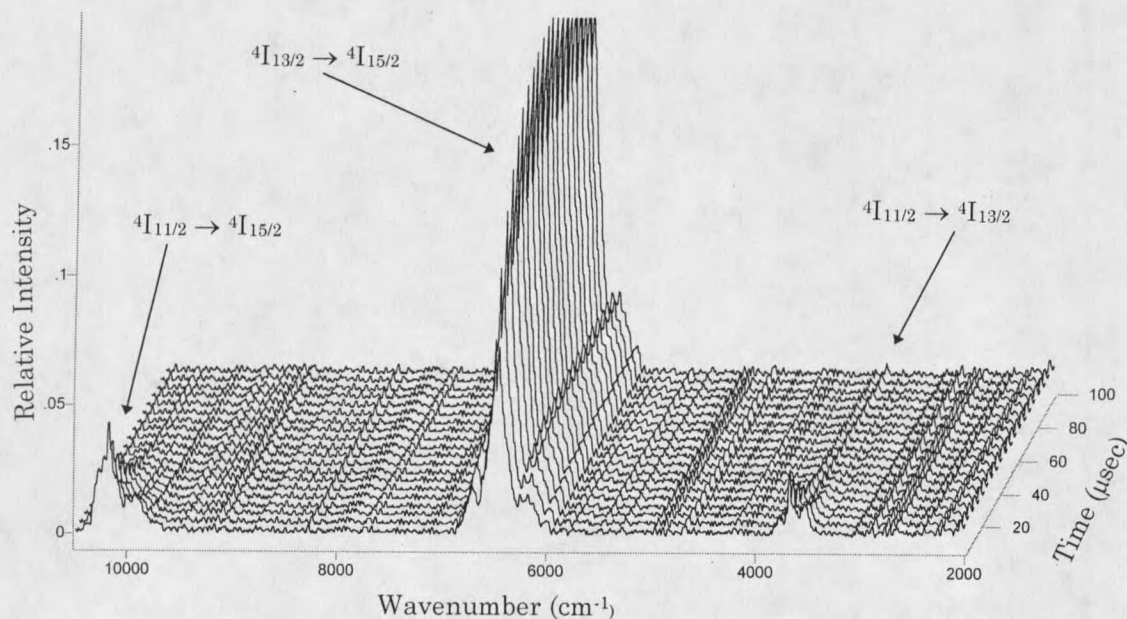


Figure 20. Temporally Resolved Emission of Er:YSO Following Excitation to the $^4I_{11/2}$ Manifold.

Pumping at or above the $^4S_{3/2}$ manifold yields three additional emission bands, as can be seen in Figure 21. These three bands also occur on the microsecond time scale, but decay even faster than the emissions from the $^4I_{11/2}$ manifold. These three bands, occurring at roughly 5800, 8000, and 11500 cm^{-1} , originate from the $^4S_{3/2}$ manifold and terminate in the $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ manifolds, respectively. Additionally, an emission band at approximately 18000 cm^{-1} ($^4S_{3/2} \rightarrow ^4I_{15/2}$, Figure 13) can be seen in the visible spectrum. Figure 21 illustrates another benefit of the temporally resolved emission method. In a time resolved experiment with temporal resolution of 5 microseconds or higher, the $^4S_{3/2} \rightarrow ^4I_{9/2}$ transition will be detected at 5800

cm^{-1} . However, in continuous spectra such as Figure 17, this emission band is hidden by the strong, long-lived ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ band. The time resolved technique enables deconvolution of emission bands that overlap spectrally but have different temporal behavior.

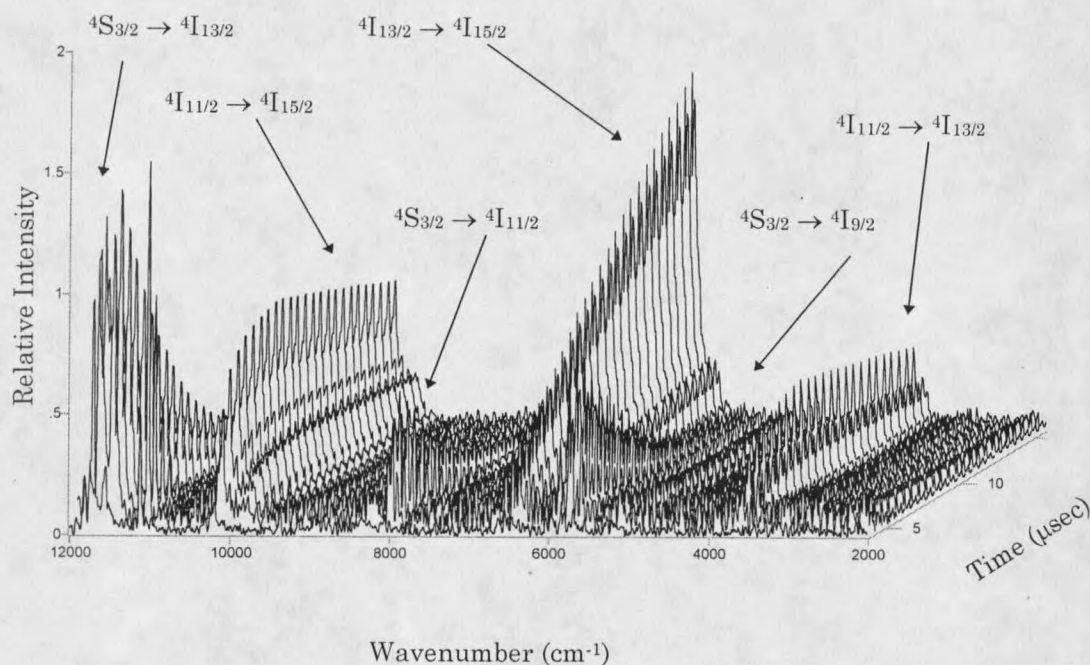


Figure 21. Temporally Resolved Emission of Er:YSO Following Excitation to the ${}^4\text{F}_{7/2}$ Manifold. The collected data set includes time from 0-130 μsec , but the data is truncated for visual clarity.

The weak emission from the ${}^4\text{F}_{9/2}$ manifold to the ground state was not observed in the time resolved spectra due to its short lifetime and low signal-to-noise ratio. In the following sections, specific results for the three materials studied are presented.

Er:YSO

The 2% Er:YSO sample was excited at the various frequencies as listed in Table 1. At each excitation frequency, experiments were run at the necessary temporal resolutions and sampling times to capture the temporal behavior of all the emission bands that occurred for a particular excitation.

Table 1. Excitation Frequencies for 2% Er:YSO.

Pump Manifold	Excitation Frequency (cm ⁻¹)
⁴ I _{13/2}	6508
⁴ I _{11/2}	10195
⁴ I _{9/2}	12606
⁴ F _{9/2}	15376
⁴ S _{3/2}	18409
² H _{11/2}	19223
⁴ F _{7/2}	20494
⁴ F _{5/2}	22095

Although there are two different Er³⁺ sites in Er:YSO, Li, Wyon, and Moncorge (39) have shown that they can be considered together in the analysis of fluorescence dynamics, since excitation of the two different sites to different degrees resulted in the same emission lineshapes (see pg. 14). Therefore, polarized temporally resolved emission spectra were not obtained in this study. In the following paragraphs, results for each of the emission transitions when pumped at the different levels will be presented.

The ⁴I_{13/2}→⁴I_{15/2} emission was detected at all pump levels. Experiments run to characterize this transition had temporal resolution of 250 μsec, and data was obtained for 66.5 msec, nearly the entire time

between laser pulses given the 15 Hz repetition rate. Signal averaging was five or ten coadditions, meaning five or ten decay events were averaged at each mirror position. Figure 22 contains two plots: a "decay trace", in which the integrated area under the transition (corrected for baseline noise) for a time slice is plotted versus time, and a "log plot", in which the logarithm of the integrated transition area is plotted instead. The integration and baseline correction methods are discussed in detail in Chapter 4. In the plots shown, most of the decay traces have been normalized to a maximum intensity value of one to facilitate comparison between different spectra. The data shown in Figure 22 were obtained by after excitation directly into the $^4I_{13/2}$ manifold. Though valuable information concerning relaxation processes can be obtained by pumping above the upper emitting level, it is best to excite the emitting level directly when determining lifetimes to prevent emission level feeding processes from influencing lifetime measurement. The straight line of the log plot shows that the decay is exponential. An exponential fit of the decay data results in an experimentally determined lifetime of 8.6 msec (experimental lifetimes for all the materials studied are summarized in Table 4 at the end of this chapter). The data in this plot are truncated after the signal has gone below the noise level.

Two emissions originating from the $^4I_{11/2}$ level appear in spectra where the $^4I_{11/2}$ manifold or higher is pumped, terminating at $^4I_{13/2}$ (emission band at approximately 3500 cm^{-1}) and $^4I_{15/2}$ (approximately 10000 cm^{-1}). Emission

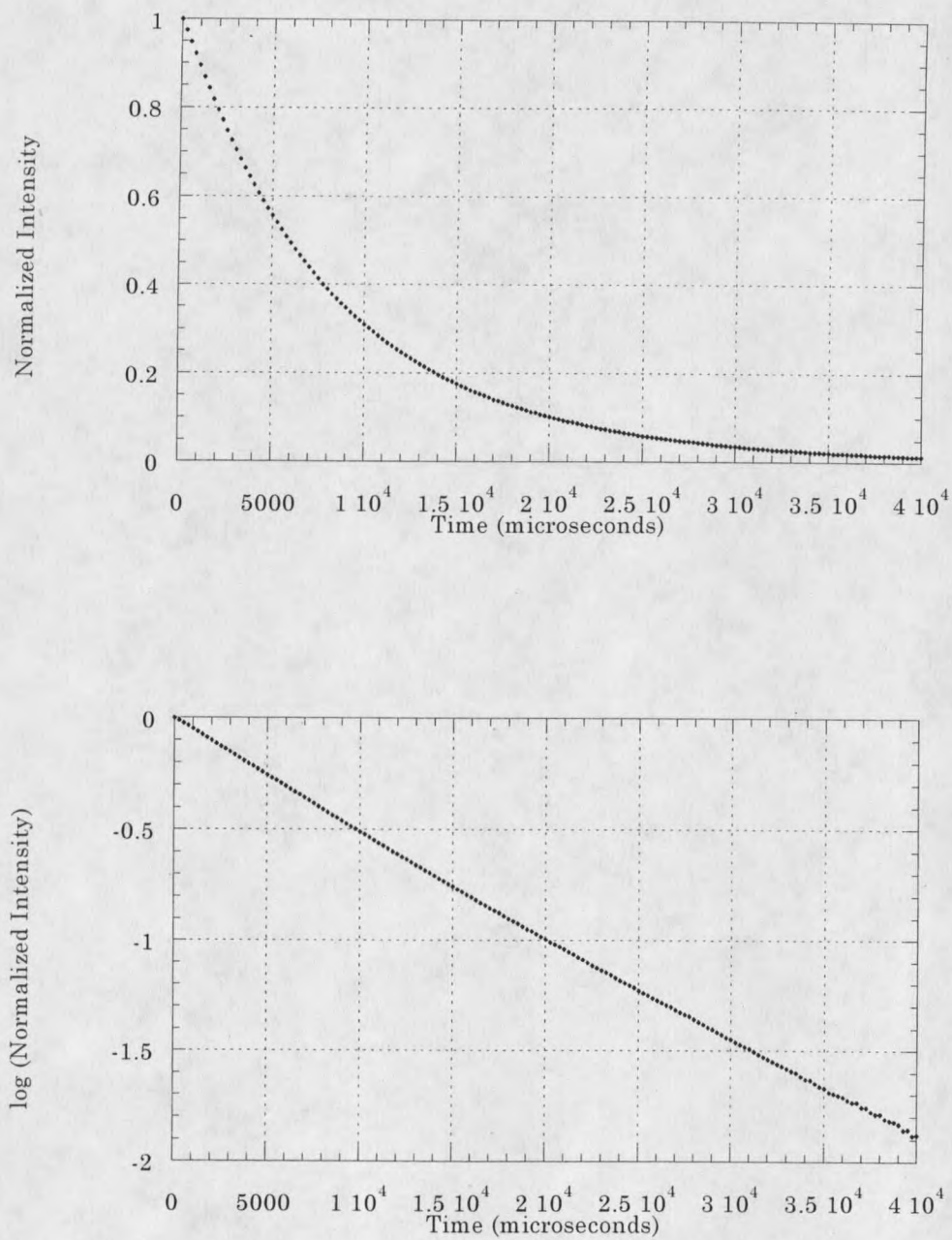


Figure 22. Decay (top) and Log of Intensity for the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ Transition in 2% Er:YSO.

from the $^4I_{11/2}$ manifold has a significantly shorter lifetime than that originating from $^4I_{13/2}$, and the experiments designed to analyze these emission bands were temporally resolved to 500 nanoseconds and had total sampling times of 120-150 microseconds. Since this higher temporal resolution required the use of a faster, 8-bit transient recorder rather than the 16-bit recorder used for the slower experiments, lower signal-to-noise resulted, necessitating more coadditions (20 to 80 for the various pump levels) for signal averaging. Figure 23 illustrates decay traces for the two emission bands. The maximum intensity for both bands is normalized to one to show the similar behavior of the two bands, which indicates that they originate from the same manifold. Experimentally determined lifetimes for the $^4I_{11/2}$ level of 2% Er:YSO ranged from 10.3 to 12.7 microseconds for all the pump levels analyzed, with values of 10.3 to 10.7 μ s for experiments run with direct $^4I_{11/2}$ excitation. The intensity of the transition terminating in the ground state is significantly higher than terminating in the $^4I_{13/2}$ level. The radiative branching ratio was determined by taking a single time slice from the experiment (an acceptable assumption since the emission bandshapes did not change over time), correcting for instrument response, and integrating the area of each emission band. The resulting branching ratio was found to be 0.91 for the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition and 0.09 for $^4I_{11/2} \rightarrow ^4I_{13/2}$. Branching ratio calculations for all the materials studied are summarized in Table 5 at the end of this chapter.

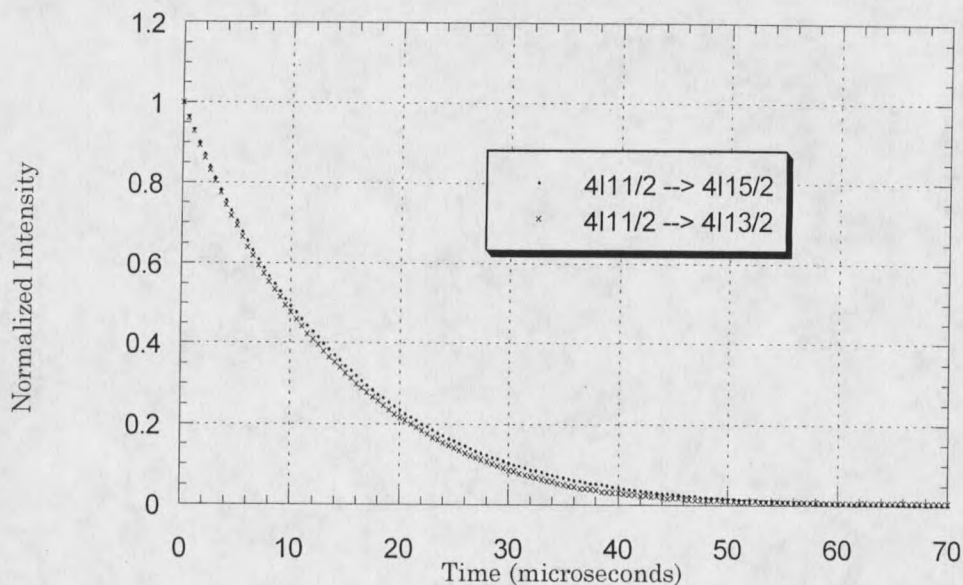


Figure 23. Decay of Emission Transitions Originating from the $4I_{11/2}$ Manifold in 2% Er:YSO.

The log plots of the above emission transitions (Figure 24) illustrate that the decays are primarily exponential. The mild degree of curvature observed in Figure 24 occurred frequently in this study and was found to be error introduced by baseline correction. The reasoning for this is discussed in the next chapter. Data points are truncated after the signal reaches the noise level.

Emission transitions originating from the $4S_{3/2}$ manifold occur when the Er:YSO was subjected to excitation to that level or higher. Spectra obtained for Er:YSO included the four emission bands originating from the

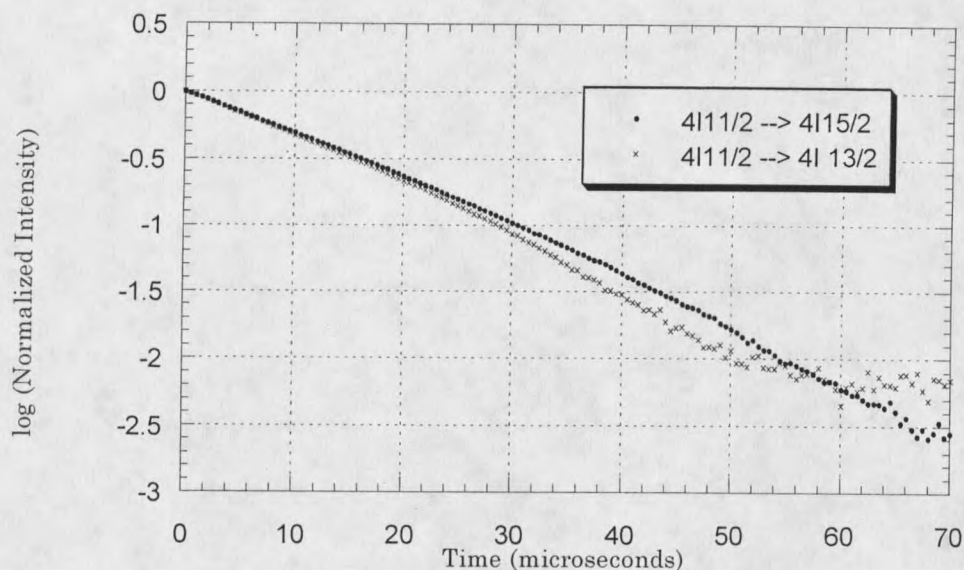


Figure 24. Log of Intensity of Emission Transitions Originating from the $4I_{11/2}$ Manifold in 2% Er:YSO.

$4S_{3/2}$ manifold that were discussed earlier in this section. Emission spectra obtained to study these transitions typically required temporal resolution of 50 nanoseconds with 400 time slices (for a total sampling duration of 20 microseconds) and 20 - 80 coadditions for signal averaging.

The IFS 66 spectrometer cannot perform time resolved experiments on both sides of the HeNe reference frequency (15798 cm^{-1}) simultaneously. The HeNe provides the reference points for where the sampling (data acquisition) is performed. Signal at higher frequencies than the HeNe are undersampled in step scan and would alias if light frequencies on both sides were detected. In continuous scan, a phase

locked loop can interpolate the HeNe curve to allow more frequent sampling which eliminates this problem. In step scan, two laser detectors are used: one to lock on a HeNe zero crossing; the other ($\sim 90^\circ$ out of phase) is used to determine the slope to tell which half wavelength is being locked on. Therefore, the strategy used in continuous scan cannot be used in step scan, and the four emission transitions originating from $^4S_{3/2}$ could not be evaluated in the same experiment. The three lower frequency transitions were observed in spectra obtained over the range of $2000 - 15700 \text{ cm}^{-1}$, and the visible transition (around 18000 cm^{-1}) was obtained in a separate experiment. IR spectra were obtained after excitation to the $^4S_{3/2}$, $^4F_{7/2}$, and $^4F_{5/2}$ levels. Since the silicon diode detector was easily saturated it was very difficult to detect emission transitions in the spectral region close to the excitation source, therefore, we were not able to obtain a time resolved emission spectrum containing the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition after pumping the $^4S_{3/2}$ manifold. However, this transition was observed in temporally resolved spectra after excitation to the $^4F_{7/2}$, and $^4F_{5/2}$ manifolds. Figure 25 shows decay traces of the three IR emission bands following $^4S_{3/2}$ excitation. The $^4S_{3/2} \rightarrow ^4I_{13/2}$ transition has the best signal-to-noise ratio, and an exponential fit based on this transition yields a lifetime of 3.5 microseconds. The $^4S_{3/2} \rightarrow ^4I_{11/2}$ transition is the weakest and the figure illustrates the effect of the lower signal-to-noise on the decay trace. Figure 25 also contains a log plot of the decays. Again, the slight curvature in the log traces is attributable to

baseline correction. Branching ratios were calculated for these radiative transitions based on spectra obtained after $^4F_{7/2}$ excitation, since a visible spectrum was obtained at that excitation level.

Er:YAG

The 4% Er:YAG sample was excited at the frequencies as listed in Table 2. Additionally, emission spectra were obtained from 2.1% Er:YAG following excitation to the $^4F_{9/2}$ manifold. The same emission transitions were observed for the same pump manifolds as in Er:YSO. Results for the fluorescence decays for the $^4I_{13/2}$, $^4I_{11/2}$, and $^4S_{3/2}$ levels are discussed in the following paragraphs.

The $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission occurred on a similar time scale in Er:YSO and Er:YAG, and experiments run to evaluate this transition were set up with similar temporal resolution, sampling duration, and number of coadditions. Figure 26 shows the integrated results of the transition after

Table 2. Excitation Frequencies for 4% Er:YAG.

Pump Manifold	Excitation Frequency (cm ⁻¹)
$^4I_{13/2}$	6797
$^4I_{11/2}$	10347
$^4F_{9/2}$	15445
$^4S_{3/2}$	18797
$^4F_{7/2}$	20494

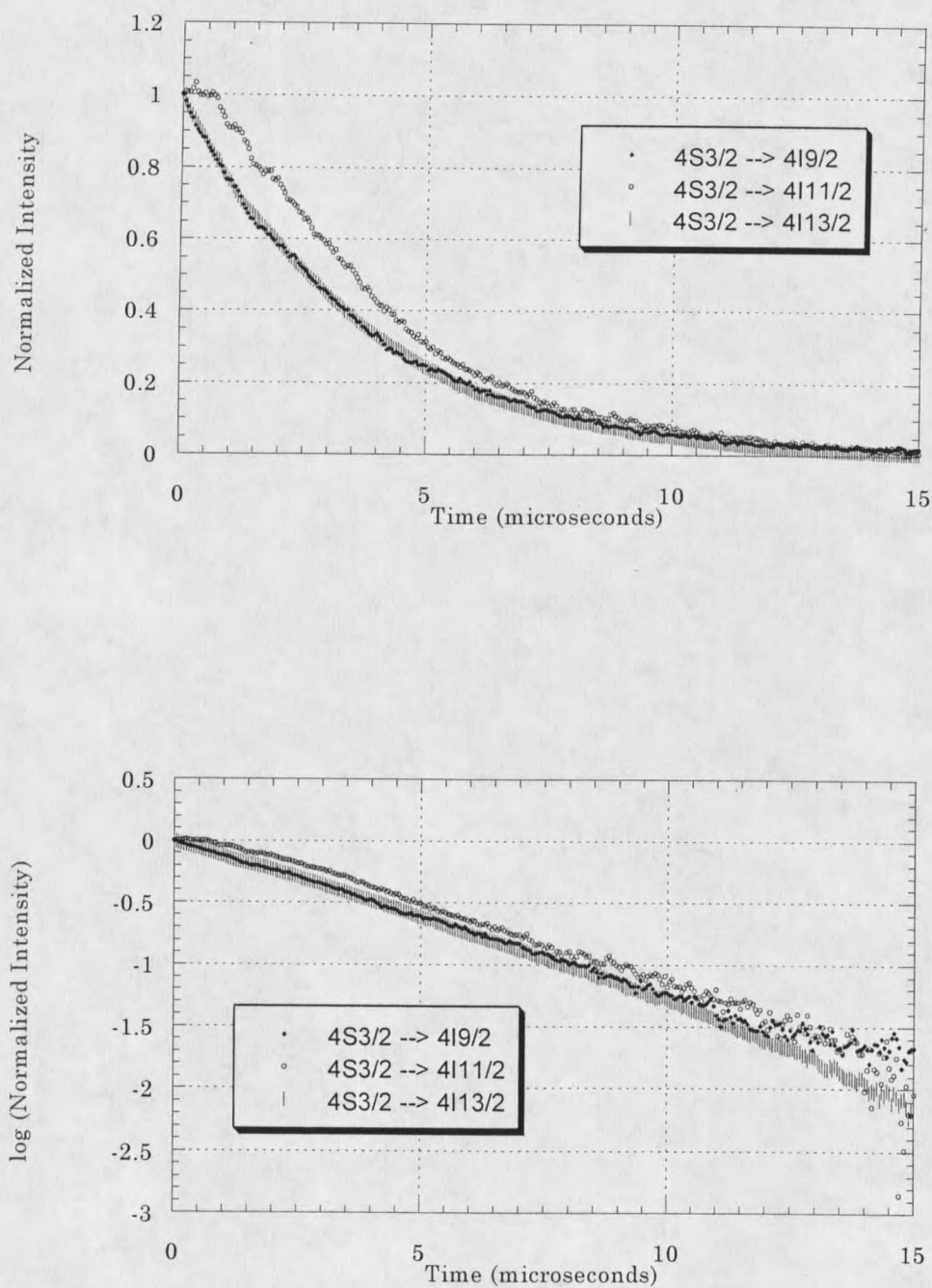


Figure 25. Decay (top) and Log of Intensity of Emission Transitions Originating from the $4S_{3/2}$ Manifold in 2% Er:YSO.

$^4F_{9/2}$ excitation for the two erbium concentrations studied. The decay profile for this transition in Er:YAG is similar regardless of excitation manifold since the emission rise time is 2-3 orders of magnitude shorter than the decay time for all the excitation levels studied.

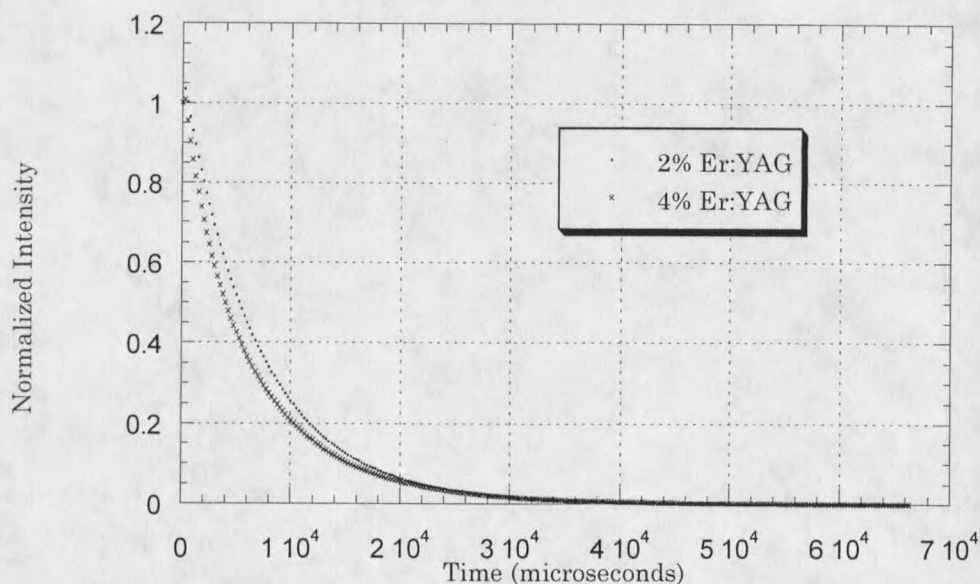


Figure 26. Decay of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ Transition for 2.1% and 4% Er:YAG.

The experimentally determined lifetimes for this transition is on the order of 6.5 - 7 milliseconds for the two samples. A difference in lifetime for the two concentrations could not be confirmed within experimental error. While the traces shown in Figure 26 would seem to indicate a shorter lifetime in the 4% sample, in another similar set of experiments the decay rate was slightly faster in the 2.1% sample. Figure 27 illustrates log plots for the

decay traces shown in Figure 26. The slight curvature seen in the log plots again is attributable to baseline correction.

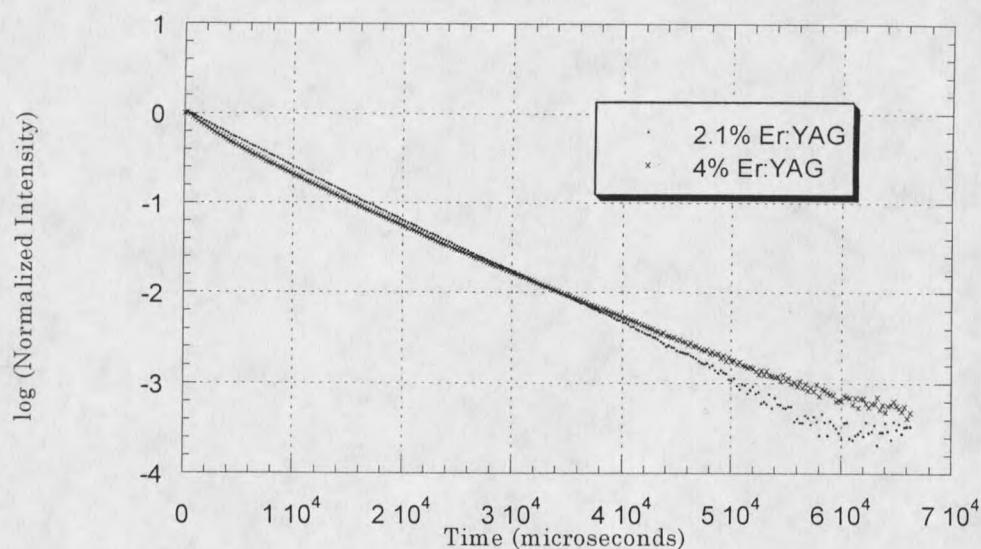


Figure 27. Log of Intensity of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Emission Transition in 2.1% and 4% Er:YAG.

The two emission transitions originating from the ${}^4I_{11/2}$ manifold decay more slowly in Er:YAG than in Er:YSO. Experiments run to evaluate these transitions were typically had 1 msec temporal resolution and 500 msec total sampling time. All other experimental parameters were similar to those for the Er:YSO experiments. Figure 28 shows the integrated transition data and log plot of the fluorescence after ${}^4I_{11/2}$ excitation. The calculated lifetime is 67.3 microseconds based on the higher intensity ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ emission, with the weaker ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ emission showing good agreement. The emission

lifetime is several times longer than that of the same transition in Er:YSO. In both materials, multiphonon relaxations dominate relaxation from the $^4I_{11/2}$ level, and the mechanism appears to be more efficient in Er:YSO. Decay results for 2.1% Er:YAG were not obtained for excitation to this manifold, but experiments run on both concentrations with $^4F_{9/2}$ excitation do not show a strong concentration dependence in the 2-4% concentration range.

Figure 29 illustrates integrated transition data and a log trace of the visible $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission. Decay from this level is also exponential, as shown by the log trace. The IR transitions from the $^4S_{3/2}$ level show similar temporal behavior. An exponential fit of this decay process for 4% Er:YAG yields a calculated lifetime of 10.7 microseconds, which is longer than the analogous process in Er:YSO (approximately 3.5 microseconds). The temporal resolution for the experiments run to analyze these transitions was 250 nsec, with a total sampling time of 150 microseconds. Other experimental parameters were the same as those for the Er:YSO experiments.

Er:LuAG

Time resolved emission spectra were obtained for 0.5% Er:LuAG after excitation to the $^4I_{13/2}$, $^4I_{11/2}$, and $^4S_{3/2}$ manifolds, using pump energies of 6525, 10385, and 18448 cm^{-1} , respectively. As with the other samples, the pump manifolds were selected since they are the emitting levels. The same

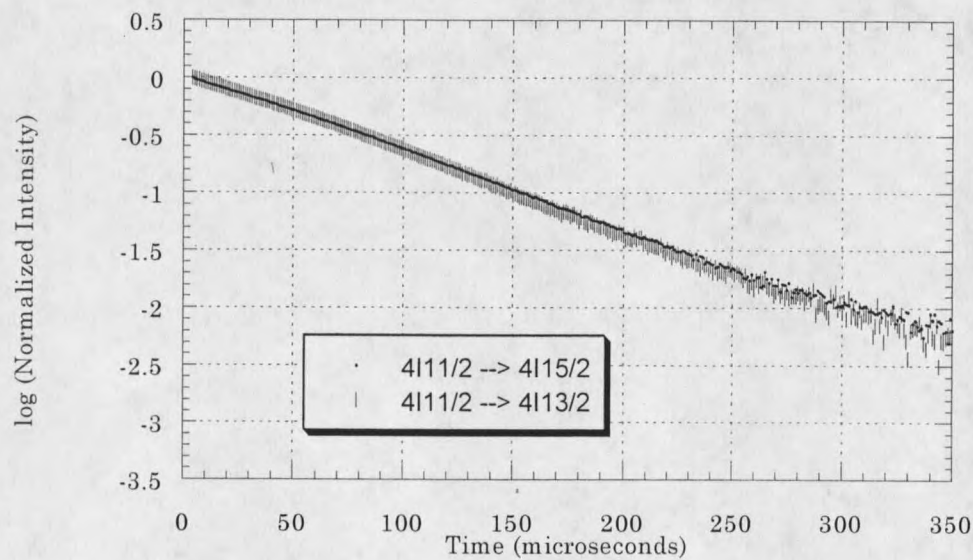
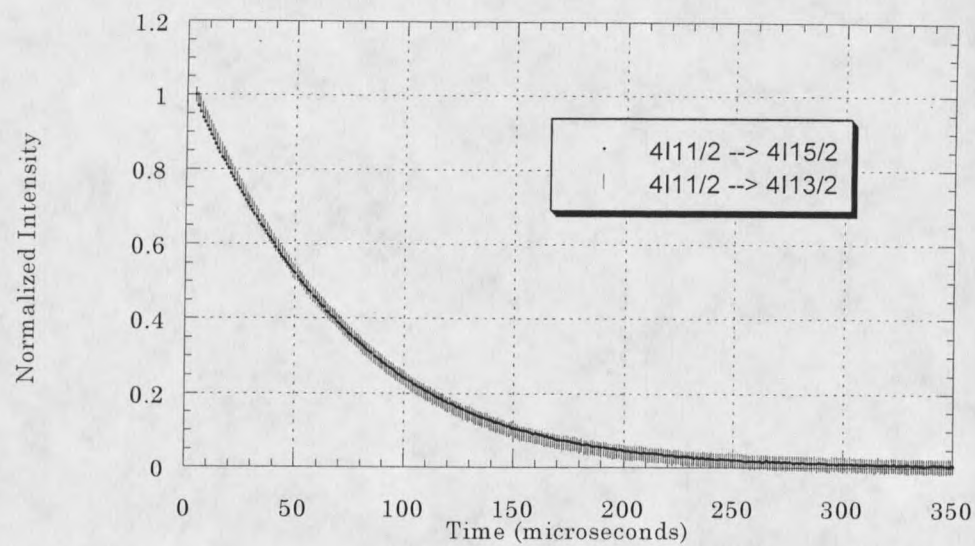


Figure 28. Decay (top) and Log of Intensity of Emission Transitions Originating from the $4I_{11/2}$ Manifold in 4% Er:YAG.

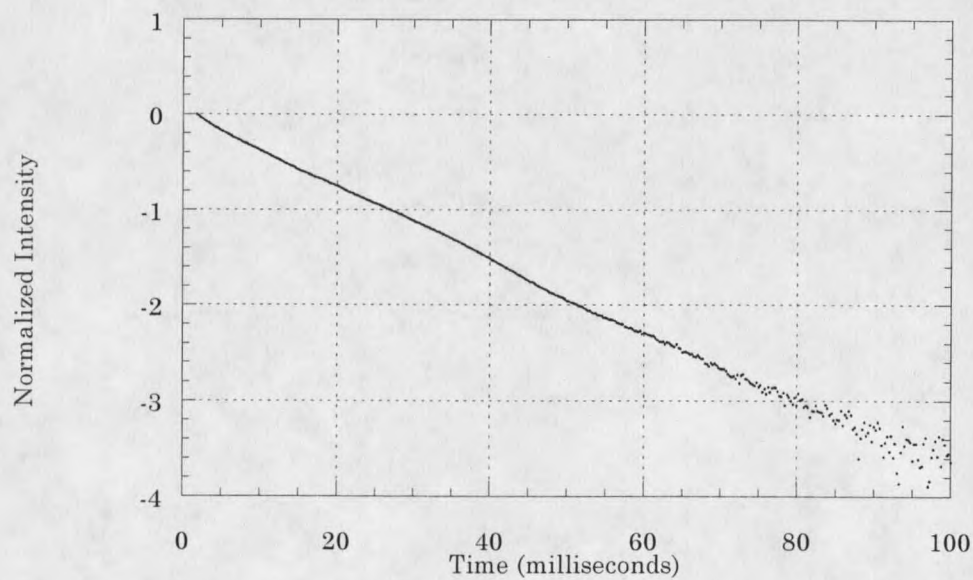
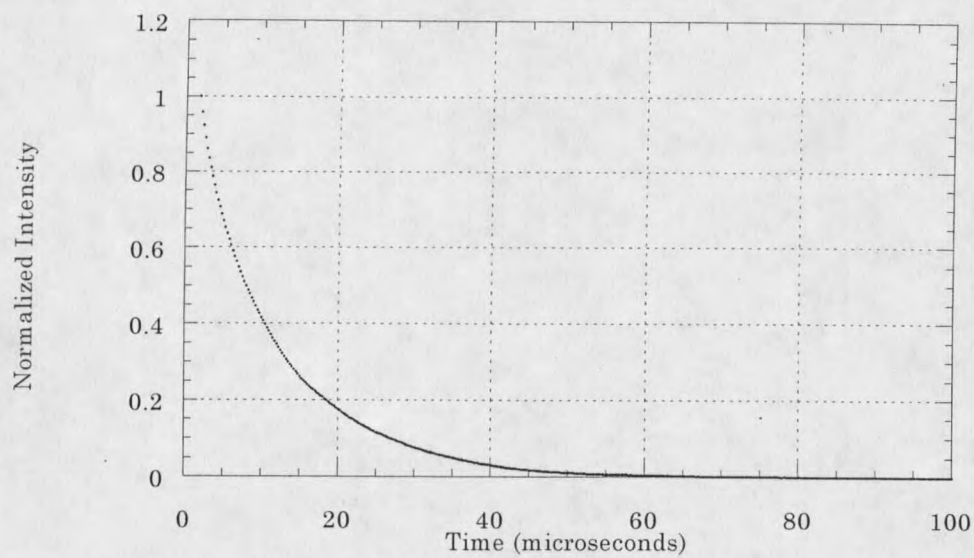


Figure 29. Decay (top) and Log of Intensity of Emission Transitions Originating from the $^4S_{3/2}$ Manifold in 4% Er:YAG.

transitions were observed in 0.5% Er:LuAG as in the other materials studied. Since the temporal behavior of the emission transitions in Er:LuAG was close to that in Er:YAG, the same experimental parameters were used in the Er:LuAG experiments as in the Er:YAG experiments. Details of the results for each of the emission transitions follow.

The integrated ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition shown in Figure 30 shows that this transition also occurs on the millisecond time scale. The signal was weaker for this material than in the other materials studied due to the lower (0.5%) erbium concentration, resulting in decreased signal-to-noise. This decay was also found to be exponential with a lifetime of 5.7 milliseconds.

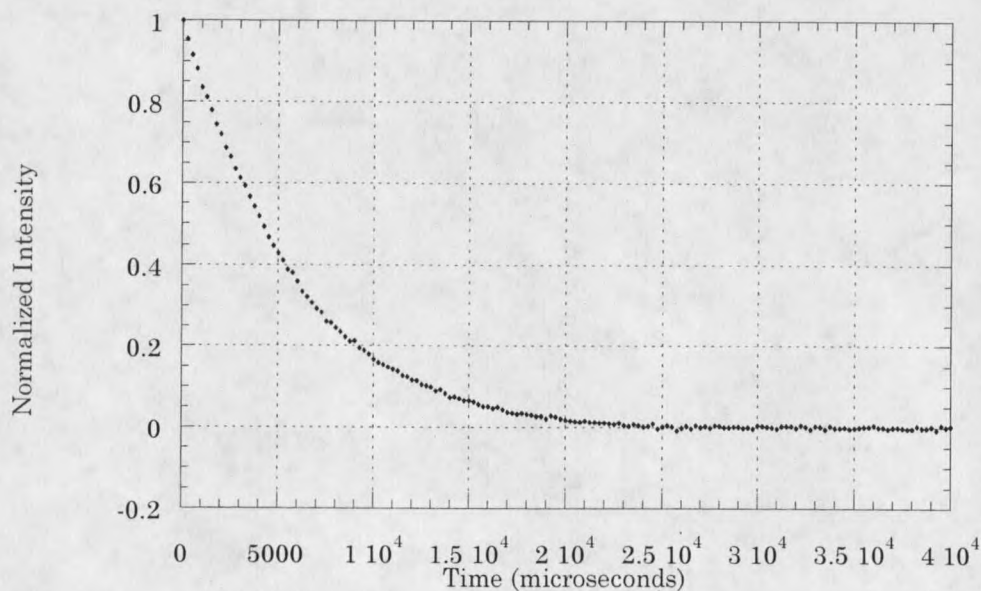


Figure 30. Decay of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Transition for 0.5% Er:LuAG.

Figure 31 shows integrated decay and log plots for the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ transition, following excitation to the ${}^4\text{I}_{11/2}$ manifold. The temporal behavior of the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ transition is similar, but the signal-to-noise ratio is slightly lower due to the lower signal intensity of the transition. The experimental lifetime is 67.7 microseconds, and the log plot is, again indicative of exponential behavior.

The three infrared emission transitions initiated from the ${}^4\text{S}_{3/2}$ level were also observed in the Er:LuAG sample. The integrated trace of the transition terminating at the ${}^4\text{I}_{13/2}$ manifold is shown in Figure 32. This emission occurred after direct excitation to the ${}^4\text{S}_{3/2}$ manifold. The log plot showed the emission decay to be exponential, and the exponential fit on the decay data yielded a calculated lifetime of 12.3 microseconds. Attempts to obtain the visible emission spectrum after excitation to the ${}^4\text{F}_{7/2}$ manifold failed due to the relatively low signal strength of the low concentration sample and saturation of the silicon diode detector by the excitation pulse. However, this visible transition could be seen by the eye.

The rise time of the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition has a exponential rise time similar to that of the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ decay lifetime, indicating that the main channel of population of the ${}^4\text{I}_{13/2}$ level is through the ${}^4\text{I}_{11/2}$ level. The rise for all three materials studied is shown in Figure 33.

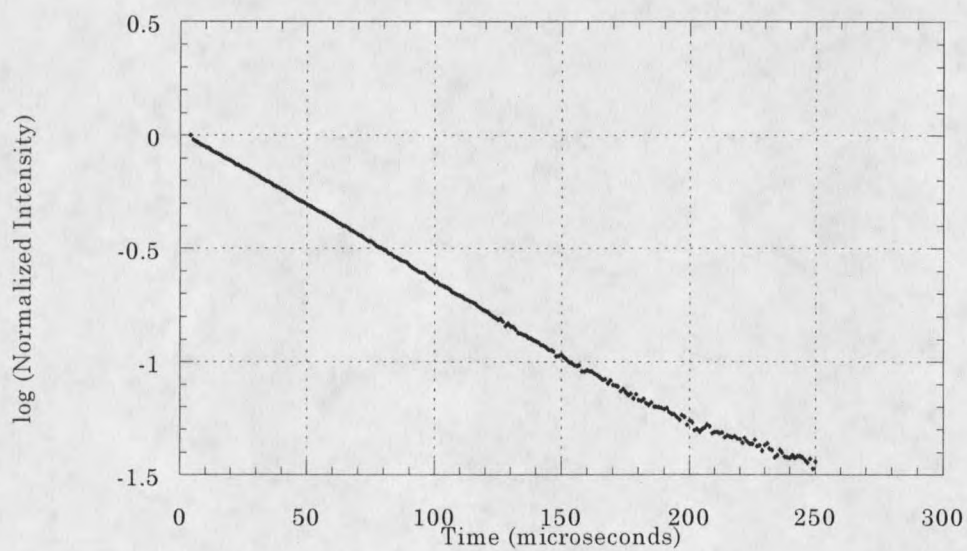
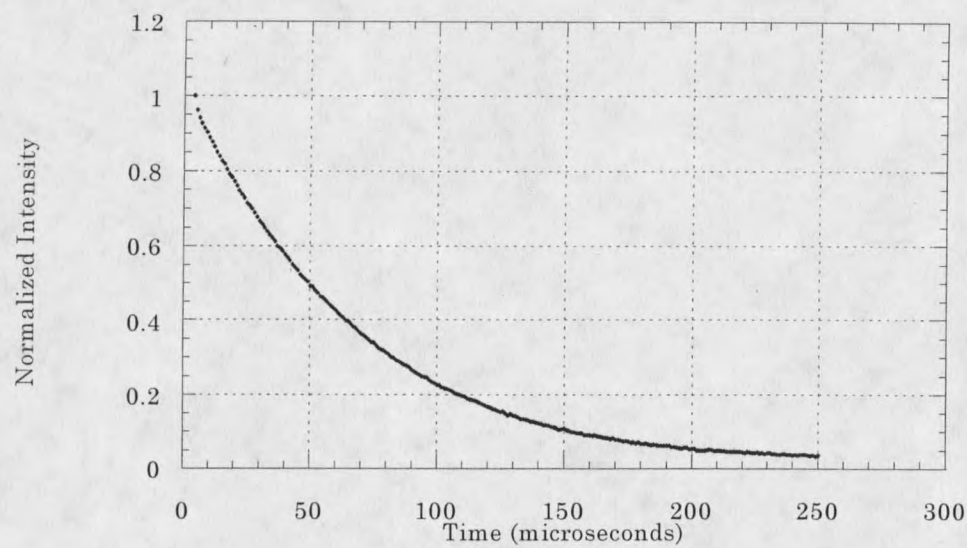


Figure 31. Decay (top) and Log of Intensity of the ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ Transition in 0.5% Er:LuAG.

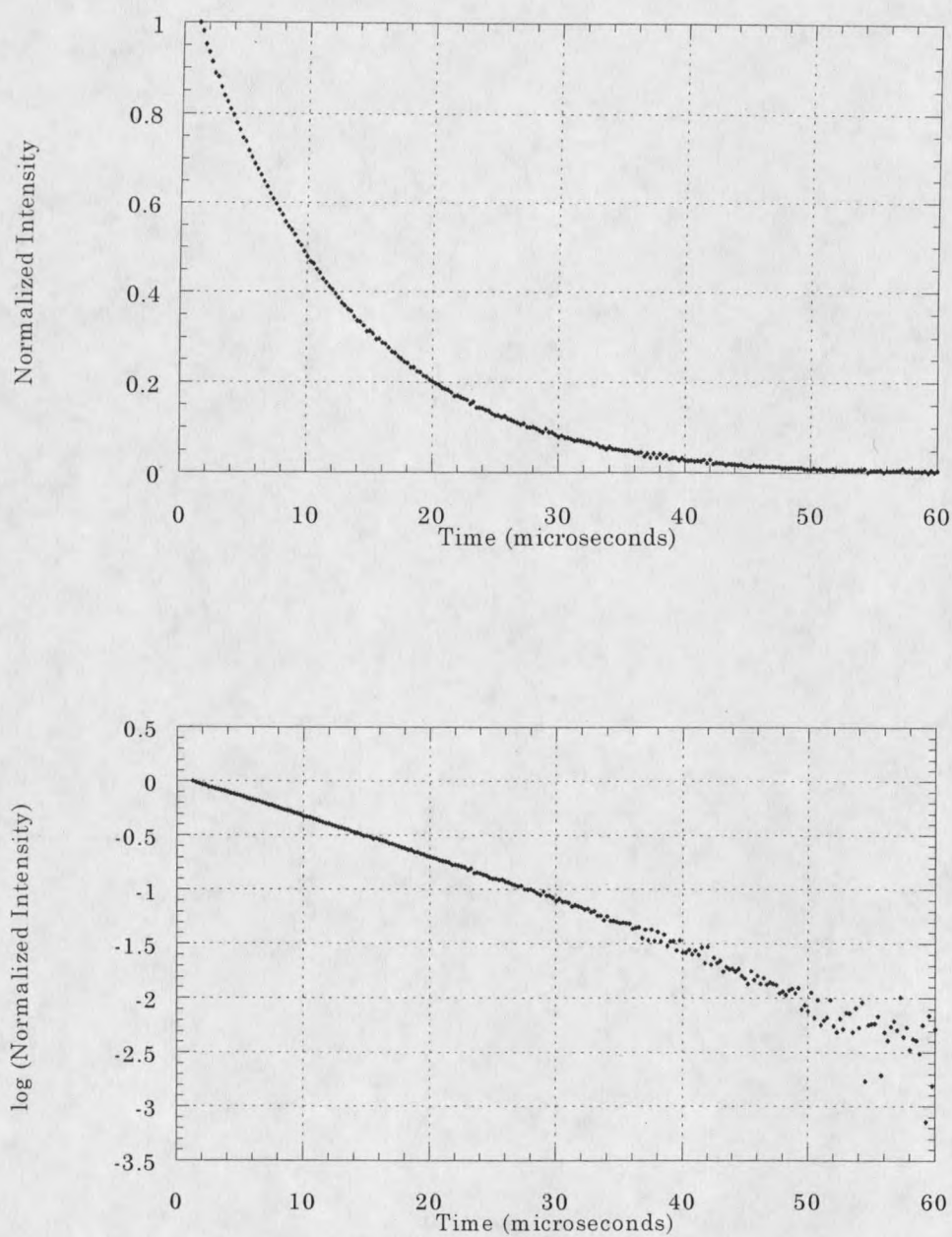


Figure 32. Decay (top) and Log of Intensity of the $^4S_{3/2} \rightarrow ^4I_{13/2}$ Transition in 0.5% Er:LuAG.

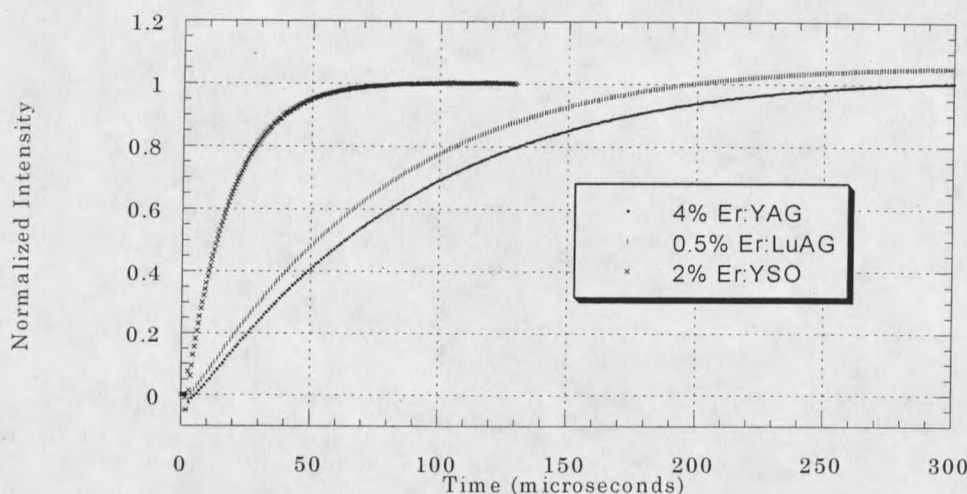


Figure 33. Rise of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ Transition for Er^{3+} in Three Crystal Hosts.

Attempts were made to study the population of the ${}^4I_{11/2}$ and ${}^4S_{3/2}$ levels by examination of the rise of emission bands initiated from these levels. However, the rise times of transitions initiated from both levels is faster than the 180 nanosecond response time of the infrared detector. Additionally, the rise time of the ${}^4S_{3/2}$ level was found to be less than 5 ns, the response time of the visible detector. The detector response times currently limit our ability to study these rapid rise times.

Table 3. Absorption Transition Frequencies in Er³⁺ Doped Materials (cm⁻¹).

<u>manifold</u>	<u>Er:YSO</u> <u><010></u>	<u>Er:YSO</u> <u>D1</u>	<u>Er:YSO</u> <u>D2</u>	<u>Er:YAG</u>	<u>Er:LuAG</u>
⁴ I _{13/2}	6428	6429	6470	6522	6493
	6452	6470	6508	6525	6519
	6470	6498	6538	6535	6525
	6508	6509	6547	6542	6541
	6538	6538	6558	6601	6549
	6592	6549	6566	6703	6559
	6699	6565	6596	6721	6602
	6727	6583	6621	6741	6721
	6752	6595	6696	6760	6741
	6768	6623	6727	6778	6764
	6784	6700	6767	6797	6783
		6725	6798	6819	6814
		6767	6849	6859	6830
				6878	6852
					6884
⁴ I _{11/2}	10157	10100	10114	10175	10180
	10183	10115	10136	10191	10208
	10193	10156	10158	10206	10230
	10209	10174	10183	10223	10251
	10235	10195	10196	10231	10262
	10252	10209	10209	10250	10315
	10270	10227	10227	10262	10326
	10283	10233	10233	10279	10337
	10296	10251	10253	10296	10348
	10315	10268	10261	10307	10360
	10343	10293	10286	10331	10365
	10382	10315	10294	10336	10380
		10333	10304	10347	10385
		10344	10316	10353	10403
			10332	10365	10417
			10343	10388	
			10384	10393	
⁴ I _{9/2}	12197	12322	12257	12225	12220
	12218	12361	12279	12240	12245

Table 3. Continued

<u>manifold</u>	<u>Er:YSO</u> <u><010></u>	<u>Er:YSO</u> <u>D1</u>	<u>Er:YSO</u> <u>D2</u>	<u>Er:YAG</u>	<u>Er:LuAG</u>
$^4I_{9/2}$	12253	12421	12322	12281	12267
	12277	12445	12349	12299	12291
	12320	12463	12358	12446	12456
	12352	12527	12375	12462	12476
	12378	12543	12423	12503	12497
	12421	12568	12444	12510	12523
	12432	12607	12464	12551	12543
	12448	12645	12491	12679	12693
	12464		12508	12691	12714
	12493		12527	12735	12767
	12534		12563	12753	
	12560		12572		
	12577		12606		
	12606		12644		
$^4F_{9/2}$	15072	15033	15000	15207	15218
	15095	15070	15051	15220	15240
	15133	15087	15118	15230	15263
	15158	15119	15133	15246	15284
	15168	15131	15156	15262	15296
	15192	15167	15168	15279	15318
	15215	15179	15179	15286	15351
	15274	15191	15193	15292	15399
	15296	15215	15215	15306	15443
	15332	15274	15274	15331	15463
	15356	15298	15301	15351	15476
	15376	15316	15317	15387	15484
	15454	15356	15333	15435	15516
	15491	15372	15355	15444	
		15395	15373	15464	
		15490	15491	15490	
$^4S_{3/2}$	18225	18182	18245	18311	18319
	18246	18228	18278	18385	18395
	18266	18243	18304	18391	18416
	18284	18267	18329	18432	18448
	18327	18283	18351	18450	

Table 3. Continued

<u>manifold</u>	<u>Er:YSO</u> <u><010></u>	<u>Er:YSO</u> <u>D1</u>	<u>Er:YSO</u> <u>D2</u>	<u>Er:YAG</u>	<u>Er:LuAG</u>
$^4S_{3/2}$	18366	18327	18363		
	18382	18366	18382		
	18410		18408		
$^2H_{11/2}$	19040	18942	18918	19013	19015
	19044	18968	18942	19032	19036
	19070	19002	18987	19050	19059
	19077	19040	19004	19069	19068
	19127	19048	19046	19090	19076
	19134	19065	19066	19110	19090
	19139	19083	19076	19126	19112
	19158	19088	19084	19146	19272
	19197	19095	19094	19262	19284
	19225	19121	19124	19279	19317
	19235	19139	19138	19304	19339
	19260	19161	19160	19319	19348
	19307	19172	19178	19338	19365
		19196	19196	19357	
		19219	19224		
		19231	19260		
		19252	19268		
		19267	19306		
		19308			
$^4F_{7/2}$	20262	20260	20259	20433	20442
	20299	20300	20343	20447	20645
	20394	20342	20369	20486	20486
	20423	20387	20387	20543	20535
	20495	20396	20395	20564	20595
	20521	20425	20425	20580	20615
	20569	20468	20469	20618	20639
	20631	20497	20496	20630	20659
		20519	20520	20640	
		20567	20610	20671	
		20609	20638		
			20653		

Table 4. Experimental Lifetimes of Transitions in Erbium Doped Materials

<u>Level</u>	<u>Material</u>	<u>Experimental Fit</u> <u>Lifetime (μsec)</u>	<u>1/e Lifetime</u> <u>(μsec)</u>
$^4I_{13/2}$	2% Er:YSO	8640	8500
	2.1% Er:YAG	6600	6800
	4% Er:YAG	6500	6500
	0.5% Er:LuAG	5700	5800
$^4I_{11/2}$	2% Er:YSO	10.5	12.0
	4% Er:YAG	67.3	73.5
	0.5% Er:LuAG	67.7	70.0
$^4S_{3/2}$	2% Er:YSO	3.5	3.7
	4% Er:YAG	10.7	11.3
	0.5% Er:LuAG	12.3	11.8

Table 5. Radiative Branching Ratios Calculated from Experimental Data.

<u>Material</u>	<u>Level</u>	<u>Transition</u>	<u>Branching Ratio</u>
2% Er:YSO	$^4I_{11/2}$	$^4I_{11/2} \rightarrow ^4I_{15/2}$	0.91
		$^4I_{11/2} \rightarrow ^4I_{13/2}$	0.09
	$^4S_{3/2}$	$^4S_{3/2} \rightarrow ^4I_{15/2}$	0.62
		$^4S_{3/2} \rightarrow ^4I_{13/2}$	0.36
		$^4S_{3/2} \rightarrow ^4I_{11/2}$	0.01
		$^4S_{3/2} \rightarrow ^4I_{9/2}$	0.01
4% Er:YAG	$^4S_{3/2}$	$^4S_{3/2} \rightarrow ^4F_{9/2}$	0 (not detected)
		$^4S_{3/2} \rightarrow ^4I_{15/2}$	0.72
		$^4S_{3/2} \rightarrow ^4I_{13/2}$	0.26
		$^4S_{3/2} \rightarrow ^4I_{11/2}$	0.01
		$^4S_{3/2} \rightarrow ^4I_{9/2}$	0.01
		$^4S_{3/2} \rightarrow ^4F_{9/2}$	0 (not detected)
0.5% Er:LuAG	$^4I_{11/2}$	$^4I_{11/2} \rightarrow ^4I_{15/2}$	0.95
		$^4I_{11/2} \rightarrow ^4I_{13/2}$	0.05

CHAPTER 4

DISCUSSION OF RESULTS

In this chapter, the method of generating the experimental decay curves shown in the previous chapter is described. Additionally, kinetic modeling of the data is presented and rate constants are determined. A new method of determining non-radiative rates and branching ratios utilizing the intensity "volume" under three-dimensional time and frequency resolved emission bands is developed. Values obtained using this method are compared to non-radiative rates and branching ratios determined from comparison of experimental emission lifetimes with calculated radiative lifetimes using Morrison's code.

Generation of Experimental Decay Curves

The experimental decay curves were generated from the temporally resolved spectra by integration using the software supplied with the Bruker spectrophotometer. The software gives the option of numerous integration techniques; of these, the method outlined here gave the best results for the data in this study.

Figure 34 is a single time slice from a temporally resolved emission spectrum. The area between lines A and B is obtained by integration and contains both signal and baseline noise. The baseline noise contribution is estimated by defining a spectral region on each side of the emission band (regions C to D and E to F) that are each equal in width to the emission band, and averaging the two integrated areas. This baseline noise is then subtracted from the initial integration to give the integrated signal. The average of two baseline regions was used to improve the results for spectra that had a "slant" in baseline intensity, since the goal was to subtract the baseline noise contributing to the area under the emission band. While this method gave the best results of the methods tried, it did not give ideal results for all spectra and small baseline correction errors still occurred. These baseline correction errors were found to lead to the slight curvature noted in some of the log plots of the integrated decay traces, as discussed in the next section.

Discussion of Long Term Curvature in Log Plots

A slight degree of curvature was noted in many of the plots when the logarithm of the integrated transition intensity was plotted versus time. Obviously, for purely exponential decay, the log plot would yield a straight line. An example of this curvature is shown in Figure 35. Both convex and

concave curvatures were observed. Figure 35 represents a typical degree of curvature; in a few instances it was considerably sharper while in other instances no curvature was noted. This curvature is attributable to baseline error introduced by the systematic baseline noise caused by source pulse-to-pulse fluctuations that was discussed in Chapter 2. Since the pulse-to-pulse intensity fluctuations of emission transitions are Fourier transformed across the entire spectral dimension as noise, the presence of one band adds noise to

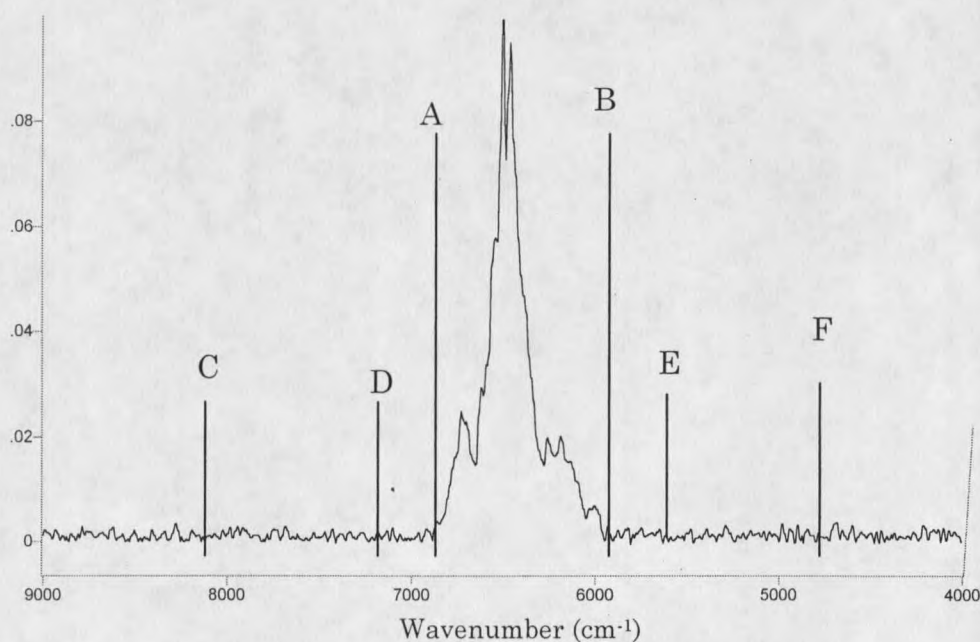


Figure 34. Illustration of Integration Method Used to Generate Decay Traces. The baseline correction is obtained by averaging the areas between lines C and D and lines E and F under the spectrum. This baseline correction value is then subtracted from the integrated area under the spectrum between lines A and B to obtain the corrected integral value.

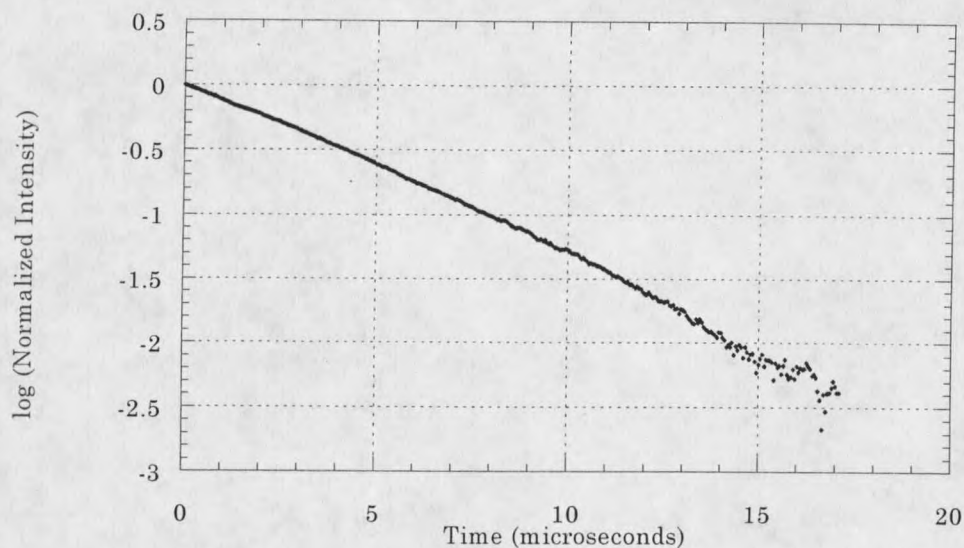


Figure 35. Curvature Observed in Logarithmic Plots of Emission Decays.

the baseline of other emission bands in the spectrum, causing error in decay traces of bands (especially those with different temporal behavior) that are manifested as curvature in log plots of decay profiles. While the fact that the noise is spread out over the entire spectrum with the Fourier transform method can be an advantage over dispersive methods, it is a disadvantage in this instance since it hurts the quality of the temporal data. Experiments run when the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition is filtered out significantly altered the curvature seen in log plots of the emission transitions from the ${}^4\text{I}_{11/2}$ level.

Two approaches to baseline correction demonstrate the connection between baseline error and the observed curvature. First, the software accompanying the Bruker spectrometer allows several different methods of

integration and baseline correction of spectra. Integrating the same spectra using a variety of methods was found to introduce and/or change the curvature in the log plots, primarily due to differences in baseline correction. The integration method described earlier in this chapter was chosen since, of the methods tried, it least frequently resulted in nonzero baselines in the integrated decay traces and led to the best agreement in temporal behavior between transitions with the same emitting level. Second, addition or subtraction of a small constant value from the decay trace after integration was successful in reducing and/or eliminating the curvature. Figure 36 shows the data from Figure 35 after this correction was implemented. As can be seen by comparison of Figures 35 and 36, the degree of curvature has been reduced substantially. This correction typically only caused a small variation in the exponential lifetime, up to a maximum of 4%. It is also possible that nonlinear detector response could contribute to the observed curvature, particularly in the earlier portions of the decay event when emission signal was stronger.

Since the depopulation of the excited states studied was found to be dominated by exponential processes (with the observed curvature explained by instrumental or signal processing errors rather than physical processes), the modeling described in the next section assumes exponential decay for all the relaxation processes.

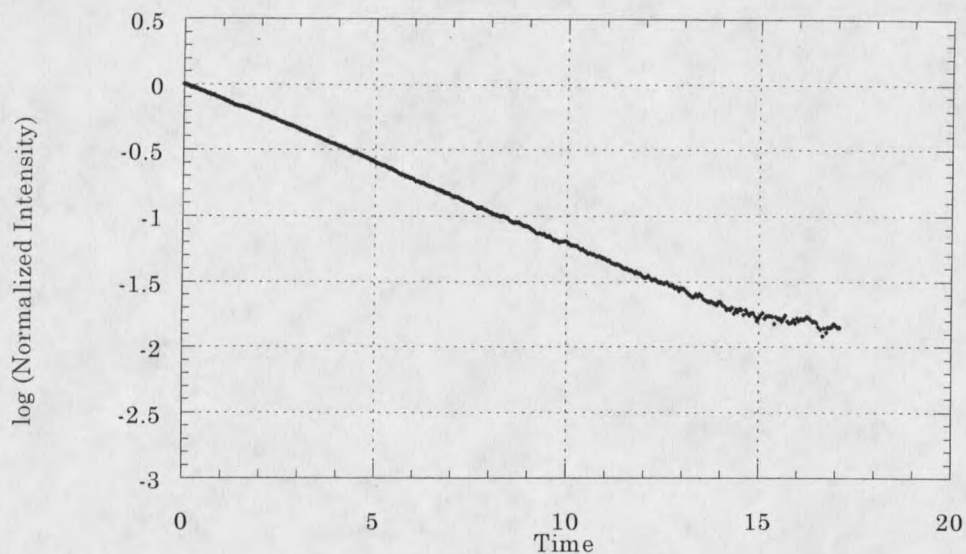


Figure 36. Data from Figure 35 After Addition of a Constant Value to the Decay Trace Data for Baseline Correction. Note the reduction in curvature compared to Figure 35.

Kinetic Modeling of Experimental Data

In this section, modeling performed to explain the decay processes responsible for the experimental results is discussed. Sets of coupled differential equations describing the population and depopulation of the energy levels studied were written and numerically solved. Both spontaneous radiative and nonradiative (multiphonon) relaxation processes are considered in the model. Similar approaches to modeling for Er:YAG (4,28,29,43,52), other erbium-doped garnets (4), and Er:YAlO₃ (20,21) can be

found in the literature. In this study, two separate cases were modeled: decay following $^4I_{11/2}$ and $^4S_{3/2}$ excitation. These two pump manifolds were considered since they are initial levels for radiative processes.

$^4I_{11/2}$ excitation

The decay transitions considered for the case of $^4I_{11/2}$ excitation are shown in Figure 37. The radiative processes (which are the same ones that were observed experimentally) are indicated by solid lines, while the wavy lines indicate multiphonon relaxation. It is assumed that the dominant multiphonon transitions are those that result in decay from one manifold to the one directly below it, therefore multiphonon processes such as the one

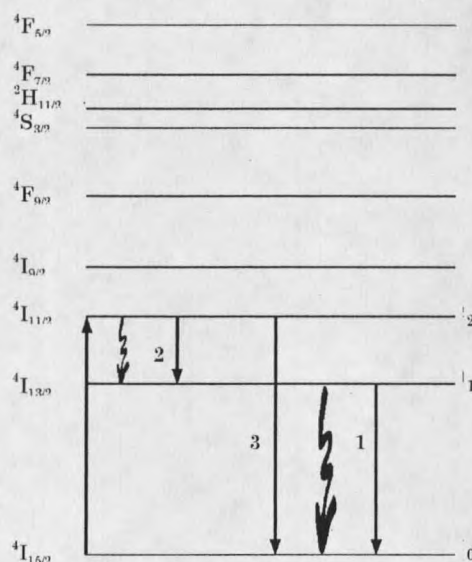


Figure 37. Decay Processes Following $^4I_{11/2}$ Excitation.

from the ${}^4I_{11/2}$ to the ${}^4I_{15/2}$ manifold are not included. For brevity, the ${}^4I_{11/2}$, ${}^4I_{13/2}$, and ${}^4I_{15/2}$ manifolds will be referred to as levels 2, 1, and 0 respectively, as indicated on Figure 37. Rate equations for the three manifold populations can be expressed as follows:

$$\begin{aligned}\frac{dN_2}{dt} &= -(A_{20} + A_{21} + W_{21})N_2 \\ \frac{dN_1}{dt} &= (A_{21} + W_{21})N_2 - (A_{10} + W_{10})N_1 \\ \frac{dN_0}{dt} &= (A_{10} + W_{10})N_1 + A_{20}N_2\end{aligned}\tag{1}$$

N_i = population of level i

A_{ij} = rate constant for spontaneous radiative emission from manifold i to j

W_{ij} = multiphonon emission from manifold i to j

The excitation pulse is short compared to the lifetimes of most of the processes, so behavior directly after excitation will be modeled.

In order to evaluate the above set of equations, values are needed for the rate constants A_{ij} and W_{ij} . The experimentally determined lifetime τ_i is related to the rate constants as follows:

$$\tau_i = \frac{1}{k_i}\tag{2}$$

$$k_i = \sum_{j=0}^{i-1} A_{ij} + \sum_{j=0}^{i-1} W_{ij}$$

where k_i is the overall rate constant for decay from manifold i .

Therefore, for manifold 2 (neglecting W_{20}):

$$\frac{1}{\tau_2} = k_2 = A_{20} + A_{21} + W_{21} \quad (3)$$

Examination of the three dimensional emission spectra for the $^4I_{11/2}$ pump manifold shows that most of the decay from levels 2 to 1 is nonradiative. This can be seen by comparing the total volume under the emission transitions (see Figure 20) for the radiative emissions for level 2 to 1 (3500 cm^{-1}) and 1 to 0 (6500 cm^{-1}). The volume under the $1 \rightarrow 0$ transition is significantly larger than the $2 \rightarrow 1$ transition, and the integration over the total volume of a band gives information about radiative depopulation. Since the total population entering a level by both radiative and nonradiative means should equal the total population leaving a level, the dominant process feeding level 1 must be nonradiative. This "total volume balance" around level 1 may be stated mathematically as follows:

Total volume of feeding processes = Total volume of depopulating processes

$$A_{21} + W_{21} = A_{10} + W_{10} \quad (4)$$

where the bold typeface indicates a total volume integral. The A_{ij} and W_{ij} symbols correspond to the same transitions as the analogous A_{ij} and W_{ij} symbols in the rate equations. Strictly speaking, W_{21} and W_{10} are not volumes since they do not correspond to radiative emission processes. Instead, each W value is numerically equal to the total volume of a hypothetical radiative emission process between the indicated initial and

terminal levels with the same probability as the nonradiative rate being evaluated. Total volume integral values for the radiative processes (A_{ij}) were determined by first integrating under the transition in the spectral dimension, after the spectrum was corrected for instrument response. This integration was done for each time slice in a temporally resolved spectrum. A plot of these integrated areas versus time gives a decay trace like that shown in Figure 22. Next, the decay trace was fit to an exponential decay equation which was then integrated over time to yield the total volume integral. Integration of baseline noise over the long exponential "tail" was found to introduce significant error, so the exponential fit equation was integrated rather than the experimental decay trace. Equation 4 can be rearranged to solve for W_{21} :

$$W_{21} = W_{10} + A_{10} - A_{21} \quad (5)$$

Results specific to the three materials modeled (4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG) are presented in the following paragraphs.

For the 4% Er:YAG sample, the experimentally determined lifetime τ_1 was found to be 6.5 ms. The theoretical radiative lifetime $\tau_{1 \text{ rad}}$, obtained from a computational method derived by Morrison et al. (37,78-80) is 13 ms. Using Equation 2 and the fact that $\tau_{1 \text{ rad}} = 1/A_{10}$, it can be found that $A_{10} = W_{10}$ for this set of experimental and theoretical radiative lifetimes. The total volume integrals of the radiative processes (A_{ij}) can be determined using the procedure described in the previous paragraph. Equation 5 can then be used

to solve for W_{21} . The branching ratio for a radiative or nonradiative process is defined as the probability that depopulation of a level will occur by that process. For example, the branching ratio for the radiative emission of level 2 to level 1 can be determined as follows:

$$B_{A_{21}} = \frac{A_{21}}{A_{21} + A_{20} + W_{21}} = \frac{A_{21}}{A_{21} + A_{20} + W_{21}} \quad (6)$$

Note the branching ratios can be calculated using either rate constants or total volume integrals. The branching ratios for depopulating level 2 using this total volume integral method are listed in Table 6.

To check the effectiveness of the total volume integral calculations, the branching ratios for level 2 were also calculated using the experimental and theoretical radiative (again obtained using the Morrison computational method) lifetimes. The relative branching ratio of A_{20} and A_{21} was calculated by using the experimental radiative branching ratio presented in Table 5. The results of these branching ratio calculations are also listed in Table 6 (under "Using Theoretical Radiative Lifetime") and show good agreement with the total volume integral calculations.

The total volume integral approach was also used to determine branching ratios for level 2 for the 2% Er:YSO sample and the 0.5% Er:LuAG sample. For Er:YSO, W_{10} was determined using theoretical radiative calculations performed by Moncorge et al (39). For Er:LuAG, since the LuAG

Table 6. Branching Ratios for Decay from $^4I_{11/2}$ Manifold in 4% Er:YAG

<u>Transition</u>	<u>Using Total Volume Integration</u>	<u>Using Theoretical Radiative Lifetime</u>
W_{21}	0.992	0.993
A_{21}	7.69×10^{-4}	7.04×10^{-4}
A_{20}	7.08×10^{-3}	6.50×10^{-3}

crystal host is similar to YAG, it was assumed that, as was the case with Er:YAG, W_{10} was approximately equal to A_{10} . Once W_{10} was determined for each material, the branching ratios were determined using the same total volume procedure used for Er:YAG and are presented in Table 7.

Once the branching ratios were obtained, the rate constant A_{ij} (or W_{ij}) can easily be obtained using the equations:

$$A_{ij} = B_{A_{ij}} k_i$$

$$W_{ij} = B_{W_{ij}} k_i \quad (7)$$

where k_i is the overall experimental rate constant.

Table 7. Branching Ratios for $^4I_{11/2}$ Manifold in 2% Er:YSO or 0.5% Er:LuAG

<u>Transition</u>	<u>2% Er:YSO</u>	<u>0.5% Er:LuAG</u>
W_{21}	0.997	0.984
A_{21}	1.85×10^{-4}	1.37×10^{-3}
A_{20}	2.42×10^{-3}	1.51×10^{-2}

Using this equation, A_{ij} and W_{ij} were calculated for all three materials modeled. Using these values and Mathematica, the system of simultaneous differential equations was solved. Table 8 contains the rate constants used in the differential equations.

Table 8. Rate Constants for Relaxation following $^4I_{11/2}$ Pumping (μsec^{-1})

<u>Transition</u>	<u>4% Er:YAG</u>	<u>2% Er:YSO</u>	<u>0.5% Er:LuAG</u>
A_{10}	7.69×10^{-5}	1.16×10^{-4}	8.77×10^{-5}
W_{10}	7.69×10^{-5}	—	8.77×10^{-5}
A_{20}	1.06×10^{-4}	2.25×10^{-4}	2.26×10^{-4}
A_{21}	1.15×10^{-5}	1.73×10^{-5}	2.04×10^{-5}
W_{21}	1.48×10^{-2}	9.30×10^{-2}	1.47×10^{-2}

The lack of entry for W_{10} for 2% Er:YSO results from the theoretical radiative lifetime value of 5.7 ms for τ_1 , which is shorter than the experimentally observed lifetime of 8.6 ms. Moncorge *et al* (39) have attributed this situation to lifetime lengthening due to radiation trapping. The allocation of probability for relaxation via radiative emission or multiphonon processes does not affect the solution of the differential equations, so the relative contribution of radiative and nonradiative decay from level one has not been explored further in this study. Decay curves for both manifolds in all three materials are shown compared to the

experimental data in Figures 38 through 41. The decay curves are shown as solid lines, while the actual experimental data points are shown. Both linear and logarithmic plots are shown for 4% Er:YAG, while only logarithmic plots are shown for the Er:LuAG and Er:YSO samples. The decay curves generated by the model show good overall agreement with the experimental data.

Summary of Total Volume Integral Modeling Method

The steps involved in the kinetic modeling calculations described in the last section are summarized as follows:

1. Rate equations for the population of each manifold included in the model are written and include rate constants for spontaneous radiative emission (A_{ij}) and multiphonon relaxation (W_{ij}).
2. Total volume balances are written around energy levels that are being both populated and depopulated in the model. For the case of $^4I_{11/2}$ excitation, the only level meeting this description is level 1 ($^4I_{13/2}$). The balance is written using the principle that the sum of the total volumes of the processes populating a level is equal to the sum of the processes depopulating the level. Total volume integrals are signified using bold typeface symbols, i.e. A_{10} .
3. The total volume integrals A_{ij} are determined from experimental data.

4. The "total volume integral" W_{10} is estimated by comparing the experimental lifetime and theoretical radiative lifetime of level one and the relationships:

$$\tau_{rad} = \frac{1}{A_{10}}$$

$$\frac{1}{\tau_{lexp}} = A_{10} + W_{10}, \text{ and}$$

$$\frac{W_{10}}{A_{10}} = \frac{W_{10}}{A_{10}}$$

5. The total volume integral balance from Step 2 is solved for upper level nonradiative processes, i.e. W_{21} .
6. Branching ratios are determined using Equation 6 (similar equations can be written for W_{ij}).

$$B_{A_{21}} = \frac{A_{21}}{A_{21} + A_{20} + W_{21}} = \frac{A_{21}}{A_{21} + A_{20} + W_{21}} \quad (6)$$

7. Rate constants A_{ij} (or W_{ij}) are then calculated using Equation 7:

$$A_{ij} = B_{A_{ij}} k_i \quad \text{or} \quad W_{ij} = B_{W_{ij}} k_i \quad (7)$$

8. The rate constants determined in Step 7 are put into the rate equations from Step 1 and solved using Mathematica.

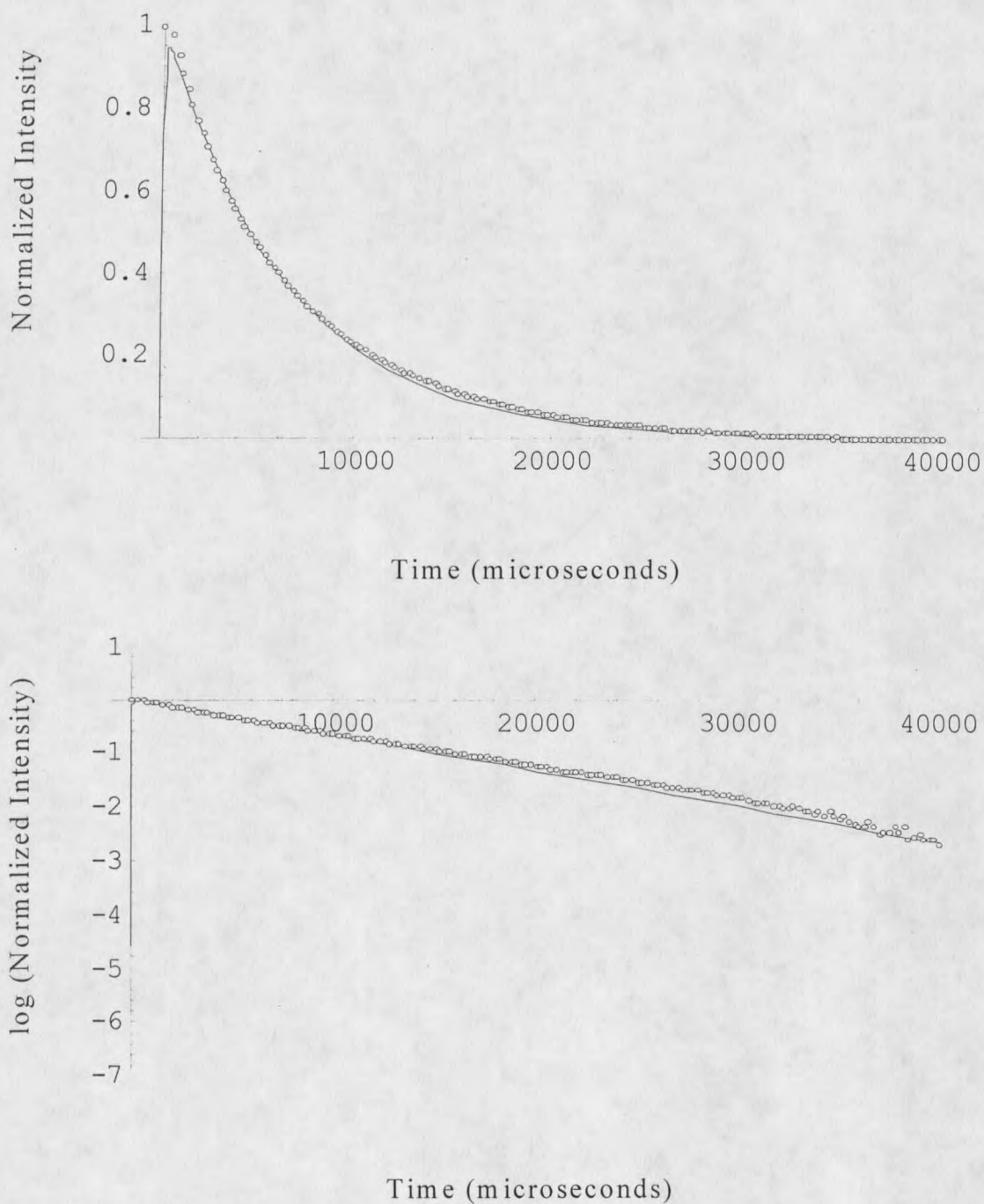


Figure 38. Linear (top) and Log Plots of Decay from the $^4I_{13/2}$ Manifold (Level 1) of 4% Er:YAG. The solid lines are modeled decay, and the points are experimental data.

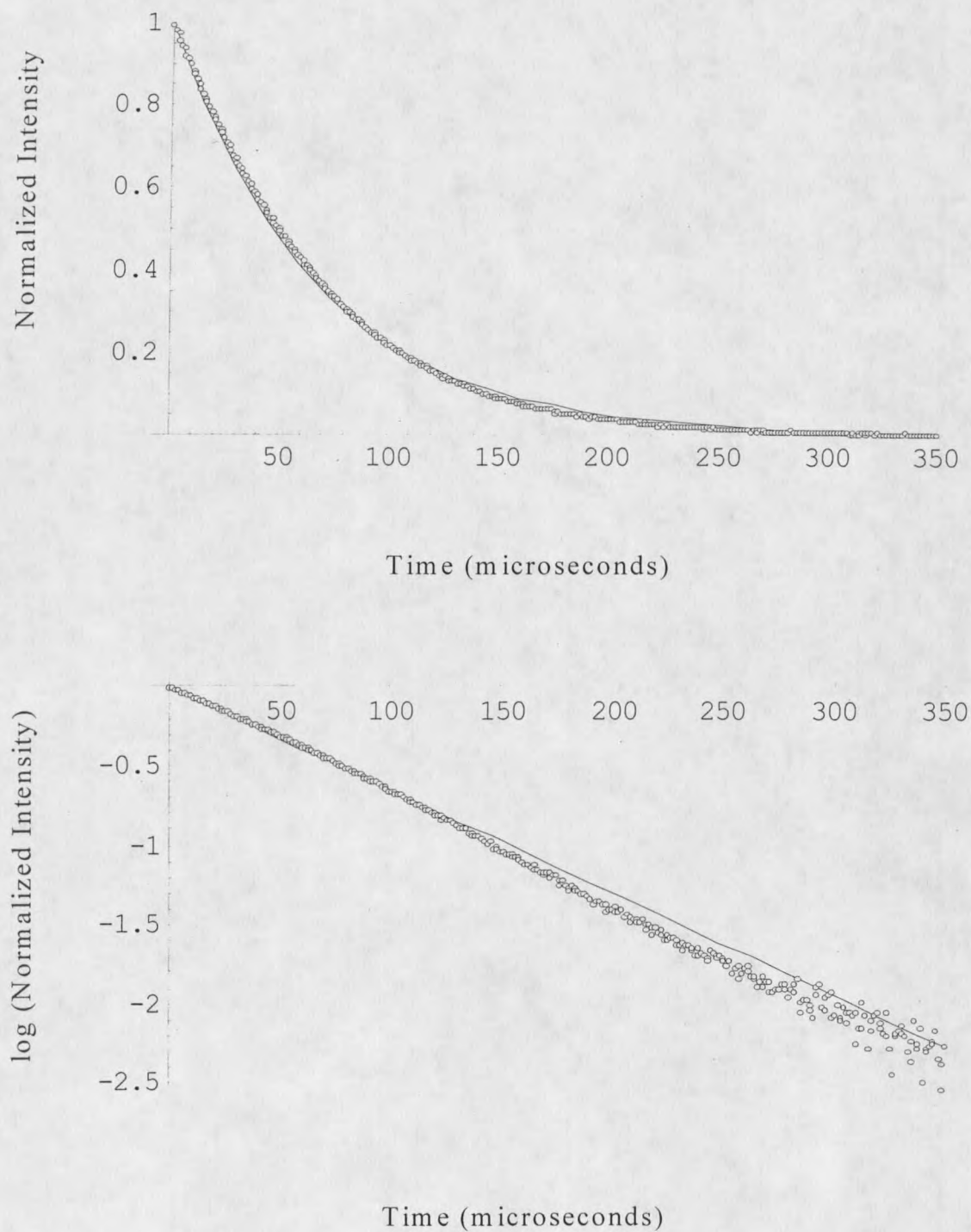


Figure 39. Linear (top) and Log Plots of Decay from the $4I_{11/2}$ Manifold (Level 2) of 4% Er:YAG. The solid lines are modeled decay, and the points are experimental data.

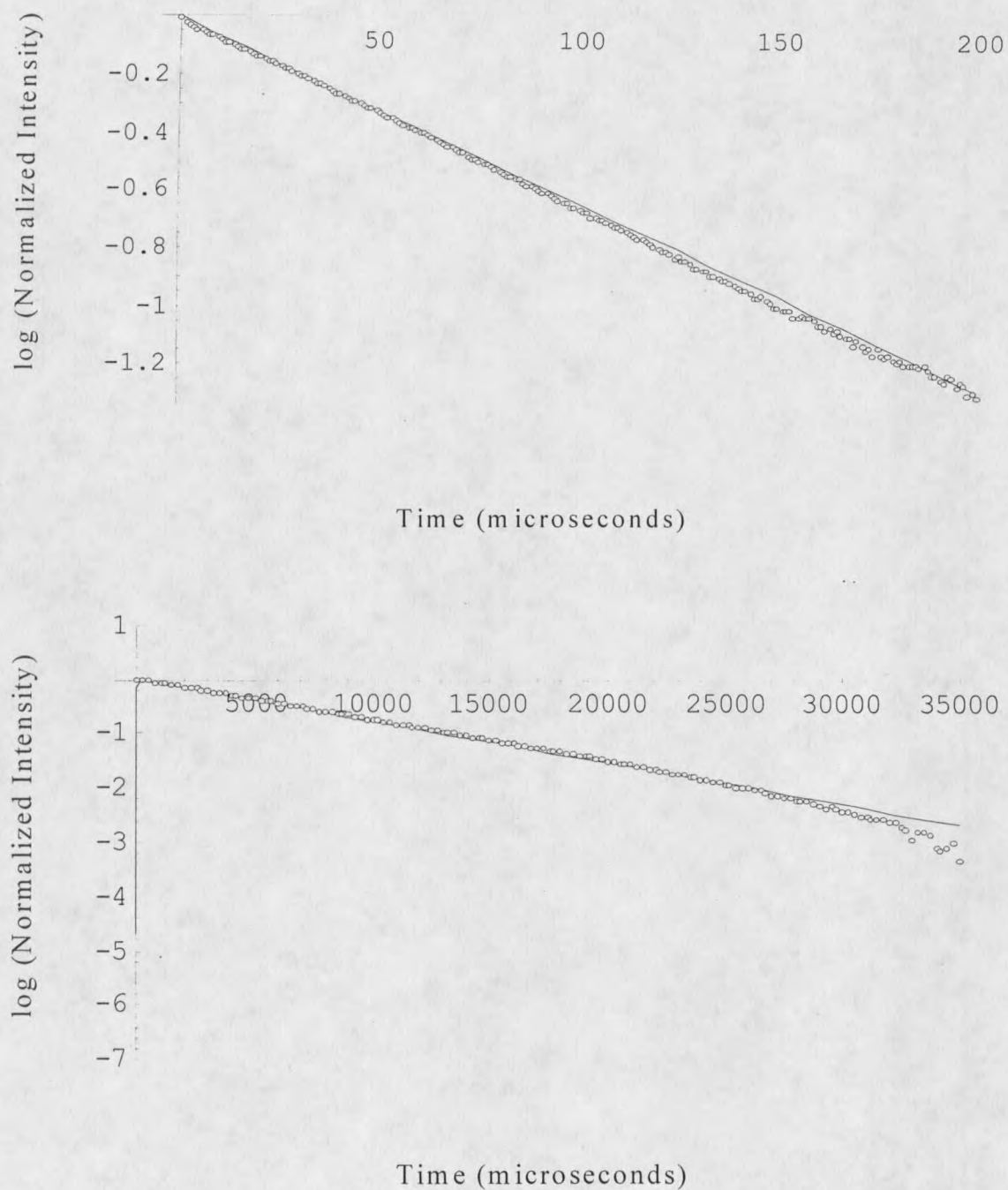


Figure 40. Logarithmic Plots of Decay from the $^4I_{11/2}$ Manifold (top) and $^4I_{13/2}$ Manifold of 0.5% Er:LuAG. The solid lines are modeled decay, and the points are experimental data.

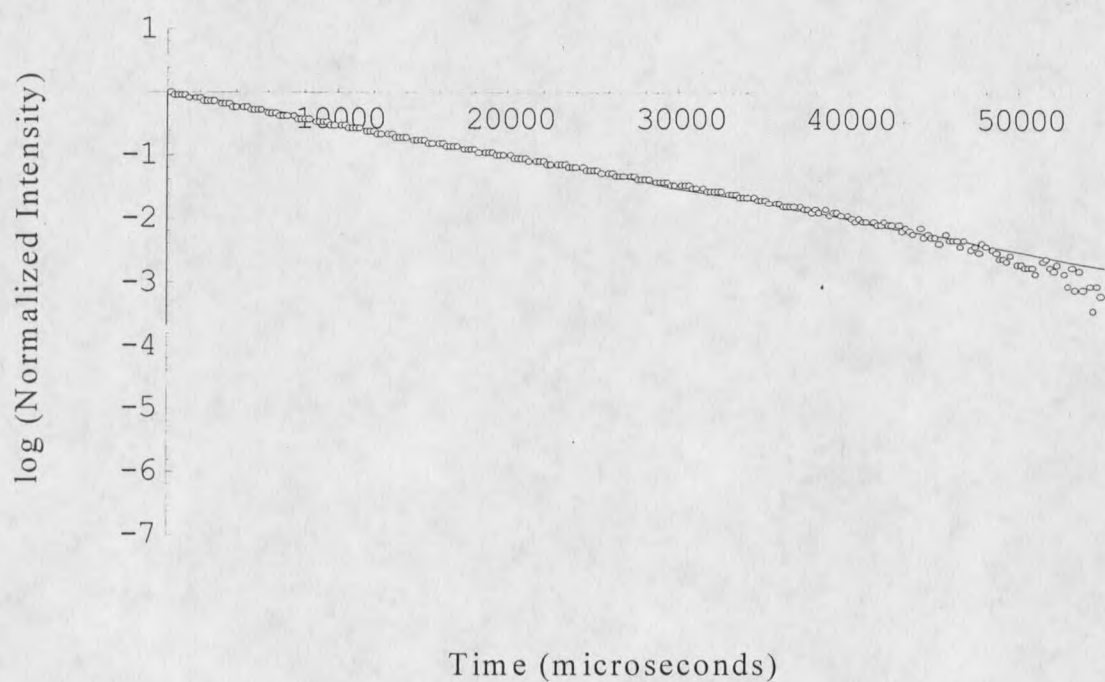
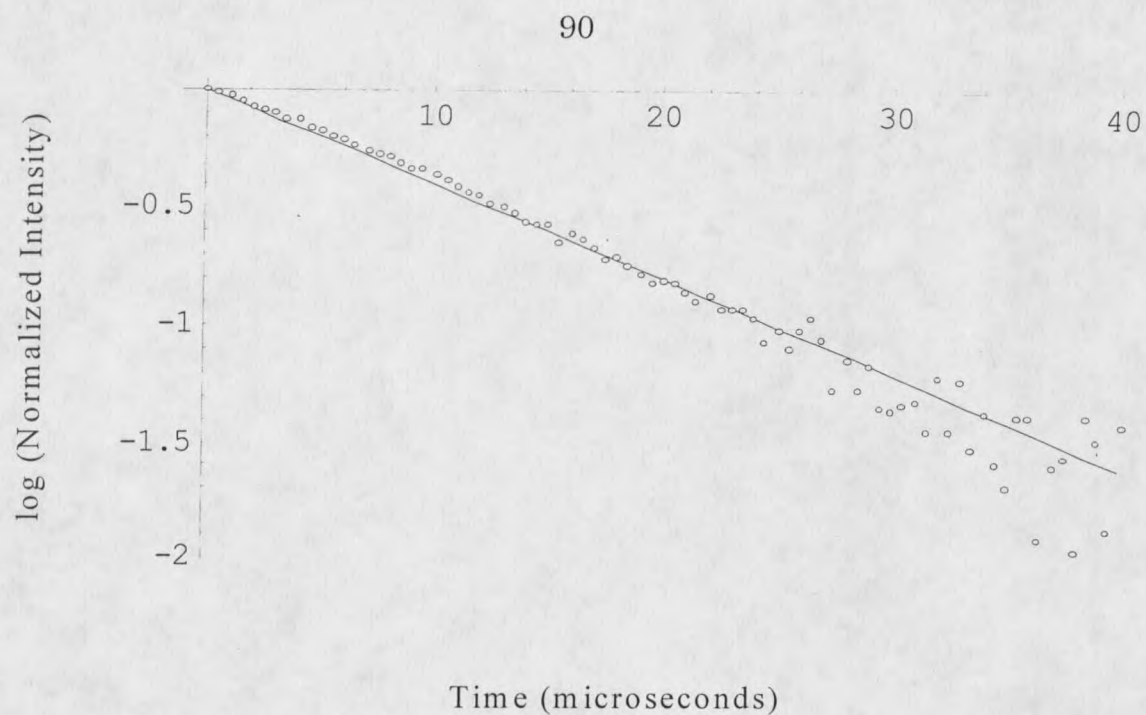


Figure 41. Logarithmic Plots of Decay from the $4I_{11/2}$ Manifold (top) and $4I_{13/2}$ Manifold of 2% Er:YSO. The solid lines are modeled decay, and the points are experimental data.

$^4S_{3/2}$ excitation

The decay transitions considered for the case of $^4S_{3/2}$ excitation are shown in Figure 42. As was the case with the $^4I_{11/2}$ model, the radiative processes are indicated by solid lines, the wavy lines indicate multiphonon relaxation, and the manifolds will be referred to as levels 0 through 5 in order of increasing energy. Rate equations for the populations of the six manifolds are expressed as follows:

$$\frac{dN_5}{dt} = -(W_{54} + A_{53} + A_{52} + A_{51} + A_{50})N_5 \quad (8)$$

$$\frac{dN_4}{dt} = W_{54}N_5 - W_{43}N_4$$

$$\frac{dN_3}{dt} = A_{53}N_5 + W_{43}N_4 - W_{32}N_3$$

$$\frac{dN_2}{dt} = A_{52}N_5 + W_{32}N_3 - (A_{20} + W_{21} + A_{21})N_2$$

$$\frac{dN_1}{dt} = A_{51}N_5 + (A_{21} + W_{21})N_2 - (A_{10} + W_{10})N_1$$

$$\frac{dN_0}{dt} = A_{50}N_5 + (A_{10} + W_{10})N_1 + A_{20}N_2$$

N_i = population of level i

A_{ij} = rate constant for spontaneous radiative emission from manifold i to j

W_{ij} = multiphonon emission from manifold i to j

Total volume balances around levels 1,2,3,and 4 (similar to Equation 4) can be stated as follows:

$$A_{51} + W_{21} + A_{21} = A_{10} + W_{10} \quad (9)$$

$$A_{52} + W_{32} = A_{21} + W_{21} + A_{20}$$

$$A_{53} + W_{43} = W_{32}$$

$$W_{54} = W_{43}$$

The W_{10} values for each material were the same ones used in the calculations for $^4I_{11/2}$ excitation in the previous section. Once W_{10} (and therefore W_{10}) were determined, the values of the other W_{ij} could be calculated by rearranging the Equations (9) and solving them sequentially as follows:

$$W_{54} = W_{43} = W_{10} + A_{10} + A_{20} - A_{51} - A_{52} - A_{53}$$

$$W_{32} = A_{53} + W_{43}$$

$$W_{21} = A_{10} + W_{10} - A_{51} - A_{21}$$

The A_{ij} are calculated from the experimental data using the same method utilized for $^4I_{11/2}$ excitation (described in the previous section). Results specific to the three samples modeled are presented in the following paragraphs.

For the 4% Er:YAG sample, branching ratios for the $^4I_{11/2}$ and $^4S_{3/2}$ manifolds are calculated using equations analogous to Equation 6 and are listed in Table 9. The branching ratios were also calculated using the experimental and theoretical radiative lifetimes for comparison with the total volume integral calculations. The relative branching ratio of A_{50} , A_{51} , A_{52} , and A_{53} was obtained from Table 5 while the relative branching ratio for A_{20}

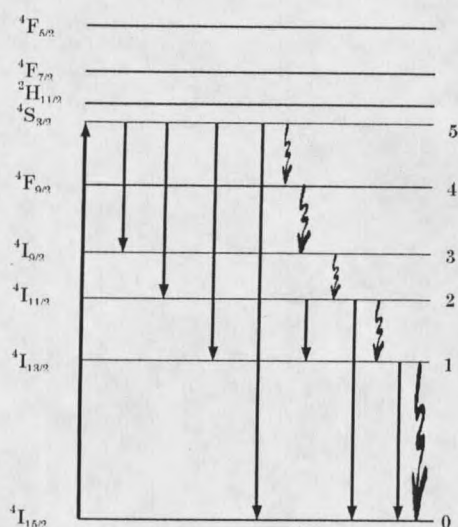


Figure 42. Decay Processes Following $^4S_{3/2}$ Excitation.

and A_{21} was obtained from emission data following $^4S_{3/2}$ pumping, to eliminate potential effects from population in other levels that might cause deviation from the $^4I_{11/2}$ manifold branching ratio after direct $I_{11/2}$ excitation. These branching ratios are also listed in Table 9 under “using theoretical radiative lifetime”. For both levels, the total volume integral method predicts less nonradiative depopulation than would be expected from comparison of the experimental and theoretical lifetimes.

The total volume integral approach was also used to determine branching ratios for the 2% Er:YSO and the 0.5% Er:LuAG samples. The Er:YSO results are presented in Table 10, and the Er:LuAG results are in

Table 9. Branching Ratios for Decay from the $^4S_{3/2}$ and $^4I_{11/2}$ Manifolds in 4% Er:YAG following $^4S_{3/2}$ Excitation.

<u>Transition</u>	<u>Using Total Volume Integration</u>	<u>Using Theoretical Radiative Lifetime</u>
W_{21}	0.834	0.993
A_{21}	4.22×10^{-3}	3.32×10^{-4}
A_{20}	0.162	6.87×10^{-3}
W_{54}	0.750	0.985
A_{53}	1.57×10^{-3}	1.65×10^{-4}
A_{52}	3.27×10^{-3}	1.97×10^{-4}
A_{51}	0.0656	4.05×10^{-3}
A_{50}	0.180	0.0111

Table 11. The Er:YSO branching ratios calculated from total volume integrals are compared with those calculated by comparison of experimentally determined lifetimes with theoretical radiative lifetimes calculated by Moncorge *et al* (39). The branching ratios from the two methods showed improved agreement over the Er:YAG results (see Table 10).

The rate constants A_{ij} and W_{ij} were calculated for all three materials modeled using Equation 7 and the overall experimental rate constants k_i and are listed in Table 12. These values were used in the set of simultaneous differential equations which were then numerically solved using Mathematica.

Table 10. Branching Ratios for Decay from the $^4S_{3/2}$ and $^4I_{11/2}$ Manifolds in 2% Er:YSO following $^4S_{3/2}$ Excitation.

<u>Transition</u>	<u>Using Total Volume</u> <u>Integration</u>	<u>Using Theoretical Radiative</u> <u>Lifetime</u>
W_{21}	0.997	0.998
A_{21}	1.93×10^{-4}	1.68×10^{-4}
A_{20}	2.89×10^{-4}	1.71×10^{-3}
W_{54}	0.992	0.994
A_{53}	7.04×10^{-5}	8.06×10^{-5}
A_{52}	1.23×10^{-4}	9.20×10^{-5}
A_{51}	2.86×10^{-3}	2.21×10^{-3}
A_{50}	4.97×10^{-3}	3.83×10^{-3}

The A_{10} and W_{10} values for all three materials are the same as those used in the $^4I_{11/2}$ model (see Table 8). The W_{32} and W_{43} values of $3.5 \mu\text{sec}^{-1}$ for 2% Er:YSO were obtained from experimental lifetime data for 1% Er:YSO taken after direct excitation into the respective levels (39). Since similar data for W_{32} was not available for Er:YAG or Er:LuAG, the same value was used for these materials. As long as W_{32} has a significantly higher value than $1/\tau_2$ (the sum of A_{20} , A_{21} , and W_{21}), which corresponds to the significantly shorter lifetime of the $^4I_{9/2}$ level compared to the $^4I_{11/2}$ level, error in the estimated value of W_{32} will have little effect on the results presented by the model. The

value for W_{43} used for Er:YAG and Er:LuAG of $0.833 \mu\text{sec}^{-1}$ was obtained from experimental data taken using a 3% Er:YAG sample (52).

Table 11. Branching Ratios for Decay from the $^4S_{3/2}$ and $^4I_{11/2}$ Manifolds in 0.5% Er:LuAG Following $^4S_{3/2}$ Excitation.

<u>Transition</u>	<u>Using Total Volume Integration</u>
W_{21}	0.993
A_{21}	5.13×10^{-4}
A_{20}	6.58×10^{-3}
W_{54}	0.996
A_{53}	4.17×10^{-5}
A_{52}	5.06×10^{-5}
A_{51}	1.02×10^{-3}
A_{50}	2.79×10^{-3}

The model-generated logarithmic decay curves for all three emitting levels of each material are compared with experimental data in Figures 43 through 47. Both linear and logarithmic plots are shown for the 2% Er:YSO sample, while only logarithmic plots are shown for the Er:YAG and Er:LuAG materials. The decay curves generated by the model show good overall agreement with the experimental data with a few notable exceptions. Since

Table 12. Rate Constants for Relaxation following $^4S_{3/2}$ Pumping (μsec^{-1}).

<u>Transition</u>	<u>4% Er:YAG</u>	<u>2% Er:YSO</u>	<u>0.5% Er:LuAG</u>
A_{10}	7.69×10^{-5}	1.16×10^{-4}	8.77×10^{-5}
W_{10}	7.69×10^{-5}	—	8.77×10^{-5}
A_{20}	2.15×10^{-3}	2.70×10^{-4}	9.71×10^{-5}
A_{21}	6.30×10^{-5}	1.80×10^{-5}	7.58×10^{-6}
W_{21}	1.25×10^{-2}	9.30×10^{-2}	1.47×10^{-2}
W_{32}	3.50	3.50	3.50
W_{43}	0.833	3.50	0.833
A_{50}	1.63×10^{-2}	1.38×10^{-3}	2.27×10^{-4}
A_{51}	5.96×10^{-3}	7.95×10^{-4}	8.28×10^{-5}
A_{52}	2.97×10^{-4}	3.42×10^{-5}	4.12×10^{-6}
A_{53}	1.43×10^{-4}	1.96×10^{-5}	3.39×10^{-6}
W_{54}	6.82×10^{-2}	0.276	0.810

only first order terms are listed in the rate equations, the logarithmic decay plots calculated using the model are straight lines. Curvature in the experimental data (attributed primarily to baseline correction error earlier in this chapter) is responsible for long term deviation from predicted behavior in several of the log plots. Also, the calculated decay curve for the $^4I_{13/2}$ level in 4% Er:YAG (see top of Figure 46) differs significantly from the experimental

data. The A_{10} and W_{10} values used in the model were the same as those used in the $^4I_{11/2}$ model, and correspond to a lifetime of 6.5 msec for the $^4I_{15/2}$ level, while the lifetime determined using the experimental data from the top of Figure 46 is 10.6 msec. This longer experimental lifetime is closer in agreement with the 9 msec lifetime level obtained on a 3% Er:YAG sample by Zhekov *et al* (52) following excitation to the $^4S_{3/2}$ level. It is possible that cross relaxation processes occurring at the higher excitation level (and not at the lower one) are partially responsible for the longer experimental lifetime, though if this were so these effects would be expected to result in more curvature in the logarithmic plot than is seen. It is also possible that the wide range of experimentally determined lifetimes results from radiation trapping, where trapping of the emitted photons lengthens the apparent emission lifetime. Deviations of this order, expected to have been caused by radiation trapping, were seen by Moncorge *et al* in low concentration Er:YSO samples (39). More work will be needed to determine the cause or causes of this deviation. Finally, the predicted and experimental logarithmic decay curve from the $^4I_{11/2}$ level in 0.5% Er:LuAG show poor long term agreement. Examination of a linear plot of the data shows this deviation is attributable to baseline correction error.

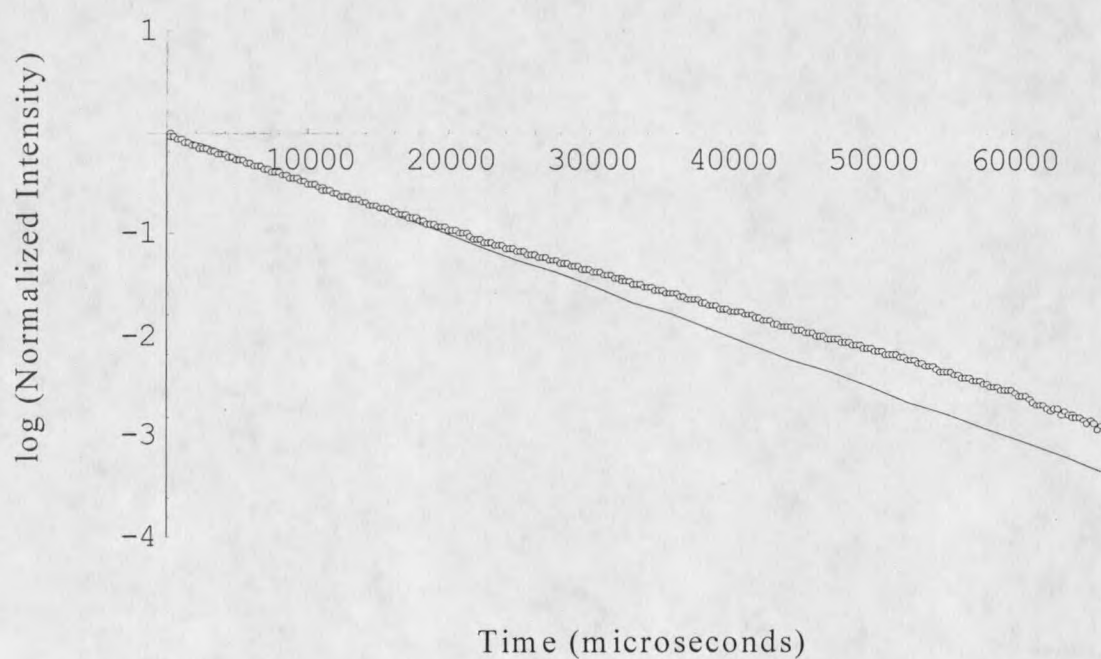
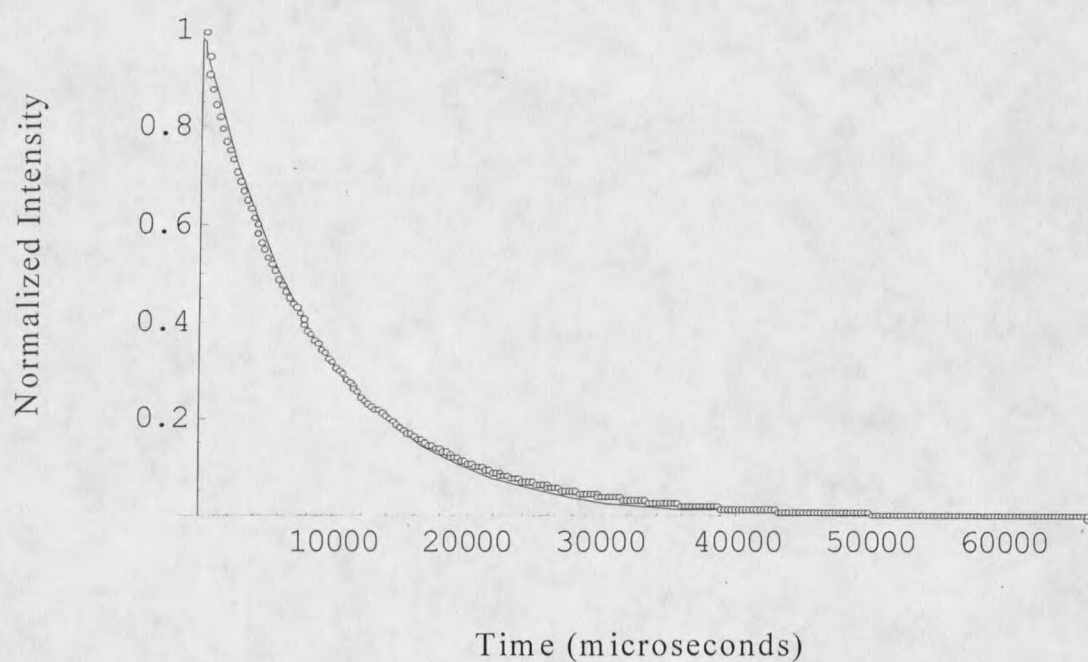


Figure 43. Linear (top) and Log Plots of Decay from the $^4I_{13/2}$ Manifold (Level 1) of 2% Er:YSO. The solid lines are modeled decay, and the points are experimental data.

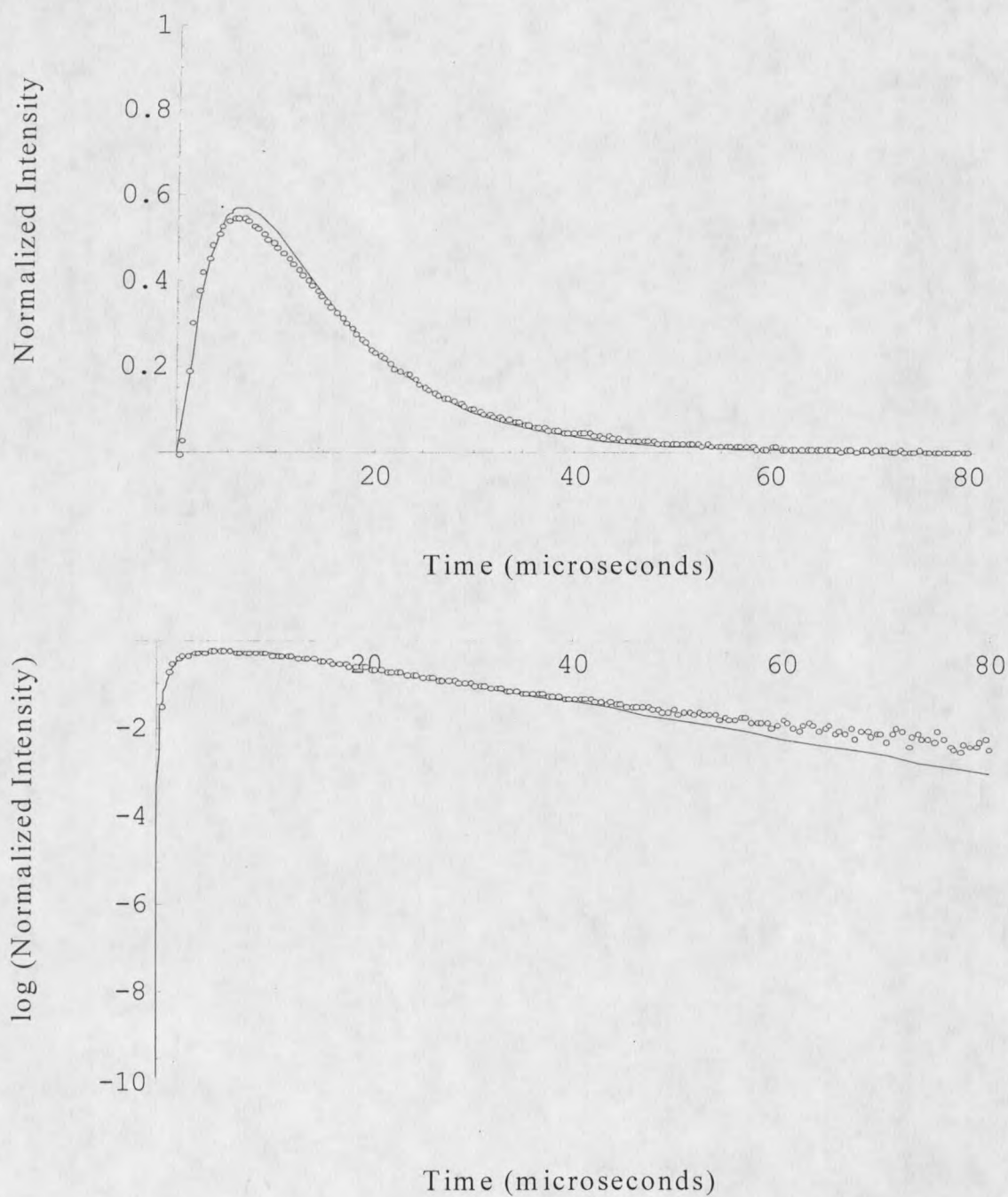


Figure 44. Linear (top) and Log Plots of Decay from the $^4I_{11/2}$ Manifold (Level 2) of 2% Er:YSO. The solid lines are modeled decay, and the points are experimental data.

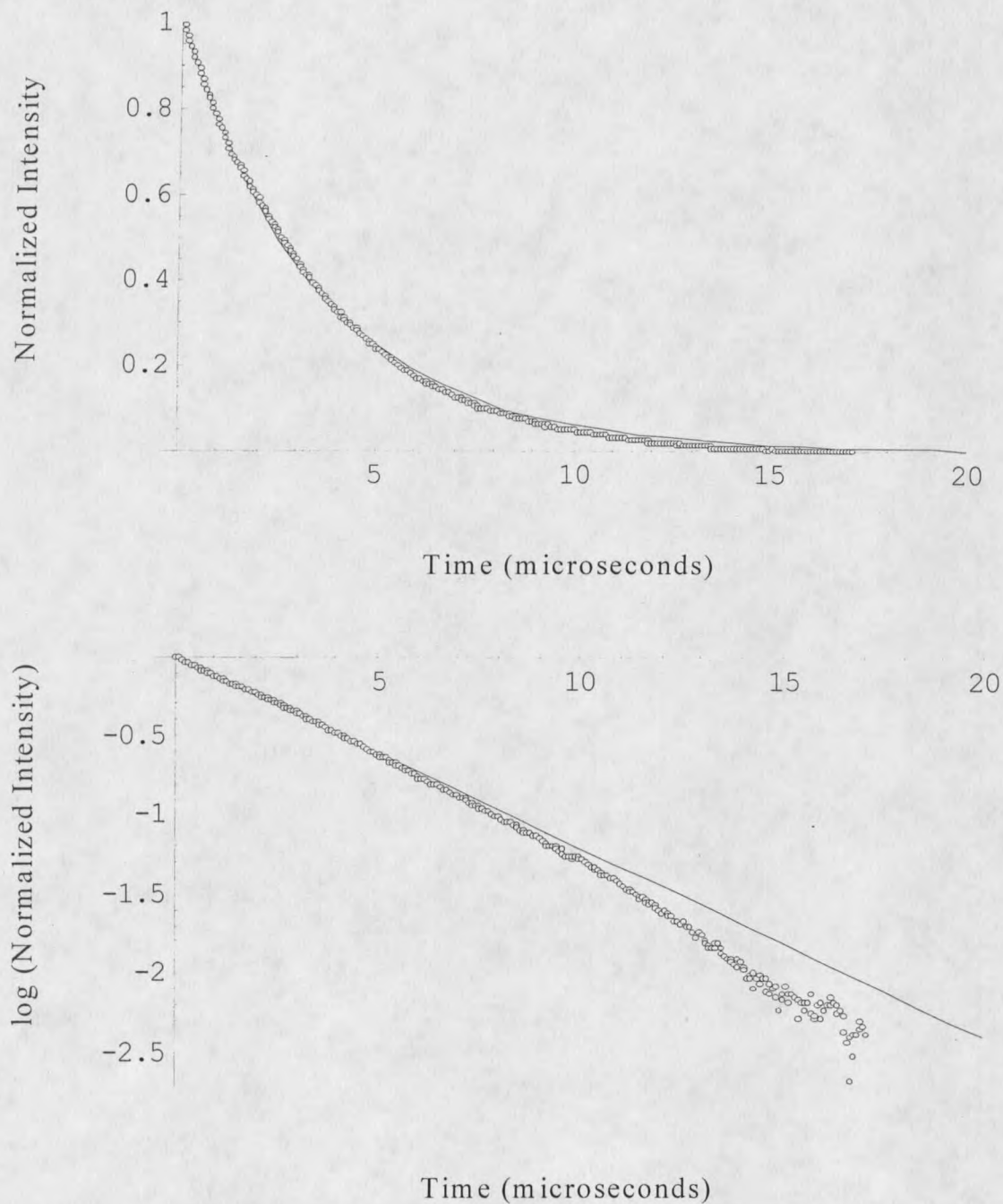


Figure 45. Linear (top) and Log Plots of Decay from the $4S_{3/2}$ Manifold (Level 5) of 2% Er:YSO. The solid lines are modeled decay, and the points are experimental data.

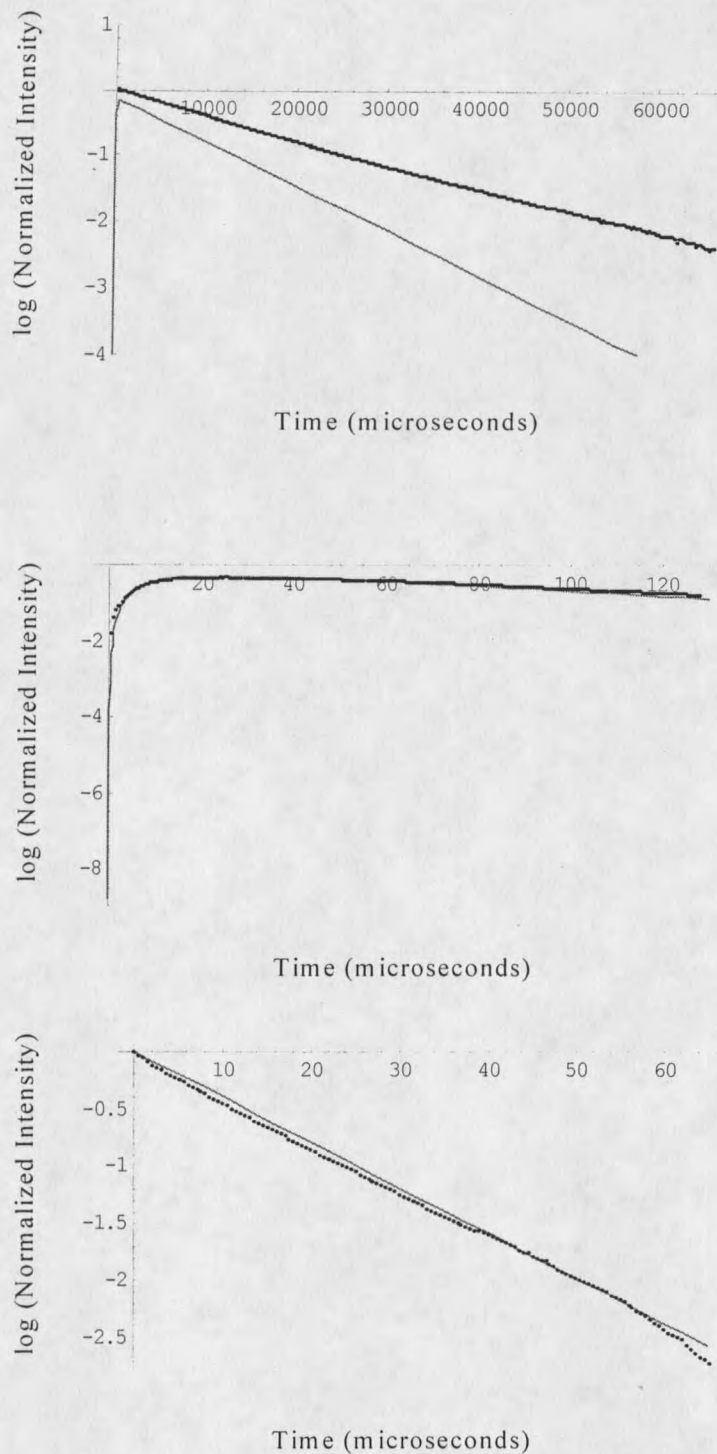


Figure 46. Log Plots of Decay from the $4I_{13/2}$ (top), $4I_{11/2}$ (center), and $4S_{3/2}$ Manifold of 4% Er:YAG. The solid gray lines are modeled decay, and the black points are experimental data.

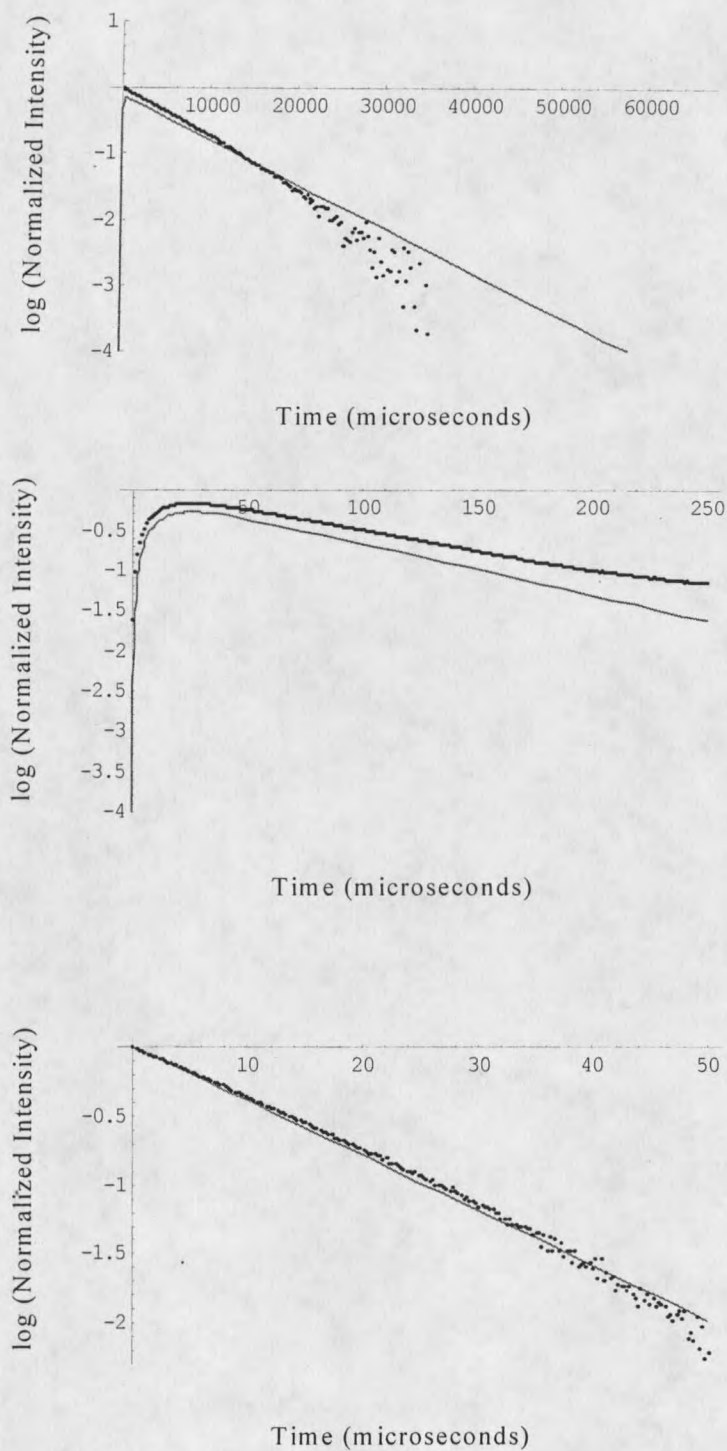


Figure 47. Log Plots of Decay from the $4I_{13/2}$ (top), $4I_{11/2}$ (center), and $4S_{3/2}$ Manifold of 0.5% Er:LuAG. The solid gray lines are modeled decay, and the black points are experimental data.

CHAPTER 5

SUMMARY

Spectroscopic analysis and kinetic modeling of relaxation processes have been completed for 2.1% and 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG at room temperature. IR and visible absorption, continuous emission, and temporally resolved emission spectra were obtained for all the materials studied using Fourier transform spectroscopy. Experimental emission lifetimes determined from the temporally resolved spectra were compared with theoretical radiative lifetimes obtained from quantum-mechanical calculations using Morrison's code to generate rate constants for the radiative and nonradiative processes involved in relaxation.¹ The rate constants were also determined via a newly developed method (using "total volume integrals"). The rate constants were plugged into sets of coupled differential equations and numerically solved using the fifth order Runge-Kutta method in Mathematica. Each of these components of the study are discussed briefly in the following paragraphs.

The experimental setup was for the most part effective in obtaining the necessary data for the investigation. The multiplex advantage of the Fourier transform method was particularly of value. In addition to providing

the usual benefit of reducing experimental time, it allowed the monitoring of several emission bands at once in the temporally resolved experiments. This capability greatly facilitated determination of branching ratios and enabled calculation and balance of the total volume integrals used in the modeling calculations. Additionally, it aided in assignment of emission transitions since transitions originating from the same manifold have a similar decay profile. The tunable source also aided in assignment and kinetic modeling by allowing the "turning on and off" of upper level emission bands by adjusting excitation wavelength. Furthermore, the system enabled compilation of room temperature absorption and emission spectra, including temporally resolved emission, following excitation into eight different excited states of erbium in the crystal hosts. These capabilities enabled compilation of the data needed to characterize the erbium doped materials studied.

Emission transitions were observed from three different manifolds: $^4I_{13/2}$, $^4I_{11/2}$, and $^4S_{3/2}$. Of these, the latter two had multiple terminal manifolds, resulting in two emission bands from $^4I_{11/2}$ and four bands from the $^4S_{3/2}$ level. Experimental emission lifetimes for all three levels were determined directly from the temporally resolved spectra. The $^4I_{13/2}$ lifetimes were found to be 6.6, 6.5, 8.6, and 5.7 msec for 2.1% and 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG, respectively. Lifetimes of 67.3, 10.5, and 67.7 μ sec were observed for 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG, respectively for the $^4I_{11/2}$ state. Experimental lifetimes of 10.7, 3.5, and 12.3

μsec were observed for the $^4\text{S}_{3/2}$ state in 4% Er:YAG, 2% Er:YSO, and 0.5% Er:LuAG. These experimental lifetimes provided overall rate constants used in the kinetic modeling.

Once excitation had taken place, relaxation was dominated by multiphonon emission and radiative emission, both exponential processes. Therefore only exponential relaxation processes were included in the kinetic model. The lack of nonexponential relaxation processes was probably largely due to the relatively low erbium concentration of the materials studied. It is well established that cross relaxation and upconversion occur in erbium doped into a variety of crystal hosts; however, these effects are more pronounced at higher concentrations (often 10% or more). Some gradual, long-term curvature attributable to baseline correction error was seen in the logarithmic decay plots.

One of the disadvantages of the Fourier transform method is the baseline noise introduced by the intensity fluctuations (this can also be of benefit as it removes noise from the signal and spreads it all over the spectrum) which can make baseline correction difficult. One possible way to address this difficulty is to use filters to reduce the baseline noise. However, this use of filters comes at the expense of the advantages provided by the ability to observe multiple emission bands simultaneously.

Quantum-mechanical calculations (using Morrison's code) allowed calculation of theoretical radiative lifetimes. Comparison of the experimental

lifetimes (due to both radiative and nonradiative relaxation processes) with the theoretical lifetimes for each level yielded the relative contribution of radiative and nonradiative processes to relaxation. This, combined with the radiative branching ratios obtained from the spectra, enabled determination of radiative and nonradiative rate constants that could be utilized for kinetic modeling.

Alternatively, the radiative and nonradiative rate constants were determined using the "total volume integral" method. The simultaneously time and frequency resolved spectra were integrated to provide intensity "volumes" under the three dimensional emission bands. "Balances" written around each energy level allowed for determination of branching ratios and rate constants. The advantage of this method is that a theoretical radiative lifetime is only needed for the first excited state (to provide the nonradiative contribution to relaxation from the level) rather than every energy level involved in the model. Alternatively, the nonradiative contribution to relaxation from the first excited state could be provided by comparison of cold (liquid helium) and room temperature experimental lifetimes. Comparison of the total volume integral method with the method utilizing theoretical lifetimes for all levels showed good agreement between the two methods.

Finally, the rate constants obtained by these methods were plugged into a set of coupled differential equations and numerically solved using the fifth order Runge-Kutta method in Mathematica. Modeling was completed

for all three host materials for the cases of excitation to the $^4I_{11/2}$ and $^4S_{3/2}$ levels. These levels were chosen since they were upper state levels that were initial levels for emission transitions. Good agreement with the experimental temporal behavior was obtained (including emission *rises* as well as decays in the case of the $^4S_{3/2}$ model) indicating the validity of the results.

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APPENDIX A

PROCEDURES USED IN QUANTUM-MECHANICAL MODELING OF
LASER MATERIALS

Introduction

This appendix describes the procedures used in the operation of computer programs developed by Morrison *et al* to predict energy levels and radiative transition probabilities, branching ratios, and lifetimes. The method has the capability to predict Stark levels for a rare earth ion in a crystalline host and calculate theoretical radiative transition intensities (either line-to-line or manifold-to-manifold). The transition intensity calculations enable determination of theoretical branching ratios and radiative lifetimes. The theoretical background of the method is discussed briefly in Chapter 1 and in more detail in References 37, 39, and 78-83. The calculations become less valid as rare earth concentration in the crystalline host is increased, since they do not consider the effects of the rare earth ion on the host. The following sections outline the functions and relationship of the computer programs that do the calculations and give directions for running each program.

Program File Organization

The calculations can be accomplished with the use of the three FORTRAN programs LATSUM, ROTATE, and NPHASE. LATSUM uses host x-ray data to calculate values for the crystal field components A_{nm} at the

rare earth site in the host crystal lattice. It works by using point charges and completing a summation over the crystal lattice. ROTATE takes the A_{nm} output from LATSUM and rotates it to the coordinate system necessary for use in the program NPHASE, providing a new, equivalent set of suitable A_{nm} . The program NPHASE can be run in different modes of operation depending on what input data is available and what output is desired from the calculations. NPHASE can use known experimentally determined energy levels and free ion wavefunctions (already contained in the code) to fit a set of crystal field parameters B_{nm} to account for host effects on the rare earth ion. Alternatively, it can be used to use a set of B_{nm} and a free ion wavefunction to calculate energy levels, radiative lifetimes, transition intensities, and branching ratios for a laser material. These different modes lend themselves to a number of computational strategies; flowsheets for two commonly used strategies are shown in Figures A1 and A2. The strategy shown in Figure A2 is useful if calculations are desired for a material for which experimental data is not readily available (Er:GGG, for example), but reliable data is available for the same active ion in a similar host (Er:YAG, for example)

Operation of the ProgramsLATSUM

The x-ray data necessary to run LATSUM are tabulated for many commonly used crystalline hosts in Reference 79. Unless otherwise noted, the input data necessary to run LATSUM are contained in this reference.

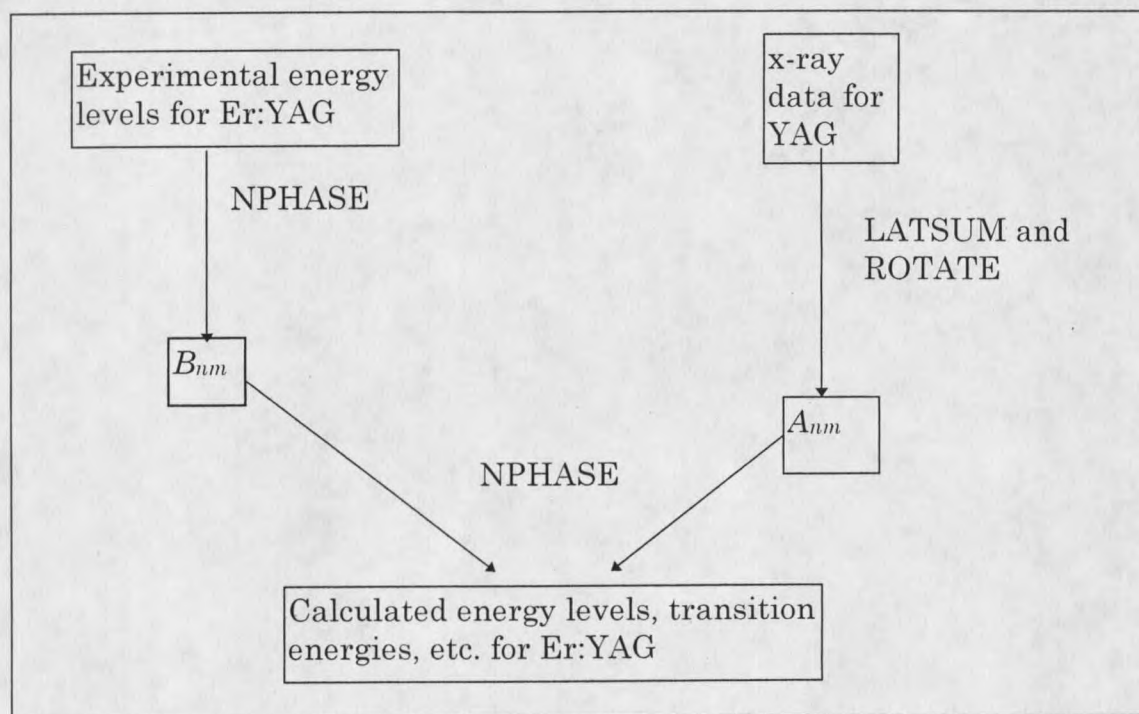


Figure A1. Flowsheet for Calculations when Experimental Energy Level Data are Available.

An example using LATSUM to determine A_{nm} for YAG follows. Once the program is running, it prompts the user for a title, simply for identification purposes; therefore, any input is suitable. Next, the program prompts for input of the space group number corresponding to the host space

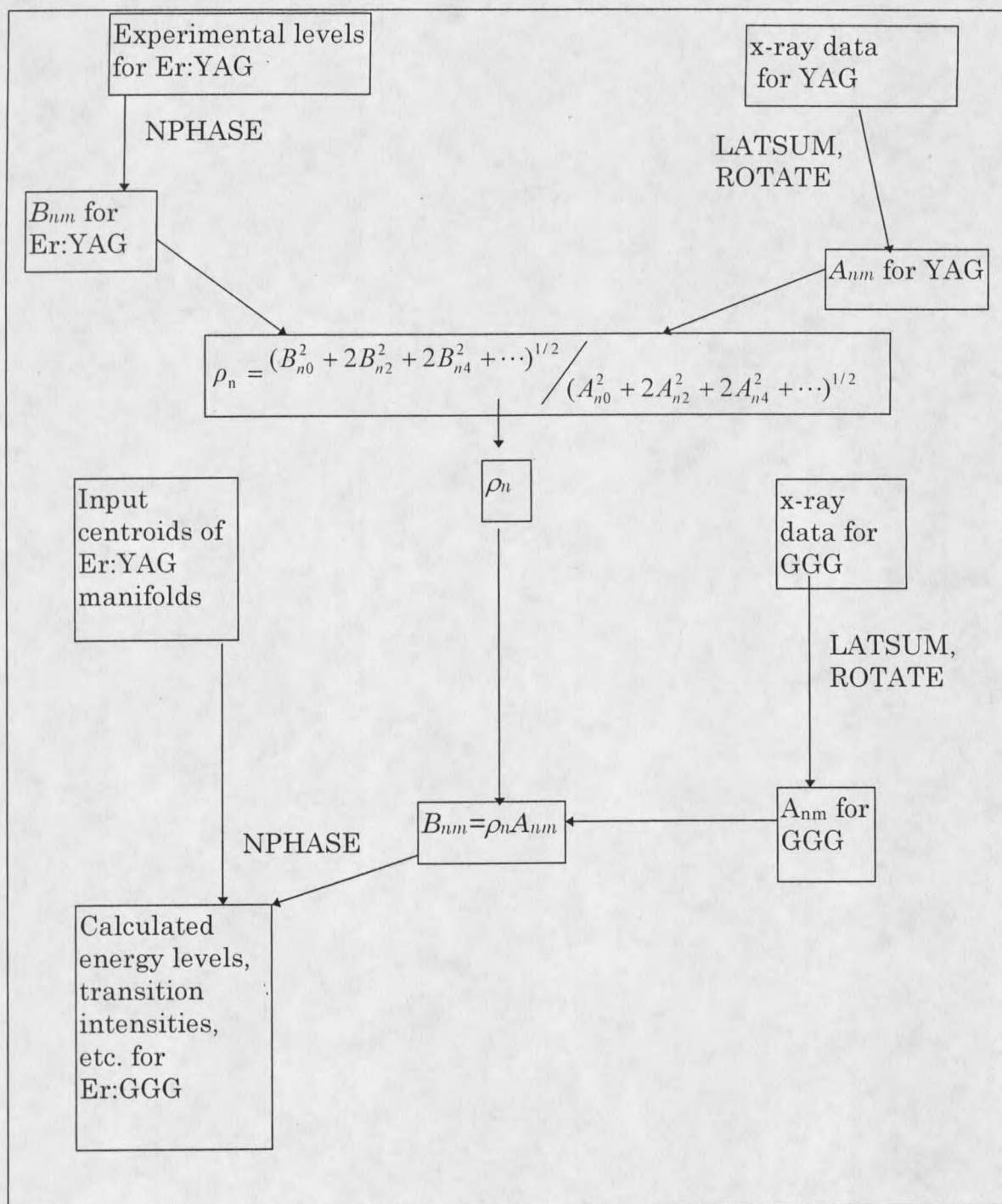


Figure A2. Flowsheet for Calculations when Experimental Energy Level Data for the Rare Earth Ion in a Similar Host are Available.

group in the International Tables (from #1 to #230, corresponding to the possible number of space groups). For YAG, this number is 230. The program then asks for the x-ray data necessary for the crystal ($a, b, c, \alpha, \beta, \gamma$ in this YAG example). The user should then type in the values of the parameters in the same order in which they were listed, i.e. 12,12,12,90,90,90. Next, the user is prompted for the number of sites. Since YAG has one yttrium site, two aluminum sites, and one oxygen site, the number 4 should be entered. The program then requests the label for site 1. The user can enter Y for yttrium. (The order is arbitrary: Al1, Al2, or O would also be suitable entries.) In response, the program asks for x, y, z, q, α for site 1. Reference 79 supplies the x, y , and z parameters; the ionic charge should be entered for q , and α denotes the polarizability for the ion. The corresponding input is 0,0.25,0.125,3,0. The polarizability input is somewhat arbitrary (80). After receiving that input, the program asks for the label for site 2, an appropriate response would be Al1. NPHASE will then again request values for x, y, z, q, α ; the appropriate response is 0,0,0,3,0. Similarly, the program will then ask for labels and x, y, z, q , and α for sites 3 and 4, respectively. Once data for the crystal sites is entered, NPHASE gives the user the option of printing nearest neighbor distances. The program then asks for the centering point in the unit cell. A point must be chosen such that the total dipole moment of the unit cell is zero. The choice will be symmetry dependent; for YAG 0,0,0 is suitable input. For more detail, see Reference

80. Finally, the program asks for the origin site, which is the site at which you wish to evaluate the A_{nm} . This will be the rare earth site, which in the case of the YAG example will be the yttrium site, arbitrarily chosen as site 1. Therefore, the input to this query is 1. At this point, LATSUM will run, and will automatically create the output file FOR009.DAT; it is recommended to rename the output file after LATSUM is run.

ROTATE

ROTATE takes the A_{nm} output from LATSUM and rotates it to the coordinate system necessary for use in the program NPHASE, which requires that the crystallographic c axis is parallel to the symmetry axis of the rare earth site. As a result, the program provides a new, equivalent set of A_{nm} for the "correct" coordinate system.

When ROTATE is started, it first asks for the name desired for the output file. Any name is suitable here; I normally named these files the crystal formula followed by the extension "ROT", as in YAG.ROT. Secondly, the program will prompt for the A_{nm} components (which unfortunately must be entered manually at this time) by asking for the tensor rank k , where $k=n$ in A_{nm} . A response of "1" will cause the program to ask, one by one, for all A_{1m} . After all A_{1m} are entered, the program will again prompt for the tensor rank, at which time 2 can be entered, causing the computer to ask for the A_{2m} . When all A_{nm} have been entered in this fashion, the user can enter "0"

in response to the tensor rank prompt, which signals to the program that all the A_{nm} are entered. After completion of this task, the program requests the input of three rotation angles— α, β , and γ . The program will then print out a set of rotated A_{nm} , and ask whether the user wants to try another set of rotation angles. Before actually trying rotation angles, it is helpful to enter 0,0,0 as the first set of “rotation angles”, since this results in a printout of the unrotated A_{nm} , giving the user the opportunity to check the manually entered A_{nm} for accuracy. Different sets of rotation angles should be tried until the properly rotated A_{nm} are obtained (criteria for properly rotated A_{nm} are described in the next paragraph); after which time, “no” can be typed when the program asks about trying another set of angles. The output will then be saved to the filename suggested by the user.

The properly rotated A_{nm} can be obtained by using the following procedure:

1. Choose the correct A_{nm} component to evaluate for each set of rotation angles: the A_{nm} to evaluate should have even, nonzero n and m , and it should not be forced to have a value of zero by symmetry. Of the components that meet these two criteria, the one with minimum n and m should be chosen.
2. The correct set of rotation angles will rotate the coordinate axes such that particular A_{nm} chosen (i.e. A_{22}) from step one become real and positive. Different sets of rotation angles should be tried until

this criteria is met. Rotation angles to try are given by the following equation:

$$\text{angle} = \pm \frac{1}{n} \arctan \left(\frac{\text{Im } A_{nm}}{\text{Real } A_{nm}} \right) \pm \frac{\pi}{n}$$

where n is a positive integer.

3. The angles given by the equation in Step 2 can be tried in any combination for rotation angles α , β , and/or γ .

NPHASE

NPHASE is the program that does the bulk of the calculations and can be run in different modes of operation, depending on what data is available and where the user is in the computational analysis (see Figures A1 and A2). When the program is started, it first prompts for a title. The choice of a title is arbitrary and has no bearing on the operation of the program. Once the title is entered, the user is directed to enter the symmetry group label at the rare earth site of the crystal host. For garnet hosts, the proper label is D2. Symmetry group labels are available in Reference 79. The program then asks whether the user wants to fit experimental energy levels. An answer of "yes" will direct NPHASE to accept input of Stark level energies in cm^{-1} , which it will use to fit a set of crystal field parameters B_{nm} to account for the host crystal field splitting of the free ions energy levels into manifolds. The program allows the user to specify the number of iterations to be used in the

fit and to choose whether the fit should be done using all the Stark levels or just the centroids of the manifolds.

NPHASE requires B_{nm} , the identity of the rare earth ion (Er, Nd, Tm, etc) and odd n A_{nm} to complete calculations of theoretical Stark levels, radiative lifetimes, and line-to-line transition probabilities. The B_{nm} can come either from a previous run of NPHASE that fits B_{nm} to experimental energy levels or from rotated A_{nm} and the relationship $B_{nm} = \rho_n A_{nm}$. The B_{nm} can either be entered manually or by selecting a file already containing the parameter values. If the B_{nm} are entered manually, NPHASE offers the option of saving them to a file of name "filename.BNM.PARM". NPHASE will then prompt the user for the identity of the rare earth ion. After the ion is selected, NPHASE will suggest a set of "default states" which are the manifolds (listed by term symbol) to be included in the calculations. The user is given the option of adding or deleting manifolds from consideration in the calculations.

Once NPHASE has these input parameters, it will do the calculations and save the output as file REHOME.DAT. Standard output includes energies of the centroids of the manifolds included in the calculations. Optional output includes radiative lifetimes for each manifold, branching ratios for transitions between manifolds, Stark-level-to-Stark-level transition probabilities (both electric dipole and magnetic dipole), and the Judd-Ofelt

parameters Ω_k . The optional output is selected by answering questions posed by the program.

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