The characterization of the radiative energy transfer process among holmium(3+) ions in yttrium(3) aluminum(5) oxygen(12)

Terri Lynn Lazarus
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THE CHARACTERIZATION OF THE RADIATIVE ENERGY TRANSFER
PROCESS AMONG Ho\(^{3+}\) IONS IN Y\(_{3}\)Al\(_{5}\)O\(_{12}\)

A Dissertation
Presented to
The Faculty of the Department of Physics
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Doctor of Philosophy

by
Terri Lynn Lazarus
1995

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NASA Langley Research Center
APPROVAL SHEET

This dissertation is submitted in partial fulfillment of
the requirements for the degree of

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ABSTRACT

This research comprises a comprehensive spectroscopic study of the characteristics of the solid state crystal YAG (Yttrium Aluminum Garnet) singly doped with Ho (Holmium) ions. An important area of solid state laser crystal research is the determination and optimization of the processes within these laser crystals which lead to efficient laser action. In most laser crystals, there is a donor ion such as Tm (Thulium) and an acceptor ion such as Ho. The donor ion generally has greater absorption than that of the acceptor at the wavelength of the pump source. The donor ion can transfer this absorbed energy to the lasing manifold, $^5I_7$, of the Ho acceptor ion. A loss process to the 2.1µm laser emission from the $^5I_7$ manifold is the radiative energy transfer of this emission to a neighboring Ho ion. The purpose of this research is to determine the dependence of this radiative energy transfer process on various macroscopic parameters of the YAG:Ho crystals.

Spectral and kinetic data were acquired over a wide range of temperatures and excitation points of the four samples available: YAG:Ho (8.5%), (3%), (1%), and (0.32%). The spectral data include absorption and luminescence. The kinetic data consist of the temporal responses to pulsed excitation.

Models for the spectral and kinetic data were developed and found to agree closely with experimental results. Moreover, these models successfully correlated the Ho - Ho radiative energy transfer with the concentration, temperature, and excitation position parameters of the YAG:Ho crystals. Using these models, one can minimize this loss process by choosing the appropriate crystal parameters and thereby, increase the efficiency of laser action.
THE CHARACTERIZATION OF THE RADIATIVE ENERGY TRANSFER
PROCESS AMONG Ho^{3+} IONS IN Y_{3}Al_{5}O_{12}
INTRODUCTION

Solid-state laser materials have extensive application in areas of research such as wind shear detection and atmospheric analysis, and for these studies a highly efficient, compact, and reliable laser material with an emission wavelength of 2.1μm is desirable. In the process of optimizing the performance of a solid-state laser material, it is useful to study the dynamics of the lasing ion or activator (acceptor), when singly doped into the crystalline host; i.e. without the aid of a sensitizer (donor), or an ion which more strongly absorbs the pump emission and subsequently transfers this energy to the lasing ion. Due to the availability of hosts singly doped with Ho ions, Yttrium Aluminum Garnet (YAG or \( \text{Y}_3\text{Al}_5\text{O}_{12} \)) was selected.

To optimize the laser emission of the Ho ion, it is important to minimize such losses as the radiative energy transfer amongst Ho ions. Therefore, a complete characterization of this process is useful. Energy transfer has been studied in transition metal ion systems, such as alexandrite, ruby, and emerald. Hasan and Manson [1] have reported on the temperature dependence of optical radiative energy transfer among Cr ions in alexandrite at low temperatures and using weakly doped (less than 0.1 at. % \( \text{Cr}^{3+} \)) samples. They found that, at helium temperatures, the crystals exhibit strong photon trapping (reabsorption) and that resonant radiative energy transfer is the dominant transfer mechanism. In addition, they concluded that the trapping had the effect of delaying the relaxation of the \( ^2\text{E} \) excited state from its intrinsic value of 1.3ms to 2 - 2.3ms.
They found that for temperatures above helium, the radiative transfer rate followed a $T^3$ dependence, in which a two-phonon-assisted non-resonant process was in effect. The data at high temperatures seemed to deviate from this dependence. From the theory developed by Holstein et al. [2], the domination of a resonant radiative transfer process in low-temperature limits was proved for Cr$^{3+}$ in emerald and for Pr$^{3+}$ in LaF$_3$. This research on alexandrite complemented earlier work by Selzer et al. [3] and Hasan et al. [4] on chromium-based materials such as ruby and emerald. Holstein et al. [5] calculated phonon assisted radiative energy transfer rates for dilute ruby, verifying the requirement for efficient energy transfer that the sample size be large compared to the mean free path for the photon participating in the transfer process.

The radiative energy transfer among the rare earth Ho ions in YAG has been extensively examined in this research as a function of Ho ion concentration, excitation point or position of the center of the pump beam spot along the sample length, and temperature. The characterization of such radiative energy transfer in terms of these macroscopic parameters provides a concrete means of maximizing the efficiency of the 2.1$\mu$m laser transition.

The summary and mathematical formulation of the various types of energy transfer between two ions, in particular between Ho and Ho, are given in Chapter 1. The spectroscopic and laser characteristics of rare earth ions, and in particular, a description of pertinent chemical and physical characteristics of Ho:YAG are given in Chapter 2. A profile of the experimental implementation and apparati is presented in Chapter 3. The experimental results are given in Chapter 4. The theoretical models of these experiments and their correlation with the results are discussed in Chapter 5. And finally, the conclusions derived
from this research as well as possibilities of future work are given in Chapter 6.
CHAPTER I
THEORY OF ENERGY TRANSFER BETWEEN RARE EARTH IONS IN SOLID
STATE MATERIALS

If a solid state crystal is pumped with photons which excite the dopant rare earth ions from their electronic ground states to higher energy excited states, then the excited ions must relax back toward their ground states through various processes which include: (a) radiative decay or spontaneous emission, (b) nonradiative decay or multiphonon emission, and (c) energy transfer to neighboring dopant ions (see Fig. 1.1). In radiative decay, the excited ion, called the donor (or sensitizer) ion, relaxes to its ground state by the emission of a photon. This photon can be absorbed by an unexcited ion, called the acceptor (or activator) ion, or can be transmitted out of the crystal unabsorbed. The acceptor ion may or may not be the same ion type as the donor ion if the crystal is codoped with other rare earth ions. In either case, the probability of the photon emitted by the donor ion being absorbed by an acceptor ion depends on the spectral overlap of the emission of the donor with the absorption of the acceptor, as well as the concentration of the acceptor ion. In nonradiative decay, the donor ion relaxes to its ground state by transforming its excitation energy into lattice phonons. In energy transfer, which is the generalization of the emission / absorption of the photon involved in radiative decay, the excitation energy emitted by the donor ion is transferred to a neighboring acceptor ion. If there is a noncongruence between the emission energy and the absorption energy, the difference is compensated for by the
emission or absorption of phonons.

This chapter will concentrate on energy transfer, predominantly based on the theoretical reviews given by Watts, Orbach, Di Bartolo, and Dexter [6, 7, 8, 9]. There are two main categories of energy transfer among ions in solids: nonradiative and radiative. In nonradiative energy transfer, the transfer process may be resonant or nonresonant. In the resonant type, the annihilation or creation of phonons does not assist in the conservation of energy in the transfer process. In the nonresonant type, energy transfer occurs accompanied by the annihilation or creation of one or two phonons. Nonradiative energy transfer is sensitized fluorescence in which the donor or more specifically, the sensitizer dopant ion improves the absorption of the host crystal in the region where the source pumping the crystal emits strongly. The strong absorption of the pump energy by the sensitizer is followed by the transfer of this energy to the acceptor or more specifically, the activator dopant ion, which in turn emits fluorescence. In nonradiative energy transfer, the emission of the sensitizer need not overlap spectrally well with the absorption of the activator. The interaction between the sensitizer and activator is instead a result of the Coulomb forces between the electrons of the two ions and is also called Van der Waals' interaction.

Radiative energy transfer also produces sensitized fluorescence. However the transfer of radiative energy or photons occurs through the good spectral overlap between the emission of the sensitizer and the absorption of the activator. In radiative energy transfer, the lifetime of the sensitizer fluorescence is not altered by the interaction with the activator. Additionally, the sensitizer emission intensity is diminished only at wavelengths corresponding to the absorption of the activator. In nonradiative energy transfer, the sensitizer emission lifetime, in contrast, decreases due to interaction with the activator. As a result, the fluorescence emanating from state involved in the transfer is
diminished uniformly due to interaction with the activator.
Fig. 1.1 (a) Radiative decay and resonant (zero-phonon) radiative energy transfer; $h\nu$ is the energy of the emitted/absorbed photon.

(b) Nonradiative decay; $\sum_i h_k$ is the energy of the multiphonon emission.
1.1 RADIATIVE ENERGY TRANSFER

In the radiative energy transfer process, the activator ions reabsorb the photons emitted by the sensitizer. The probability or quantum yield of this reabsorption is given by [9],

\[
\eta_T = A_L \left\{ v \int f_S(E) \left[ 1 - \exp(-c_A L \sigma_A(E)) \right] \, dE \right\}
\]

(1.1.1)

where,

- \( v \) = volume of the cell pumped within the sample (cm\(^3\))
- \( L \) = dimension of the pump cell along the sample length (cm)
- \( A_L \{ \} \) = average over \( L \) of \{ \}
- \( f_S(E) \) = normalized line shape of sensitizer emission (cm\(^{-3}\))
- \( c_A \) = activator concentration (cm\(^{-3}\))
- \( \sigma_A(E) \) = absorption cross section of activator (cm\(^2\))
  (typically on the order of \(10^{-24} \text{ cm}^2\) for Ho\(^{3+}\))
- \( E \) = energy (cm\(^{-1}\))

So,

\[
\eta_T = A_L \left\{ v \int f_S(E) \, dE \right\} - A_L \left\{ v \int f_S(E) \exp(-c_A L \sigma_A(E)) \, dE \right\}
\]

= \( A_L \{ v \} - A_L \{ v \int f_S(E) \exp(-c_A L \sigma_A(E)) \, dE \} \) (1.1.2)
Taking, \( e^{-x} \ll 1 \sim 1 - x \),

\[
\eta_T = \frac{L \nu}{2} c_A \int f_s(E) \sigma_A(E) \, dE
\]

Hence, the probability of radiative energy transfer depends on the size and shape of the crystal volume, the concentration of the activator ions, and the spectral overlap of the sensitizer emission with the activator absorption.

A specific kind of radiative energy transfer, of primary importance in this research, is the radiative interaction between ions of the same type, in particular between activator and activator. In this case, the energy emitted by one activator is "self absorbed" by another at least once before exiting the crystal. The spectral line shapes with the highest probability of reabsorption are those that terminate in the most populous state, i.e., the ground state. Another important consequence of reabsorption is the increase in the measured lifetime of the metastable state from which the reabsorption line originates. In general, reabsorption has greater effect at low temperatures.
1.2 NONRADIATIVE ENERGY TRANSFER (ENERGY MIGRATION)

Nonradiative energy transfer can be examined in a fundamental way as follows. Under the assumption of an isolated two-ion system comprised of a sensitizer ion and an activator ion, the state of the system without energy transfer or any other interaction between the two ions is given by,

\[ \Psi_0 = \phi_S^0 \phi_A^0 \]  

To examine how the state of this system changes when there is nonradiative energy transfer between the ions, the state before transfer, "the initial state," and the state after transfer, "the final state," must be considered. State i, the initial state, is such that the sensitizer is in its excited state, \( \phi_S^e \), and the activator is in its ground state, \( \phi_A^0 \). State f, the final state, is such that the sensitizer is in its ground state, \( \phi_S^0 \), and the activator is in its excited state, \( \phi_A^e \). The participation of two electrons, one from the sensitizer and one from the activator, is assumed in this transfer of energy or transition from the initial to final states. Via the Pauli principle, these initial and final states are given respectively by,

\[ \Psi_i = \left[ \phi_S^e(r_1) \phi_A^0(r_2) - \phi_S^0(r_2) \phi_A^e(r_1) \right] / \sqrt{2}, \]

\[ \Psi_f = \left[ \phi_S^0(r_1) \phi_A^e(r_2) - \phi_S^e(r_2) \phi_A^0(r_1) \right] / \sqrt{2} \]  

Since the nonradiative energy transfer interaction is Coulombic (Van der Waals') in nature, the interaction between the electrons of the sensitizer and activator is given by the following Hamiltonian:

\[ H = \frac{1}{\sqrt{2}} \left[ \phi_S^e(r_1) \phi_A^0(r_2) - \phi_S^0(r_2) \phi_A^e(r_1) \right] \]
where \( i \) represents the electrons of one of the ions and \( j \), the electrons of the other ion. The probability rate of non-radiative energy transfer is then:

\[
P_{SA} = (2\pi)^2 \int \psi_i^* H \psi_j \delta \nu \rho(E = E_i) / \hbar,
\]

where \( \delta \nu \) is the elemental probability volume, \( \rho \) is the density of states, and \( \hbar \) is Planck's constant. Expanding \( H \) in a Taylor series about \( R \), the relative separation between the sensitizer and activator nuclei (see Fig. 1.2), we have the following terms. The lowest order term, or leading term, in the expansion represents an electric dipole - dipole interaction and is proportional to \( R^{-3} \). The second order term represents an electric dipole - quadrupole interaction and is proportional to \( R^{-4} \). The third order term represents an electric quadrupole - quadrupole interaction and is proportional to \( R^{-5} \). Similarly, there are other terms in the multipole expansion of \( H \) which are proportional to \( R^{-n} \), where \( n = 6, 7, 8, \ldots \), but make a negligible contribution to the overall interaction. Another term of interest is the exchange interaction. The exchange exists due to the presence of cross terms in the matrix element of this interaction term, where the electrons involved in the transfer switch ions during the transfer. A final term of interest is the electric dipole - magnetic dipole interaction which exists because of the motion of the sensitizer electrons causing a magnetic field about the activator.

The following derivation provides a means of calculating the nonradiative energy transfer from measured quantities. The intrinsic fluorescence lifetime of the sensitizer, in the absence of the activator, will be taken as \( \tau_S \). When the
activator is introduced, the fluorescence lifetime of the sensitizer becomes

\[ \frac{1}{\tau_f} = P_{SA} + \frac{1}{\tau_S}. \]  

(1.2.5)

Thus, \( P_{SA} \) can be experimentally determined from the measured values of \( \tau_f \) and \( \tau_S \). Similarly, the average nonradiative energy transfer efficiency can be determined from experiment by,

\[ \eta_T = \int N e^{-Nv} \frac{P_{SA}}{(P_{SA} + 1 / \tau_S)} \delta v, \]

(1.2.6)

where \( N e^{-Nv} \delta v \) is the probability that an activator is in a spherical shell with respect to the sensitizer defined by \( (v, v + \delta v) \), \( N \) is the total density of activators, \( v = 4\pi R^3/3 \), and \( v \) varies from zero to infinity.

In the following section, the average nonradiative energy transfer efficiency will be calculated for the dominant transfer mechanism, electric dipole - electric dipole. In the last section, nonresonant or phonon assisted nonradiative energy transfer will be discussed.

![Fig. 1.2 Vectorial position of the activator with respect to the sensitizer.](image)
1.2.1 ELECTRIC DIPOLE - DIPOLE TRANSFER

The probability rate of nonradiative energy transfer, as derived by Dexter [9] in terms of the spectral overlap between sensitizer emission and activator absorption, is given by

\[ P_{SA} = \frac{(2\pi)^3}{\hbar^2} \left| \langle \phi_S^e | \phi_A^0 | H | \phi_S^0 \phi_A^e \rangle \right|^2 \int f_S(\omega) F_A(\omega) \delta\omega, \]  

(1.2.7)

where \( f_S(\omega) \) and \( F_A(\omega) \) are the normalized sensitizer emission and activator absorption line shapes. If only the interaction between one electron in the sensitizer and one electron in the activator is examined, the Taylor series expansion of the leading term in the Coulombic Hamiltonian reduces to

\[ e^2 / (\varepsilon R^3) \left[ \mathbf{r}_S \cdot \mathbf{r}_A - 3 (\mathbf{r}_S \cdot \mathbf{R})(\mathbf{r}_A \cdot \mathbf{R}) / R^2 \right], \]  

(1.2.8)

where \( \varepsilon \) is the dielectric constant of the host lattice. This expression represents the energy resulting from the interaction between the sensitizer dipole, \( \mathbf{e}_S \mathbf{r}_S \), and the activator dipole, \( \mathbf{e}_A \mathbf{r}_A \), when separated by \( \mathbf{R} \). Averaging the energy transfer probability rate over all \( \mathbf{R} \) yields dependence on the squares of the matrix elements

\[ \langle \phi_S^e | \mathbf{r}_S | \phi_S^0 \rangle \text{ and } \langle \phi_A^0 | \mathbf{r}_A | \phi_A^e \rangle \]  

(1.2.9)

which implies transitions within both the sensitizer and the activator that are electric dipole in nature. The sensitizer matrix element can be derived from the sensitizer spontaneous emission rate, \( A_{21}^S \), which is simply the reciprocal of the sensitizer fluorescence lifetime when the vibronic transitions are negligible.

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The activator matrix element can be derived from the integrated activator absorption cross section. The probability rate of this type of nonradiative energy transfer then becomes

\[ P_{SA}(dd) = \frac{(3h^4c^4)}{(64\pi^5)} \frac{1}{\tau_S} Q_A \left( \frac{1}{R^6} \right) \left( \frac{1}{\epsilon^2} \right) \int \sigma_S(E) f_A(E) \frac{1}{E^4} \delta E, \]

(1.2.10)

where \( \tau_S \) is the sensitizer fluorescence lifetime and \( Q_A \) is the activator integrated absorption cross section, \( \int \sigma_A(E) \delta E \). The average transfer efficiency can then be calculated from (1.2.6).

The previous results are applicable when the sensitizer ion concentration is relatively low. As the concentration increases, the tendency for sensitizer - sensitizer energy transfer increases. Hence, the density of sensitized activators increases beyond that for sensitizer - activator transfer alone, causing a dependency of the transfer rate on sensitizer concentration, particularly when the sensitizer ion is an ion in the host lattice.
1.2.2. PHONON ASSISTED NONRADIATIVE ENERGY TRANSFER

\[ \int f_s(\omega) F_a(\omega) \, d\omega \propto \Delta \omega_{sa} (\omega_s^\theta - \omega_a^\theta) \]

For \( \Delta \omega_{sa} \) small (sharp lines) and \( (\omega_s^\theta - \omega_a^\theta) \) large (well separated), i.e., when \( T \) is low (line shapes change from Lorentzian to Gaussian), the overlap integral and therefore \( P_{sa} \) decrease.
CHAPTER II
PROPERTIES OF THE YAG:Ho\textsuperscript{3+} SAMPLES USED EXPERIMENTALLY

Energy transfer amongst Ho\textsuperscript{3+} ions in singly - doped YAG:Ho\textsuperscript{3+} has been examined in this research. In this crystal system, when an energy transfer occurs, one Ho\textsuperscript{3+} ion acts as the donor of the energy absorbed from the pump source, and the other Ho\textsuperscript{3+} ion acts as the acceptor of the donor emission. Since one Ho\textsuperscript{3+} ion does not absorb the pump emission any better than the other, the term "donor" is used here rather than "sensitizer." Fig. 2.1 gives the energy levels of Ho\textsuperscript{3+} in YAG. From this diagram, it can be seen that when a YAG:Ho\textsuperscript{3+} sample is pumped with a 460nm argon ion laser, the Ho\textsuperscript{3+} 5F\textsubscript{3} manifold is populated by electrons from the ground 5I\textsubscript{8} manifold. Also, when a sample is pumped with a 542nm dye laser, the Ho\textsuperscript{3+} 5S\textsubscript{2} manifold is populated by the ground state electrons. When either pumping scheme is used, one of the decay channels available is the Ho\textsuperscript{3+} 5I\textsubscript{7} to 5I\textsubscript{8} 2.09\textmu m emission.

In doubly doped YAG:Tm\textsuperscript{3+},Ho\textsuperscript{3+}, the higher the concentration of Ho\textsuperscript{3+}, the greater the chance of Ho\textsuperscript{3+} - Ho\textsuperscript{3+} energy transfer, which reduces the fraction of available Ho\textsuperscript{3+} acceptor ions for Tm\textsuperscript{3+} - Ho\textsuperscript{3+} transfer. By studying
singly doped YAG:Ho$^{3+}$, the upper bound for this Ho$^{3+}$ - Ho$^{3+}$ process (which acts as a loss to the sensitized 2.09μm laser emission) can be characterized.

The samples used in this research are as follows:

a) YAG:Ho$^{3+}$ (0.32% at.)

b) YAG:Ho$^{3+}$ (1% at.)

c) YAG:Ho$^{3+}$ (3% at.)

d) YAG:Ho$^{3+}$ (8.5% at.).

All of these samples were grown by A. A. Kaminskii at the Institute of Crystallography, Russian Academy of Science.
Fig. 2.1 Energy levels for Ho$^{3+}$ in YAG [14].
2.1 OPTICAL CHARACTERISTICS OF YAG

YAG is a commonly used inorganic insulating material which can act as a host for optically active defects or dopant ions such as Ho$^{3+}$. YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) belongs to the oxide category of such materials, where the strength of crystal bonding is between that of ionic (e.g., alkali halides) and covalent (e.g., diamond) crystals. All such insulators have a significant energy gap from the highest filled electron band to the lowest empty electron band, which can be bridged by an ultraviolet photon. Hence, YAG appears transparent since it does not interact with optical photons and is characterized as "optically inert."

The index of refraction of YAG was obtained by private communication from N. P. Barnes [10] and is as follows:

$$n^2(\lambda) = 2.08745 + 1.2081 \frac{\lambda^2}{(\lambda^2 - 0.02119)} + 17.2049 \frac{\lambda^2}{(\lambda^2 - 1404.45)}$$  \hspace{1cm} (2.1.1)

Other material and optical properties of YAG, shown in Table 2.1 below, are given by Kaminskii [11].
#### TABLE 2.1

PHYSICAL PROPERTIES OF THE LASER CRYSTAL HOST YAG

| MECHANICAL | Molecular weight | 593.59 |
| Density (g cm\(^{-3}\)) | 4.55 |
| Hardness (Mohs) | 8.25 - 8.5 |
| Hardness (Knoop, kg mm\(^{-2}\)) | 1320 - 1380 |
| Elastic modulus (N m\(^{-2}\)) | 33.3 x 10\(^{10}\) |
| Poisson's ratio | 0.3 |
| Breaking strain (kg cm\(^{-2}\)) | 1.75 - 2.1 |

| THERMAL | Melting point (°C) | 1930 +/- 20 |
| Debye temperature (K) | 700 - 750 |
| Thermal conductivity | 0.13 |
| Specific heat (cal g\(^{-1}\) K\(^{-1}\)) | 0.14 - 0.15 |
| Thermal expansion | 8.2 || [100] |
| | 7.7 || [110] |
| | 7.8 || [111] |
| Thermal diffusion (cm\(^2\) s\(^{-1}\)) | 0.046 |
| Optical transparency range (μm) | 0.24 - 6 |

OPTICAL

| Linear dispersion δn/δT | 9.86 +/- 0.04 |
| (10\(^{-6}\) K\(^{-1}\)) |  |
TABLE 2.1 (CONTINUED)

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<tr>
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<td>$Al^{3+}_{II}$ - (S$_4$)</td>
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<tr>
<td>Structure</td>
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2.2 PROPERTIES OF RARE EARTH IONS IN SOLIDS

The active ion in solid state lasers is usually an impurity ion which when introduced into the crystal host replaces a given host ion. A common type of impurity ion is the rare earth ion, which has been successfully introduced in its trivalent ionic state in various vibronic solid state laser materials. The rare earths occur as two groups, lanthanides and actinides, each consisting of fourteen elements. Ho is in the lanthanide series, which is associated with the filling of the 4f shell. In their neutral state, lanthanides have the following electronic configuration:

\[
\begin{align*}
1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} f^n s^2 5p^6 d^m 6s^2 & = \\
(Pd \text{ core})^{46} f^n s^2 5p^6 d^m 6s^2 & = (2.2.1)
\end{align*}
\]

where \( n = 2, 3, 4, ..., 13 \) and \( m = 1, 2 \). Their atomic numbers range from \( Z = 58 \) (Ce) to \( Z = 70 \) (Yb). The electronic configuration of these ions in their trivalent state becomes:

\[
(Pd \text{ core})^{46} f^n s^2 5p^6 .
\]  

(2.2.2)

The partially filled 4f shell is then shielded by the filled 5s and 5p shells from the external crystal field. The optical characteristics of Lanthanide rare earth ions are derived from the absorption and fluorescence spectra of the crystals into which they are doped. It is the transitions of electrons in this shielded and partially filled 4f shell that cause the various lines in these spectra.
Because of this shielding of the 4f electrons from the crystal field, the crystal field splitting is small relative to the spin-orbit interaction. Therefore, we use the weak crystal field scheme to calculate the splitting of the ion energy levels due to crystal field interaction. Hence, the energy of a given manifold of total angular momentum J, as well as the splitting of this manifold into 2J+1 levels due to spin-orbit coupling, is relatively independent of the external crystal field or host.

Electrons in these levels can relax to lower levels via radiative or nonradiative transitions. The totally radiative or zero-phonon transition is due to the interaction of external radiation or photons with the ion and occurs through the emission of a photon. The probability of this radiative transition is in leading order electric dipole-dipole for rare earths. However, the nonradiative transition is due to the interaction of the external oscillating crystal field or phonons with the ion and occurs through the emission of a phonon.

The theory concerning rare earth ions with respect to their energy level splittings and radiative or nonradiative transition probabilities will be discussed in the following three sections. The energy level theory has been extracted primarily from the works of Wybourne [15], Imbusch [16], and Di Bartolo [17]; the radiative transition theory from Weber [18]; and the nonradiative transition theory from Imbusch [16] and Weber [18].
2.2.1 CALCULATION OF ENERGY EIGENFUNCTIONS AND EIGENVALUES

To calculate the energy wavefunctions and levels of the 4f\textsuperscript{n} configuration, we first determine the matrix elements of the Hamiltonian without the influence of the crystal field interaction; i.e., of the free ion. This Hamiltonian is as follows:

\[ H_j = H_0 + H_{ES} + H_{SO} \]

\[ = \sum_{i=1}^{n} \left[ \left( -\frac{\hbar^2}{2m} \right) \nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{j>i} \frac{e^2}{r_{ij}} \right] + \sum_{i=1}^{n} \frac{\xi (r_i) s_i \cdot l_i}{r_i} \]  \hspace{1cm} (2.2.3)

The first term represents the kinetic energy of the 4f\textsuperscript{n} electrons. The second term gives the potential energy of these electrons due to their attraction to the nucleus. The combination of the first and second terms yields the unperturbed Hamiltonian, \( H_0 \). The third term represents the repulsive Coulomb interaction of the electrons, that is, the electrostatic perturbation potential. The fourth term gives the perturbative spin-orbit interaction. The eigenstates of \( H_j \) are also eigenstates of the operators which commute with \( H_j \); i.e., \( L^2, S^2, J_z, J_z, \) and \( P \) (parity). Since the spin-orbit interaction is much smaller than the electrostatic interaction, we can employ the Russell-Saunders approximation and use the \( L S J M_J \) representation to take the matrix elements of the free ion Hamiltonian, \( H_j \).

Due to the shielding of the 4f\textsuperscript{n} electrons, by the outer 5s and 5p shells,
from the electrons and nuclei of neighboring ions in the lattice, the crystal field interaction is much smaller than the electrostatic interaction. In fact, the crystal field interaction is smaller than the spin - orbit interaction. Therefore, it suffices to use the L S J M_j representation to take the matrix elements of the perturbative crystal field interaction as well. This approach in calculating the crystal field splittings is called the “weak crystal field scheme.”

When the free ion is introduced into a weak crystal field, each term $2S+1L_j$ with degeneracy $2J + 1$, is split into irreducible crystal field terms such that the sum of the degeneracies of the crystal terms is $2J + 1$. The perturbative crystal field interaction term is given by the Hamiltonian

$$H_C = \sum_i eV(r_i)$$

(2.2.4)

Some of the effects of the crystal field perturbation are:

(a) $H_C$ not commuting with $H_J$,
(b) connection of $H_J$ states having equal parity, and
(c) interaction between distinct: J levels, terms, or configurations.
2.2.2 RADIATIVE TRANSITIONS IN RARE EARTH IONS

If a rare earth ion is excited to a state \( i \), it relaxes to a given terminal state \( j \) radiatively or nonradiatively. The total measured decay probability rate from excited state \( i \) is given by

\[
1 / \tau_i = \sum_j (A_{ij} + W_{ij}) , \quad (2.2.5)
\]

where \( A_{ij} \) and \( W_{ij} \) are the radiative and nonradiative, respectively, decay rates of the ion from original state \( i \) to all possible terminal states \( j \). Radiative transitions may occur through either entirely electronic or phonon-assisted vibronic transitions. These transitions are both electric and magnetic dipole in nature. In general, the spontaneous emission rate of dipole radiation between two \( J \) levels is given by

\[
A(J; J') = \left[ \frac{64\pi^4v^3\chi}{3hc(2J + 1)} \right] S(J; J') , \quad (2.2.6)
\]

where \( v \) is frequency and \( \chi \) is a factor which corrects the refractive index for the particular host crystal. In electric dipole transitions, an approximation for \( \chi \) is

\[
\chi_{ed} = n (n^2 + 2)^2 / 9 , \quad (2.2.7)
\]

and in magnetic dipole transitions, \( \chi \) is approximated by

\[
\chi_{md} = n^3 . \quad (2.2.8)
\]

\( S(J; J') \), derived from Judd [19] - Ofelt [20] theory, is the line strength for a dipole transition between SLJ states. For electric dipole transitions, \( S(J; J') \) is given by
\[ S_{ed}(J; J') = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} \left( \frac{fN\alpha S}{|U^{(\lambda)}|} \right) \left( \frac{fN\alpha' S'L'J'}{|U^{(\lambda)}|} \right)^2 \]  

(2.2.9)

where \(|U^{(\lambda)}|\) are matrix elements of tensor operators, and \(\Omega_{\lambda}\) are phenomenological intensity parameters. For magnetic dipole transitions, \(S( J; J' )\) is given by

\[ S_{md}(J; J') = \mu_B^2 \left( \frac{fN\alpha S}{L + 2S} \right) \left( \frac{fN\alpha' S'L'J'}{|U^{(\lambda)}|} \right)^2 \]  

(2.2.10)

where \(\mu_B\) is the Bohr magneton,

\[ \mu_B = \frac{e\hbar}{2mc} . \]  

(2.2.11)

The eigenvectors employed in the matrix elements are with respect to an intermediate coupling scheme and are comprised of linear combinations of SLJ vectors. These eigenvectors are reasonably independent of the host material.

The accuracy of \(S(J; J')\) as determined from the Judd-Ofelt method depends on the energy gap separating the \(J\) and \(J'\) manifolds. When the energy gap is small, \(W_{ij}\) is typically much larger than \(A_{ij}\). Therefore, discrepancies in \(S(J; J')\) and hence in \(A_{ij}\) have little impact on \(W_{ij}\). When the energy gap is large, \(W_{ij}\) is much smaller than \(A_{ij}\). Hence, \(W_{ij}\) is more susceptible to errors in \(S(J; J')\).

The spontaneous emission rate of dipole radiation between two \(J\) levels can also be calculated from the experimentally determined absorption cross section, \(\sigma\), as follows:

\[ A(J; J') = \left( \frac{8\pi n^2 v^2}{c^2} \right) \left[ \frac{(2J' + 1)}{(2J + 1)} \right] \int \sigma(v) \delta v . \]  

(2.2.12)

The latter formulation is the approach used in this thesis.
2.2.3 NONRADIATIVE TRANSITIONS IN RARE EARTH IONS

When rare earth ions are doped into crystal hosts, their electronic states undergo changes due to static and dynamic distortions of the host lattice. The ions that neighbor the dopant ion vibrate about their respective average positions, causing not only a static crystal field, but also a dynamic field. The Hamiltonian of the ion / lattice system is given by

\[ H = H_J + V_C + H_L \]  \hspace{1cm} (2.2.13)

where \( H_J \) is the free ion Hamiltonian of the dopant rare earth ion given by (2.2.3), \( V_C \) is the interaction energy of the ion with the lattice crystal field, and \( H_L \) is the Hamiltonian associated with the lattice. \( V_C \) is actually described by

\[ V_C = V_C^O + V_C^V \]  \hspace{1cm} (2.2.14)

where \( V_C^O \) is the static term which represents the interaction that would exist if all the ions were fixed in their average positions, and \( V_C^V \) is the dynamic term which represents the interaction when the vibrating ions cause a time-varying crystal field. The states of the rare earth dopant ion with respect to the Hamiltonian in (2.2.13) depend on the strength of the coupling between the dopant and neighboring ions. The occurrence of nonradiative decay is due to the interaction, \( V_C \), between the dopant ion and the lattice. The probability or strength of nonradiative decay depends on the energy gap from the excited state to the next lower level of the transition. Therefore, the nonradiative decay probability depends on the strength of the coupling between the dopant ion and the lattice. For rare earths, this coupling is considered weak. When the
coupling is weak, the nonradiative transition behavior can be studied using perturbation theory.

In the perturbation approach, the eigenstates of the Hamiltonian, $H_J + V_{C^0} + H_L$, are the basis states. These states are represented by $|i, n>$ where $|i>$ are the eigenstates of both the free ion Hamiltonian, $H_J$, and the static ion-lattice interaction, $V_{C^0}$; $|n>$ are the eigenstates of the lattice Hamiltonian, $H_L$.

The dynamic ion-lattice interaction, $V_C^V$, is considered as a perturbation. The lattice vibrations are assumed independent of the electronic states of the ion.

The object of this approach is to calculate the nonradiative transition probability from $|i, n>$ to $|f, m>$ as a function of the $V_C^V$ perturbation. $V_C^V$ can be expressed as a power series in $\varepsilon$,

$$V_C^V = \varepsilon + \varepsilon^2 + \ldots = \sum_k V_k \varepsilon^k$$  \hspace{1cm} (2.2.15)

where $\varepsilon$ is the strain or the displacement of the near-neighbor separation from its equilibrium value, and $V_1, V_2$, etc. are functions of the electronic coordinates of the dopant ion. The total strain $\varepsilon$ is defined as follows:

$$\varepsilon = \sum_{\omega} \varepsilon_{\omega} = \sum_{\omega} \sqrt{(\hbar \omega / 2Mv_{\omega}^2)} (a_{\omega} + a^{+}_{\omega})$$  \hspace{1cm} (2.2.16)

where $\varepsilon_{\omega}$ is the strain associated with a lattice vibration of a given frequency $\omega$, $M$ is the crystal mass, $v_{\omega}$ is the speed of sound at a given frequency $\omega$, and $a_{\omega}$ and $a^{+}_{\omega}$ are annihilation and creation operators for phonons of frequency $\omega$. 

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respectively. If only the first term in $V_C^V$ is considered, then the perturbation is linear in $a_\omega$ and $a_\omega^+$, which results in processes in which one phonon is created. If the second term in $V_C^V$ is incorporated into first-order perturbation theory, two-phonon processes result. Two-phonon processes can also result from the use of the first term in $V_C^V$ in second-order perturbation theory. In the general case, the $n^{th}$-order term in first-order perturbation theory results in an $n$-phonon relaxation process. In the opposite sense, the first-order term in $n^{th}$-order perturbation results in the same process. Intermediate terms in intermediate-order perturbation result in similar phonon relaxation processes.

In general, the probability of nonradiative transitions can be characterized in terms of the energy gap from the excited state to the next lower level. This probability can be understood through the order of perturbation required. A typical energy of highest energy active phonons is on the order of 500 cm$^{-1}$. An example of an energy gap involved in visible radiative transitions, such as green, is on the order of 18,000 cm$^{-1}$. Hence, if a nonradiative transition were to occur across such a gap, it would require the creation of approximately 36 phonons, which implies the need for a large number of terms in perturbation theory for determination of the nonradiative probability. The larger the gap the phonons must bridge, the higher the number of phonons required, and therefore, the more terms needed in perturbation theory. The more perturbative terms needed, the less the probability of the nonradiative transition. Therefore, the larger the gap, the smaller is the nonradiative transition probability.

To quantify this dependence of nonradiative transition probability on gap,
the probability of an $n$-phonon relaxation process, $W(n)$, can be calculated. If it is assumed that the ratio of the $n$th to the $(n-1)$th probability is constant such that,

$$\frac{W(n)}{W(n-1)} = \gamma << 1$$  \hspace{1cm} (2.2.17)

which is a property of the host crystal and independent of $n$, then $W(n)$ has an exponential dependence on $n$. Denoting the gap by $\Delta E$ and the energy of the dominant phonon by $\hbar \omega$, and assuming the gap is bridged by $n$ phonons, then $\Delta E = n\hbar \omega$. Thus,

$$W = A \exp \left( -\frac{\Delta E}{\hbar \omega} \right)$$  \hspace{1cm} (2.2.18)

where $W$ is the nonradiative transition probability across the gap. The value of $\hbar \omega$ is constant for a given host material. The value of $A$ depends on the host material as well as the dopant ion.

This nonradiative decay rate for trivalent rare earth dopant ions can be compared to the typical radiative decay time, $10^{-4}$ to $10^{-2}$s, for these ions. It is generally found that the critical gap corresponds to an energy of about 7 phonons. That is, for gaps smaller than the critical gap, the excited state of the dopant rare earth ion will decay to the next lowest state nonradiatively, while for larger gaps, the state will decay radiatively.
2.3 OPTICAL CHARACTERISTICS OF Ho³⁺ IN YAG

The following properties of Ho³⁺, when doped into Y₃Al₅O₁₂ and hence placed under the influence of the ambient crystal field, were gathered from Kaminskii's *Laser Crystals*.

The unit cell of a garnet structure compound, A₃B₅O₁₂, has eight formula units. The B atoms occupy two kinds of sites with respect to oxygen: 16 octahedral a positions (C₃ᵥ), and 24 tetrahedral d positions (S₄); a body-centered cubic lattice is formed by the a sites. The A ions occupy dodecahedral c positions (D₂). The Ln³⁺ ions, which determine the laser properties of the crystals, lie mainly in these c positions. Thus, Ho³⁺ ions occupy the c positions shown in Fig. 2.2. And finally, the oxygen ions occupy 96 general h positions (C₂).

![Fig. 2.2 Garnet crystal structure depicting how Ho³⁺ is doped into YAG](image-url)
Two laser emission channels for $\text{Ho}^{3+}$ in garnets can be seen between manifolds as shown in Fig. 4.3. This figure ignores crystal field splitting. Only the splitting due to electrostatic and spin-orbit interaction is considered.

Fig. 2.3  Induced transitions of $\text{Ln}^{3+}$ ions in crystals with garnet structure [13].
CHAPTER III
EXPERIMENTAL SET-UP

This research incorporated three basic experiments:

1. absorption as a function of temperature;
2. continuous luminescence as a function of concentration, pump position, and temperature;
3. lifetime of pulsed emission as a function of concentration, pump position, and temperature.

The materials used in this research were Ho:YAG crystals that were grown in concentrations of 8.5, 3, 1, and 0.32% at. through the joint effort of Christopher Newport College and the Institute of Crystallography at the Russian Academy of Science. These crystals were then cut into rectangular cross section slabs with the dimensions of 8.73mm x 2.10mm x 2.62mm. In what follows: the slab length, 8.73mm, is represented by “L”; the slab width, 2.10mm, is represented by “W”; and the slab height, 2.62mm, is represented by “H.”

In the continuous luminescence experiments, the Ho:YAG sample was pumped transverse to its length by an ~460nm cw argon ion laser. In the lifetime experiments, the sample was pumped transverse to its length by an ~542nm 10ns pulsed dye laser. In both experiments, the emission traveling within the sample along its length was measured at one end of the sample by placing an aperture with the shape of the sample cross section in front of the detector. In what follows, we shall call “pump position” the distance along the length of the sample between the end of the sample nearest the detector and
the center of the pump spot. "Pump position" will be represented by the variable "X."
3.1 ABSORPTION AS A FUNCTION OF TEMPERATURE

The temperature dependent absorption measurements were performed with a:

1. Perkin-Elmer Lambda 9 UV / VIS / NIR spectrophotometer;
2. LFE Model 232 automatic temperature controlled sample heater;
3. RMC-Cryosystems LTS-22 Series closed cycle cryogenic refrigerator system.

3.1.1 THE SPECTROPHOTOMETER

The spectrophotometer can be programmed to record absorption spectra within a total wavelength range of 185-3200nm. It is accompanied by two interchangeable light sources: a deuterium lamp for the UV (ultraviolet) range; and a tungsten-halogen lamp for the VIS (visible) and NIR (near infrared) ranges. Also included, are two interchangeable detectors: a photomultiplier for the UV and VIS ranges; and a PbS detector for the NIR range.

The spectrophotometer can measure the absorption in terms of “absorbance” or “optical density, O.D.” defined as,

\[ \text{O.D.} = \log_{10}(\frac{l_i}{l_0}), \]

where,
\[ I_0 = I_i \exp(-\alpha W) = I_i \exp(-\sigma N W) \]

where \( I_i \) is the intensity of the light incident upon the slab, \( I_0 \) is the intensity of the light transmitted along the width \( W \) of the slab, \( \alpha \) is the absorption coefficient, \( \sigma \) is the absorption cross section, and \( N \) is the concentration of Ho in YAG.

### 3.1.2 THE SAMPLE HEATER

The sample heater can be set in the temperature range of 295-550 K. The actual sample heating element consists of a soldering iron in which the tip was modified to hold a sample.

### 3.1.3 THE REFRIGERATION SYSTEM

The refrigeration system provides cryogenic temperature in the range from \(~10K\) to \(295\) K without the use of liquid helium or nitrogen (closed-cycle cooler).
3.2 CONTINUOUS LUMINESCENCE AS A FUNCTION OF
CONCENTRATION, PUMP POSITION, AND TEMPERATURE

The diagram for this experimental set-up is shown in Fig. 3.1. The continuous luminescence set-up consists of the following segments:

1. excitation
2. measurement
3. temperature control
4. detection and amplification
5. data capture

3.2.1 EXCITATION

Excitation was achieved using a Lexel Model 85 - 0.5 Argon ion laser. The specifications for this laser are given in Table 3.1. This laser light is focused on the widest face and at various pump positions along the sample length. The fluorescence is detected transverse to the incident beam, through the end face of the sample nearest the detector.

3.2.2 MEASUREMENT

This arrangement begins with a lens capable of moving parallel to the
sample length, thus changing the position of the focused pump beam along the sample length. The luminescence from the sample end nearest the detector is first chopped and then focused onto the entrance slit of a SPEX Industries Model 1681B Mini-Mate 3/4 m scanning monochromator. A 600 groove/mm plane grating blazed at 2 μm was mounted in this monochromator for scanning in the IR (infrared) region.

3.2.3 TEMPERATURE CONTROL

The cooled sample temperature was controlled by mounting the sample in a CTI-Cryogenics Model 12 cold head, which was supported with a Model SC-21 compressor. Using a Lake Shore Cryotronics Model DRC-80C digital thermometer / controller, the temperature of the sample in the cold head was varied between 30 and 300 K.

The heated sample temperature was controlled by using the sample heater and attached temperature controller mentioned in section 3.1.2. The heated sample temperature was varied between 300 and 500 K.

3.2.4 DETECTION AND AMPLIFICATION

The fluorescence from the monochromator was detected using a liquid nitrogen cooled SPEX Industries Model 1428 PbS detector. The electrical signal was then amplified by a Stanford Research Systems Model SR510 lock-in amplifier.
3.2.5 DATA CAPTURE

The wavelength of the monochromator was varied by and the signal from the lock-in amplifier was processed with respect to the wavelength by a SPEX Industries Model DM1B Laboratory Controller / Data Processor. The luminescence spectra were obtained directly from this instrument.
3.3 LIFETIME OF PULSED EMISSION AS A FUNCTION OF
CONCENTRATION, PUMP POSITION, AND TEMPERATURE

The diagram for this experiment is shown in Fig. 3.2. The lifetime set-up
consists of the following segments.

1. excitation
2. measurement
3. temperature control
4. detection and amplification
5. data capture

3.3.1 EXCITATION

Excitation was achieved with a Quantel International Model TDL51
tunable dye laser pumped by a Quantel International Model 660A-10 Nd:YAG
laser. The specifications for these lasers are shown in Tables 3.2 and 3.3. In
these pulsed emission measurements, the decay times are much longer than
the ~10 ns pulse widths of these lasers. The laser light is focused on the widest
face and at various pump positions along the sample length. The fluorescence
is detected transverse to the incident beam, through the end face of the sample
nearest the detector.
3.3.2 MEASUREMENT

This set-up begins with a lens capable of moving parallel to the sample length, thus changing the position of the focused pump beam along the sample length. The luminescence from the sample end nearest the detector is then focused onto the face of the detector.

3.3.3 TEMPERATURE CONTROL

The cooling and heating of the sample was performed as described in section 3.2.3.

3.3.4 DETECTION AND AMPLIFICATION

The luminescence from the sample end nearest the detector was focused onto the center of a 2.1 μm notch filter which was centered on and covering the face of a Judson Infrared Inc. Model J12TE2 InAs detector. The signal from this detector was then amplified by an EG&G PARC amplifier in series with an Analogic Data Precision Model D1000 dual amplifier.
3.3.5 DATA CAPTURE

The signal from the D1000 amplifier was then transient digitized by and stored in an Analogic Data Precision Model D6000 waveform analyzer.
Fig. 3.1. Schematic of the continuous luminescence experimental set-up
### TABLE 3.1

**SPECIFICATIONS OF THE LEXEL MODEL 85 - 0.5 ARGON ION LASER**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fundamental tuning range</td>
<td>457.9 - 514.5 nm</td>
</tr>
<tr>
<td>Beam diameter (514.5 nm TEM(_{00}), at 1/e(^2) points)</td>
<td>1.1 mm</td>
</tr>
<tr>
<td>Beam divergence (514.5 nm TEM(_{00}), full angle)</td>
<td>0.7 mrad</td>
</tr>
<tr>
<td>Beam polarization ratio</td>
<td>&gt; 100:1, E - vector vertical</td>
</tr>
<tr>
<td>Fundamental mode power:</td>
<td></td>
</tr>
<tr>
<td>multiline</td>
<td>0.5 W</td>
</tr>
<tr>
<td>single line (457.9 nm)</td>
<td>20 mW</td>
</tr>
<tr>
<td>Amplitude power stability (avg. variation in 1 hr period):</td>
<td></td>
</tr>
<tr>
<td>in light control</td>
<td>&lt; +/ - 0.2 %</td>
</tr>
<tr>
<td>in current control</td>
<td>&lt; +/ - 2 %</td>
</tr>
<tr>
<td>Optical Noise (10 Hz to 2 MHz):</td>
<td></td>
</tr>
<tr>
<td>typical in light control</td>
<td>&lt; 0.5 % rms</td>
</tr>
<tr>
<td>maximum ripple in current control</td>
<td>&lt; 1.5 % rms</td>
</tr>
<tr>
<td>typical high frequency component</td>
<td>&lt; 0.3 % rms</td>
</tr>
<tr>
<td>typical high frequency with etalon</td>
<td>&lt; 0.15 % rms</td>
</tr>
<tr>
<td>Input voltage range</td>
<td>190 - 245 v</td>
</tr>
</tbody>
</table>
Fig. 3.2. Schematic of the pulsed emission lifetime experimental set-up
## TABLE 3.2
SPECIFICATIONS OF THE QUANTEL INTERNATIONAL MODEL TDL51
TUNABLE Nd:YAG - PUMPED DYE LASER

Energy output per pulse:

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Energy Output (mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>560</td>
<td>37</td>
</tr>
<tr>
<td>790</td>
<td>8</td>
</tr>
</tbody>
</table>

Repetition rate: up to 50 pps
<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy output per pulse:</td>
<td></td>
</tr>
<tr>
<td>1064 nm</td>
<td>390 mJ</td>
</tr>
<tr>
<td>532 nm</td>
<td>150 mJ</td>
</tr>
<tr>
<td>Repetition rate:</td>
<td></td>
</tr>
<tr>
<td>Optimized rate</td>
<td>10 pps</td>
</tr>
<tr>
<td>Maximum rate</td>
<td>20 pps</td>
</tr>
<tr>
<td>Pulse duration:</td>
<td></td>
</tr>
<tr>
<td>1064 nm</td>
<td>10 ns</td>
</tr>
<tr>
<td>Shot to shot stability:</td>
<td></td>
</tr>
<tr>
<td>1064 nm</td>
<td>+ / - 2.5 %</td>
</tr>
<tr>
<td>Linewidth:</td>
<td></td>
</tr>
<tr>
<td>1064 nm</td>
<td>0.8 cm⁻¹ FWHM</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>&lt; 6 mm</td>
</tr>
<tr>
<td>Beam divergence</td>
<td>&lt; 0.5 mrad for 84 % of laser energy</td>
</tr>
<tr>
<td>Shot to shot jitter</td>
<td>&lt; + / - 500 ps from external sync pulse</td>
</tr>
</tbody>
</table>
CHAPTER IV
EXPERIMENTAL RESULTS

4.1 ABSORPTION MEASUREMENTS

Absorption spectra were measured for YAG:Ho(3 %) as functions of temperature between 77 K and 500 K. The absorption length used was the width of the Ho(3 %) slab, 2.10 mm. The low temperature spectra (77 K - 295 K) were taken by placing the slab in the RMC-Cryosystems LTS-22 Series closed cycle cryogenic refrigerator dewar which was then lowered into the Perkin-Elmer Lambda 9 spectrophotometer sample chamber. The high temperature spectra (295 K - 500 K) were taken by placing the slab on the LFE Model 232 automatic temperature controlled sample heater which was also lowered into the Perkin-Elmer sample chamber. Fig. 4.1 - Fig. 4.10 corresponding to these ten temperature - dependent absorption spectra are shown on the following pages.
Fig. 4.1 Infrared \( ^5I_8 \rightarrow ^5I_7 \) transmission spectrum of YAG:Ho(3\%), \( T = 77 \) K.
Fig. 4.2 Infrared $^{5}I_{8} \rightarrow {^5}I_{7}$ transmission spectrum of YAG:Ho(3 %), $T = 120$ K.
Fig. 4.3 Infrared (5_{18} \rightarrow 5_{17}) transmission spectrum of YAG:Ho(3%), T = 160 K.
Fig. 4.4 Infrared ($^5I_8 \rightarrow ^5I_7$) transmission spectrum of YAG:Ho(3 %), $T = 200$ K.
Fig. 4.5 Infrared \((^5I_8 \rightarrow ^5I_7)\) transmission spectrum of YAG:Ho(3 %), \(T = 295\text{K}\) (from low temperature measurement).
Fig. 4.6 Infrared \( ^5I_8 \rightarrow ^5I_7 \) transmission spectrum of YAG:Ho(3 %), \( T = 295 \text{ K} \) (from high temperature measurement).
Fig. 4.7  Infrared (5\textsuperscript{1}G\textsubscript{8} \rightarrow 5\textsuperscript{1}T\textsubscript{7}) transmission spectrum of YAG:Ho(3\%), \( T = 350 \) K.
Fig. 4.8 Infrared \((4_{18} \rightarrow 5_{17})\) transmission spectrum of YAG:Ho(3%), \(T = 400\) K.
Fig. 4.9 Infrared (5^1G -> 5^1I) transmission spectrum of YAG:Ho(3%), T = 450 K.
Fig. 4.10 Infrared $(^5_{1G} -> ^5_{1F})$ transmission spectrum of YAG:Ho(3 %), $T = 500$ K.
These spectra were taken in the form of "transmittance" spectra which can be explained with respect to "absorption" by the following equations:

\[ I_{out} = I_{in} \ e^{-\sigma N L} \]  \hspace{1cm} (4.1.1)

where \( I_{in} \) is the intensity of the radiation incident upon the sample, \( \sigma \) is the absorption cross section (cm\(^2\)), \( N \) is the concentration of Ho\(^{3+}\) in YAG (ions / cm\(^{-3}\)), \( L \) is the absorption length or sample thickness (cm), and \( I_{out} \) is the intensity of the radiation transmitted through the sample thickness. Also,

\[ T = \frac{I_{out}}{I_{in}} = 1 - A = e^{-\sigma N L} \leq 1 \]  \hspace{1cm} (4.1.2)

where \( T \) is the transmittance, and \( A \) is the absorbance. Hence, we measure

\[ T(\lambda) = e^{-\sigma(\lambda) N L} \]  \hspace{1cm} (4.1.3)

The spectral quantity that is actually used in later calculations is

\[ \alpha(\lambda) = \sigma(\lambda) \ N \]  \hspace{1cm} (4.1.4)

where \( \alpha(\lambda) \) is the absorption coefficient (cm\(^{-1}\)). Therefore, these latter spectra were calculated from the measured transmittance spectra as follows:

\[ \alpha(\lambda) = -\ln[T(\lambda)] / L \]  \hspace{1cm} (4.1.5)

where \( L = 0.21 \) cm, and \( N = 3 \% = 4.14 \times 10^{20} \) cm\(^{-3}\). Fig. 4.11 - Fig. 4.20 corresponding to these ten temperature-dependent absorption coefficient spectra are shown on the following pages.
Fig. 4.11 Infrared (5I_8 \rightarrow 5I_7) absorption coefficient spectrum of YAG:Ho(3%), T = 77 K.
Fig. 4.12 Infrared (2s_g \rightarrow 5_{17}) absorption coefficient spectrum of YAG:Ho(3%), T = 120 K.
Fig. 4.13 Infrared ($^5I_8 \rightarrow ^5I_7$) absorption coefficient spectrum of YAG:Ho(3 %), $T = 160$ K.
Fig. 4.14 Infrared \((\tilde{5}_{18} \rightarrow 5_{17})\) absorption coefficient spectrum of YAG:Ho(3\%), \(T = 200\) K.
Fig. 4.15 Infrared $^{5I_8 \rightarrow 5I_7}$ absorption coefficient spectrum of YAG:Ho(3 %), $T = 295$ K (from low temperature measurement).
Fig. 4.16  Infrared ($^5I_8 \rightarrow ^5I_7$) absorption coefficient spectrum of YAG:Ho(3 %), T=295 K (from high temperature measurement).
Fig. 4.17  Infrared ($^5I_8 \rightarrow ^5I_7$) absorption coefficient spectrum of YAG:Ho(3 %), $T = 350$ K.
Fig. 4.18 Infrared ($^5I_8 \rightarrow ^5I_7$) absorption coefficient spectrum of YAG:Ho(3 %), $T = 400$ K.
Fig. 4.19  Infrared ($^5I_{18} \rightarrow ^5I_{17}$) absorption coefficient spectrum of $	ext{YAG:Ho}(3\%)$, $T = 450 \text{ K.}$
Fig. 4.20 Infrared $^{5}I_{8} \rightarrow ^{5}I_{7}$ absorption coefficient spectrum of YAG:Ho(3 %), $T = 500$ K.
From these spectra, it is evident that the minimal transmission or maximal absorption occurs in the region of 1.9 $\mu$m. As the temperature is increased, absorption in the 2.1 $\mu$m region intensifies. The overall dependence of absorption on temperature can be seen by examining the variation of the integrated absorption cross section, $\int \sigma(\lambda) \delta(\lambda)$, with temperature, which is shown below in Fig. 4.20a.

![Graph showing the integrated absorption cross section as a function of temperature.](image)

**Fig. 4.20a** Infrared ($^5I_8 \rightarrow ^5I_7$) integrated absorption cross section of YAG:Ho(3 %) as a function of temperature.
This figure shows that in general, the integrated absorption cross section increases with temperature. This finding is consistent with the previous temperature-dependent absorption spectra where absorption intensified in the 2.1 \( \mu \text{m} \) region as temperature increased.
4.2 LUMINESCENCE MEASUREMENTS

Luminescence spectra were taken at room temperature \((T = 295 \text{ K})\) for each of the four YAG:Ho\(^{3+}(c)\) slabs \((c = 0.32, 1, 3, 8.5 \%)\) at the nine pump positions along each slab \((X = 0.3125 \text{ to } 8.3125 \text{ mm}, \Delta X = 1 \text{ mm})\).

To observe how the overall luminescence varies with pump position for each Ho\(^{3+}\) concentration or slab, the following treatment was made on each of these spectra. Each of the slabs were pumped with the same intensity. Since the portion of this pump intensity absorbed by a slab increases with the concentration of absorbers or Ho\(^{3+}\) ions in the slab, a method was devised to condition the spectra from different slabs such that they appear to have absorbed the same portion of pump intensity. These spectra all have in common the wavelength at which minimum absorption of pump radiation takes place. This wavelength was found experimentally from the absorption spectrum of YAG:Ho(3 \%) at 295 K. In particular, this wavelength (2122 nm) corresponded to that of the minimum local maximum of absorbance. Each of the spectra were then normalized with respect to the intensity of each spectra at this wavelength and are shown in Fig. 4.21 - Fig. 4.52 on the following pages.
Fig. 4.21 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(8.5%) at 295 K, X = 0.3125 mm.
Fig. 4.22  Luminescence spectrum $5_{17} \rightarrow 5_{18}$ of YAG:Ho(8.5%) at 295 K, $X = 1.3125$ mm.
Fig. 4.23 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(8.5 %) at 295 K, X = 2.3125 mm.
Fig. 4.24  Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(8.5 %) at 295 K, $X = 3.3125$ mm.
Fig. 4.25 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(8.5 %) at 295 K, $X = 4.3125$ mm.
Fig. 4.26 Luminescence spectrum \( ^5I_7 \rightarrow ^5I_8 \) of YAG:Ho(8.5 \%) at 295 K, \( X = 5.3125 \) mm.
Fig. 4.27  Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(8.5 %) at 295 K, $X = 6.3125$ mm.
Fig. 4.28 Luminescence spectrum $5^{1}g \rightarrow 5^{1}g$ of YAG:Ho(8.5 %) at 295 K, $X = 7.3125$ mm.
Fig. 4.29  Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(8.5%) at 295 K, $X = 8.3125$ mm.
FIG. 4.30 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(3 %) at 295 K, $X = 0.3125$ mm.
Fig. 4.32 Luminescence spectrum $5_{17} \rightarrow 5_{18}$ of YAG:Ho(3 %) at 295 K, $x = 2.3125$ mm.
Fig. 4.33  Luminescence spectrum \( ^5I_7 \rightarrow ^5I_8 \) of YAG:Ho(3 \%) at 295 K, \( X = 3.3125 \) mm.
Fig. 4.34 Luminescence spectrum \( ^5I_7 \rightarrow ^5I_8 \) of YAG:Ho(3 %) at 295 K, \( X = 4.3125 \) mm.
Fig. 4.35 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(3 %) at 295 K, $X = 5.3125$ mm.
Fig. 4.36 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(3 %) at 295 K, $X = 6.3125$ mm.
Fig. 4.37 Luminescence spectrum $5_{17} \rightarrow 5_{18}$ of YAG:Ho(3\%) at 295 K, $X = 7.3125$ mm.
Fig. 4.38 Luminescence spectrum $5_{17} \rightarrow 5_{18}$ of YAG:Ho(3%) at 295 K, X = 8.3125 mm.
Fig. 4.39  Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(1 %) at 295 K, X = 0.3125 mm.
Fig. 4.40 Luminescence spectrum $5_{17} \rightarrow 5_{18}$ of YAG:Ho(1%) at 295 K, $X = 1.3125$ mm.
Fig. 4.41 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(1 %) at 295 K, $X = 2.3125$ mm.
Fig. 4.12  Luminescence spectrum $5/7 \rightarrow 5/8$ of YAG:Ho(1 %) at 295 K, $X = 3.3125$ mm.
Fig. 4.43 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(1 %) at 295 K, X = 4.3125 mm.
Fig. 4.44  Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(1 %) at 295 K, $X = 5.3125$ mm.
Fig. 4.45 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(1%) at 295 K, $X = 6.3125$ mm.
Fig. 4.46 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(1 %) at 295 K, $X = 7.3125$ mm.
Fig. 4.47 Luminescence spectrum $5_{17}^{1} \rightarrow 5_{18}^{1}$ of YAG:Ho(1%) at 295 K, $X = 8.3125$ mm.
Fig. 4.48 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$ of YAG:Ho(0.32 %) at 295 K, $X = 0.3125$ mm.
Fig. 4.49 Luminescence spectrum $5I_7 \rightarrow 5I_8$ of YAG:Ho(0.32 %) at 295 K, $X = 2.3125$ mm.
at 295 K, $X = 4.3125$ mm.
Fig. 4.51 Luminescence spectrum $5_{17} \rightarrow 5_{18}$ of YAG:Ho(0.32 %) at 295 K, $X = 6.3125$ mm.
Fig. 4.52 Luminescence spectrum $^5l_7 \rightarrow ^5l_8$ of YAG:Ho(0.32 %) at 295 K, $X = 8.3125$ mm.
From these 295 K spectra, the following observations have been made concerning the dependence of luminescent intensity on Ho\(^{3+}\) concentration and pump position. First, for each concentration or slab, as the pump position is increased, the luminescent intensity decreases. This decrease is appreciable in the vicinity of 1.9 µm, which is the region of maximum absorption for YAG:Ho. This decrease is more and more dramatic as the concentration is increased. If we compare the spectra of the highest and lowest concentrations (8.5 % and 0.32 %) at the same pump position nearest to the detector (0.3125 mm), we notice that there is no significant difference. If we compare the spectra of the highest and lowest concentrations at the same pump position fartherest from the detector (8.3125 mm), we observe that the 8.5 % luminescence is much less than that of 0.32 %.
These 295 K luminescence spectra were then integrated with respect to wavelength and examined as functions of concentration and pump position as shown in Fig. 4.53 below.

Fig. 4.53  Wavelength - integrated luminescent intensity vs. concentration and pump position at 295 K.
From Fig. 4.53 above, the following observations have been made. At the closest pump position to the detector, $X = 0.3125$ mm, it is evident that all the spectra (for all Ho$^{3+}$ concentrations) share the same integrated emission. Indeed, all the spectra have been successfully conditioned for equal absorption of pump radiation. However, for each $X > 0.3125$ mm, as the Ho$^{3+}$ concentration increases above 0.32 %, the integrated emission decreases. Hence, although the slabs appear to absorb and subsequently emit the same amount of pump radiation at each pump position, the number of absorbers per unit slab length increases with slab concentration. Therefore, the number of additional reabsorptions / reemissions of 2.1 $\mu$m radiation increases per unit slab length. As the number of reemissions per unit length increases, so does the loss of initial pump radiation through the sides of the slab per unit length. Thus, for each $X > 0.3125$ mm, the integrated emission (the fraction of initial pump radiation seen by the detector) decreases with increasing concentration above 0.32 %. In short, this figure defines the net reduction in integrated emission due to a given increase in concentration at a particular pump position. It also shows that for each concentration, the integrated emission decreases with increasing pump position.

A spectral model was developed (explained in Ch. 5) to calculate radiative energy transfer rates between Ho$^{3+}$ ions using spectral measurements (absorption and luminescence) as functions of temperature. Hence, luminescence spectra, corresponding in concentration ( YAG:Ho(3 %) ) and temperature ( 77 - 500 K ) with the absorption spectra in Fig. 4.11 - Fig. 4.20, were measured. As with all the other measured luminescence spectra, the YAG:Ho(3 %) slab was pumped along the slab width (2.10 mm). The low
temperature spectra (77 K - 295 K) were taken by placing the slab in the CTI-Cryogenics Model 12 cold head, which was supported with a Model SC-21 compressor. This cold head was placed in the excitation / emission path such that the slab maintained the same position as in Fig. 3.1. Using a Lake Shore Cryotronics Model DRC-80C digital thermometer / controller, the temperature of the sample in the cold head was varied between 77 and 295 K. The high temperature spectra (295 K - 500 K) were taken by placing the slab on the LFE Model 232 automatic temperature controlled sample heater which was then placed in the set-up described in Fig. 3.1, maintaining the slab position. Fig. 4.54 - Fig. 4.63 corresponding to these ten temperature-dependent luminescence spectra are shown on the following pages. These spectra show that as the temperature is increased, the luminescent intensity decreases due to increased phonon decay from the $^5I_7$ manifold. It is evident that the room temperature spectra taken from both the high and low temperature measurements suffered an overall attenuation in luminescent intensity with respect to the corresponding spectrum from the previous room temperature measurements. This reduction in signal has been attributed to the additional housing and different surface mounting of the sample that is required for the high and low temperature measurements.
Fig. 4.54 Luminescence spectrum $^5I_7 \rightarrow ^5I_8$; $T = 77$ K.
Fig. 4.55  Luminescence spectrum $5_{17} \rightarrow 5_{18}$; $T = 120 \text{ K.}$

$X = 4.3125 \text{ mm}$

Intensity (A.U.) vs. Wavelength (nm)
Fig. 4.56 Luminescence spectrum $5^1 \rightarrow 5_{10}^0$; $T = 160$ K.
Fig. 4.57 Luminescence spectrum $5^1_7 \rightarrow 5^1_8$; $T = 200$ K.
Fig. 4.58  Luminescence spectrum $^5I_7 \rightarrow ^5I_8$; $T = 295$ K (from low temperature measurement).
Fig. 4.59 Luminescence spectrum $5^1_g \rightarrow 5^1_f$; $T = 295 K$
(from high temperature measurement).

YAG:Ho(3 %) mm

Wavelength (nm)

Intensity (A.U.)
Fig. 4.60  Luminescence spectrum $5_I^7 \rightarrow 5_I^8$; $T = 350$ K.
Fig. 4.61 Luminescence spectrum $5_{17} \rightarrow 5_{18}$; $T = 400$ K.
Fig. 4.62 Luminescence spectrum $5_{17} \rightarrow 5_{18}$; $T = 450$ K.

Intensity (A.U.)

YAG:Ho (3 %)

$x = 4.3125$ mm

Wavelength (nm)
4.3 LIFETIME MEASUREMENTS

Pulsed luminescence studies were performed for each of the concentrations or slabs as functions of both pump position and temperature. These measurements were taken by examining the temporal $\text{Ho}^{3+} \rightarrow \text{5I}_7 \rightarrow \text{5I}_8$ luminescent response to pulsed excitation, unlike the continuous luminescence experiments where the spectral (wavelength) response to cw (continuous wave) excitation was of interest. From these pulsed studies, decay curves of luminescent intensity vs. time were obtained. The time constant resulting from the best exponential fit to the long tail segment of each decay curve was taken as the lifetime of the $\text{5I}_7$ manifold under each measurement condition of concentration, pump position, and temperature.

As in the continuous luminescence experiments, each slab was pumped along its width (2.10 mm). The low temperature decay curves (77 K - 295 K) were obtained by placing each slab in the CTI-Cryogenics Model 12 cold head, which was supported with a Model SC-21 compressor. This cold head was placed in the excitation / emission path such that the slab maintained the same position as in Fig. 3.2. Using a Lake Shore Cryotronics Model DRC-80C digital thermometer / controller, the temperature of the sample in the cold head was varied between 77 and 295 K. The high temperature decay curves (295 K - 500 K) were obtained by placing the slab on the LFE Model 232 automatic
temperature controlled sample heater which was then placed in the set-up described in Fig. 3.2, maintaining the slab position.

Fig. 4.64 below shows the lifetimes of the pulsed luminescence at 295 K as functions of concentration when pumped at the nearest position to the detector.

![Graph showing lifetime vs. concentration](image)

**Fig. 4.64** Lifetime of the Ho$^{3+}$ 5$^1_7$ emission vs. concentration at $T = 295$ K, $X = 0.96$ mm (nearest to the detector).
This graph indicates that as the Ho$^{3+}$ concentration increases up to 3 %, the lifetime increases as well. At concentrations of 8.5 % and above, the lifetimes are diminished with respect to that at 3 %. The pump was then maintained at the nearest position to the detector, and the lifetimes were examined for each concentration as functions of temperature. The resulting iso-concentration curves are shown in Fig. 4.65 below.

Fig. 4.65 Lifetime of the Ho$^{3+}$ $^5l_7$ emission vs. temperature and concentration, $X = 0.96$ mm (nearest to the detector).
This figure indicates that the maximum lifetime of the Ho\(^{3+}\) pulsed emission occurs around 295 K for each concentration. The concentration dependence of these lifetimes seen at 295 K in Fig. 4.64 is preserved for temperatures at and above 295 K in this figure. This 295 K concentration dependence is not maintained at temperatures well below 295 K. In fact, for temperatures below 200 K, the relative magnitude of the lifetimes for each concentration are somewhat reversed and have less variance with respect to those at 295 K and above. On the following page, Table 4.1 lists the numerical measured values of the lifetimes at the nearest pump position as functions of concentration and temperature.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Concentration (% Ho:YAG)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>77</td>
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<td>120</td>
<td>7315.270</td>
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<td>160</td>
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<tr>
<td>200</td>
<td>7576.189</td>
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<tr>
<td>350</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>7429.418</td>
</tr>
<tr>
<td>450</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>6760.691</td>
</tr>
</tbody>
</table>
5.1 SPECTRAL MODEL: ANALYSIS OF ABSORPTION AND LUMINESCENCE RESULTS

The dynamics of 2.1 µm photons traveling within a given Ho:YAG slab as they are reabsorbed and remitted after the initial absorption of pump radiation were theoretically modeled. One of the products of this model was the accurate prediction of the actual measured luminescence spectrum for a given concentration, pump position, and temperature. Through this prediction, the corresponding absorption and luminescence spectra were correlated. This correlation is shown in the following description of the spectral model, entitled the "luminescence" model since a theoretical luminescence spectrum is calculated.

The following figure and table define the constants and parameters for the luminescence model.
\( X \) = pump position or emission path length

\( L, W, H \) = Ho:YAG slab dimensions (length, width, and height)

\( x, y, z \) = coordinates of reference frame, the origin of which is the point of incidence of the pump beam on the slab (pump along \( y \), detect along \( x \))

\( S_{\text{far}} \) = cantilevered end of slab fartherest from the detector

\( R_{\text{far}} \) = reflectivity of \( S_{\text{far}} = 100\% \)

\( S_{\text{near}} \) = free end of slab nearest to the detector

\( R_{\text{near}} \) = reflectivity of \( S_{\text{near}} = \left[ \frac{n - 1}{n + 1} \right]^2 \)

\[ = 8.21\% \] for \( n = 1.802 \) for YAG @ 2.1 \( \mu \text{m} \)

\( = R \)

Fig. 5.1 Schematic of slab pumping for luminescence detection
| **TABLE 5.1**  
PARAMETERS FOR THE LUMINESCENCE MODEL |
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$I(\lambda)$</td>
</tr>
<tr>
<td>$I_0(\lambda)$</td>
</tr>
<tr>
<td>$I_0^+(\lambda)$</td>
</tr>
<tr>
<td>$I_0^-(\lambda)$</td>
</tr>
<tr>
<td>$\alpha(\lambda)$</td>
</tr>
<tr>
<td>$d$</td>
</tr>
<tr>
<td>$\kappa$</td>
</tr>
</tbody>
</table>

The algorithm describing the dynamics of 2.1 μm photons as they travel within the slab (starting at the excitation point or pump position and ending at $S_{near}$ where they exit to the detector) over a rectangular volume of length $d$ having the same cross section as the slab is given as follows. For emission initially towards the detector,

$$I^{+}(d,\lambda) = \kappa I_0^+\lambda)e^{-\alpha(\lambda)d} + \kappa^2 I_0^+\lambda)(1 - e^{-\alpha(\lambda)d}), \quad (5.1.1)$$

and for emission initially away from the detector,
Here, $\kappa l_0^+(\lambda)$ or $\kappa l_0^-(\lambda)$ represents the TIR radiation incident upon the first cell of length $d$ towards or away from the detector, respectively. Hence, the first term in each equation describes the TIR radiation transmitted to the next cell of length $d$ in either direction with respect to the detector. The second term in each equation is derived from the TIR radiation reabsorbed over the first cell of length $d$ in either direction. If we assume that all of this reabsorbed radiation is later remitted as $2.1 \mu m$ photons in all directions, then the TIR portion of this remission is given by the second term. If we factor out the incident TIR radiation in each equation, they become,

$$I^+(d,\lambda) = \kappa l_0^+(\lambda) [ e^{-\alpha(\lambda)d} + \kappa (1 - e^{-\alpha(\lambda)d}) ]$$

$$I^-(d,\lambda) = \kappa l_0^-(\lambda) [ e^{-\alpha(\lambda)d} + \kappa (1 - e^{-\alpha(\lambda)d}) ] .$$

When $I^+(d,\lambda)$ or $I^-(d,\lambda)$ is incident upon the next cell of length $d$ in either direction, the same algorithm, multiplication of incident intensity by

$$A(\lambda) = [ e^{-\alpha(\lambda)d} + \kappa (1 - e^{-\alpha(\lambda)d}) ] ,$$

is performed on each term in the previous two equations, resulting in

$$I^+(2d,\lambda) = \kappa l_0^+(\lambda) [ e^{-\alpha(\lambda)d} + \kappa (1 - e^{-\alpha(\lambda)d}) ]^2$$

$$I^-(2d,\lambda) = \kappa l_0^-(\lambda) [ e^{-\alpha(\lambda)d} + \kappa (1 - e^{-\alpha(\lambda)d}) ]^2 .$$

Next, the inclusion of all such cells, except for those with perturbatively small contribution to the detected luminescence, was performed. First we considered
the initial TIR emission traveling towards the detector, \( k l_{0}^{+}(\lambda) \), with respect to the path length required to diminish its intensity below a given threshold as it travels within the slab. From the previous two equations, it is known that this diminished intensity is a function in general of both its path length and wavelength. Hence, we define this intensity as \( I^{+}(x^{+}, \lambda) \), where \( x^{+} \) is the path length over which this intensity diminishes beyond detection, depending of course on the pump position, \( X \). Since the length of the slab is much greater than either dimension of the slab cross section, we consider \( x^{+} \) to include only the TIR rays along the slab axis. On the average, the actual path length is longer. We pick a limit for \( x^{+} \) based on the number of reflections at \( S_{\text{near}} \) after which negligible contribution is yielded to the detected luminescence. In other words, we find an integer, \( m \), such that \( R^{m} \sim 0 \). Thus,

\[
\begin{align*}
m = 2 & \quad \rightarrow \quad R^{m} = 0.67 \% \\
3 & \quad 0.06 \\
4 & \quad 0.004 \\
5 & \quad 0.0004 \\
6 & \quad 0.00003
\end{align*}
\]

Let the limit for \( x^{+} \) be \( m = 5 \). For \( m = 5 \), \( I^{+}(x^{+}, \lambda) \) travels back and forth along the slab a distance of:

\[
x^{+} = X + 2L + 2L + 2L + 2L = X + 8L
\]

\[
m = 1 \quad 2 \quad 3 \quad 4 \quad 5
\]

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On the basis of significant contribution to detected luminescence, we do not consider the remissions from each d cell derived from \( I^+(x^+,\lambda) \) in the negative x direction.

Next we considered the initial TIR emission traveling away from the detector, \( \kappa I_0^-(\lambda) \), with respect to the path length required to diminish its intensity below a given threshold as it travels within the slab. The previous treatment was applied to the resulting diminished intensity, defining it as \( I^-(x^-,\lambda) \). Again, we consider \( x^- \) to include only the TIR rays along the slab axis and let the limit for \( x^- \) be \( m = 5 \). For \( m = 5 \), \( I^-(x^-,\lambda) \) travels back and forth along the slab a distance of:

\[
x^- = (X+d) + 2L + 2L + 2L + 2L = (X+d) + 8L \sim X + 8L
\]

Again, we do not consider the remissions from each d cell derived from \( I^-(x^-,\lambda) \) in the negative x direction. In actuality, we consider the initial intensity for \( I^-(x^-,\lambda) \) to be:

\[
I^-(d,\lambda) = \kappa I_0^- (\lambda) \left[ e^{-\alpha(\lambda)d} + \kappa(1 - e^{-\alpha(\lambda)d}) \right],
\]

rather than \( \kappa I_0^-(\lambda) \).

We may now begin to synthesize the theoretical luminescence spectrum,

\[
I(\lambda) = I^+(\lambda) + I^-(\lambda), \quad (5.1.8)
\]

where,

\[
I^+(\lambda) = \sum_{m=1}^{5} I^+_m(\lambda) \quad \text{and} \quad I^-(\lambda) = \sum_{m=1}^{5} I^-_m(\lambda) \quad (5.1.9)
\]
Each of the five terms in \( I^+(\lambda) \) and in \( I^-(\lambda) \) represent the intensities transmitted to the detector through the five respective normal incidences at \( S_{near} \). These terms are defined as functions of powers of \( A(\lambda) \), see (5.1.5), as follows.

\[
I^+_1(\lambda) = \kappa I_0^+(\lambda) [A(\lambda)]^{n_1^+} (1 - R) \tag{5.1.10}
\]

\[
I^+_2(\lambda) = R \kappa I_0^+(\lambda) [A(\lambda)]^{n_1^+} [A(\lambda)]^{n_2^+} (1 - R) \tag{5.1.11}
\]

\[
I^+_3(\lambda) = R^2 \kappa I_0^+(\lambda) [A(\lambda)]^{n_1^+} [A(\lambda)]^{n_2^+} [A(\lambda)]^{n_3^+} (1 - R) \tag{5.1.12}
\]

\[
I^+_4(\lambda) = R^3 \kappa I_0^+(\lambda) [A(\lambda)]^{n_1^+} [A(\lambda)]^{n_2^+} [A(\lambda)]^{n_3^+} [A(\lambda)]^{n_4^+} (1 - R) \tag{5.1.13}
\]

\[
I^+_5(\lambda) = R^4 \kappa I_0^+(\lambda) [A(\lambda)]^{n_1^+} [A(\lambda)]^{n_2^+} [A(\lambda)]^{n_3^+} [A(\lambda)]^{n_4^+} [A(\lambda)]^{n_5^+} (1-R) \tag{5.1.14}
\]

\[
n_1^+ = \frac{X}{d} ; \quad n_2^+ = n_3^+ = n_4^+ = n_5^+ = 2 \frac{L}{d} = n^+ \tag{5.1.15}
\]

\[
\Gamma_1(\lambda) = I^-(d,\lambda) [A(\lambda)]^{n_1^-} (1 - R) \tag{5.1.16}
\]

\[
\Gamma_2(\lambda) = R I^-(d,\lambda) [A(\lambda)]^{n_1^-} [A(\lambda)]^{n_2^-} (1 - R) \tag{5.1.17}
\]

\[
\Gamma_3(\lambda) = R^2 I^-(d,\lambda) [A(\lambda)]^{n_1^-} [A(\lambda)]^{n_2^-} [A(\lambda)]^{n_3^-} (1 - R) \tag{5.1.18}
\]

\[
\Gamma_4(\lambda) = R^3 I^-(d,\lambda) [A(\lambda)]^{n_1^-} [A(\lambda)]^{n_2^-} [A(\lambda)]^{n_3^-} [A(\lambda)]^{n_4^-} (1 - R) \tag{5.1.19}
\]

\[
\Gamma_5(\lambda) = R^4 I^-(d,\lambda) [A(\lambda)]^{n_1^-} [A(\lambda)]^{n_2^-} [A(\lambda)]^{n_3^-} [A(\lambda)]^{n_4^-} [A(\lambda)]^{n_5^-} (1-R) \tag{5.1.20}
\]

\[
n_1^- = \frac{(X + d)}{d} ; \quad n_2^- = n_3^- = n_4^- = n_5^- = 2 \frac{L}{d} = n^- = n^+ = n \tag{5.1.21}
\]

Therefore,

\[
I^+(\lambda) = \kappa I_0^+(\lambda) [A(\lambda)]^{n_1^+} (1 - R) \{ 1 + R [A(\lambda)]^{n_1^+} + R^2 [A(\lambda)]^{2n_1^+} + R^3 [A(\lambda)]^{3n_1^+} + R^4 [A(\lambda)]^{4n_1^+} \} , \tag{5.1.22}
\]
\[ l'(\lambda) = (1 - R) \left\{ 1 + R [A(\lambda)]^{n_1} + R^2 [A(\lambda)]^{2n_1} + R^3 [A(\lambda)]^{3n_1} + R^4 [A(\lambda)]^{4n_1} \right\} . \] (5.1.23)

Hence, the detected luminescence for a given concentration, pump position, and temperature is known theoretically as,

\[ l(\lambda) = (1 - R) \left\{ 1 + R [A(\lambda)]^{n_1} + R^2 [A(\lambda)]^{2n_1} + R^3 [A(\lambda)]^{3n_1} + R^4 [A(\lambda)]^{4n_1} \right\} \kappa I_0^+ (\lambda) [A(\lambda)]^{n_{1+}} + I^-(d, \lambda) [A(\lambda)]^{n_{1-}} \} \] (5.1.24)

The remaining parameters for this luminescence model are specified as follows. First, the experimental luminescence spectrum selected for a case study in this model was that corresponding to YAG:Ho(3%), \( X = 4.3125 \text{ mm} \) (a pump position moderately near the detector), and \( T = 295 \text{ K} \). Hence, the absorption coefficient spectrum used in the model was that corresponding to YAG:Ho(3%) and \( T = 295 \text{ K} \) (see Fig. 4.15). The initial TIR emission traveling towards the detector, \( \kappa I_0^+ (\lambda) \), was taken to be the luminescence spectrum measured for YAG:Ho(3%), \( X = 0.3125 \text{ mm} \) (the pump position along the slab length nearest the detector), and \( T = 295 \text{ K} \). As for the initial TIR emission traveling away from the detector, \( \kappa I_0^- (\lambda) \), its value in the model was taken to be the same as that of \( \kappa I_0^+ (\lambda) \).

The value of \( \kappa \), the fraction of the initial hemispherical emission after absorption of pump radiation that is TIR either towards or away from the detector was calculated as follows. First, \( \kappa \) for an elliptical cross section slab whose total major axis length is 2.62 mm and whose total minor axis length is 2.10 mm is calculated. Since the actual slabs are of rectangular cross section 2.62 mm by 2.10 mm, the actual value of \( \kappa \) will be slightly less than that for the elliptical
cross section slab. We define $\kappa$ as the ratio of the solid angle of TIR (either towards or away from the detector) to the solid angle corresponding to the total initial hemispherical emission (either towards or away from the detector),

$$\kappa = \frac{\mu_{\text{TIR}}}{\mu_{\text{total}}}.$$  
(5.1.25)

Further,

$$\mu_{\text{TIR}} = \int_{\phi = -(\Pi/2)}^{(\Pi/2)} \phi \int_{\theta = \theta_c}^{\Pi - \theta_c} \sin \theta \d \theta \d \phi$$  
(5.1.26)

and,

$$\mu_{\text{total}} = \int_{\phi = -(\Pi/2)}^{(\Pi/2)} \int_{\theta = 0}^{\Pi} \sin \theta \d \theta \d \phi.$$  
(5.1.27)

Since $n = 1.802$ for YAG at 2.1 $\mu$m, then by Snell’s law,

$$\phi_c = \theta_c = \sin^{-1} \left( \frac{1}{n} \right) = 33.67^\circ,$$  
(5.1.28)

are the critical angles of TIR within the slab along its width and height, respectively. From these values, we find that $\kappa \approx 0.4499$.

Lastly, the value for the parameter $d$ was chosen such that it was on the order of the slab’s cross sectional dimensions (or such that $\alpha(\lambda) d \sim 1$) and such that the best fit of theoretical to experimental luminescence spectra was achieved. This value of $d$ was found to be 2.5 mm. Figure 5.2 on the next page shows the close comparison of the theoretical with experimental luminescence spectra for YAG:Ho(3 %), $X = 4.3125$ mm, and $T = 295$ K.
Fig. 5.2 Theoretical (a) and measured (b) luminescence spectra for YAG:Ho(3 %), $X = 4.3125$ mm, and $T = 295$ K.
5.2 SPECTRAL MODEL: CALCULATION OF RADIATIVE ENERGY TRANSFER RATES

The Ho $^5\text{I}_7$ radiative energy transfer rate as a function of temperature was derived from the previously described spectral model as follows. Recall that the portion of the initial luminescence emission toward the detector remaining inside the crystal after a distance $d$ is given by

$$I^+(d,\lambda) = \kappa l_0^+(\lambda) \left[ e^{-\alpha(\lambda)d} + \kappa (1 - e^{-\alpha(\lambda)d}) \right]$$

(5.1.3)

In this equation, $d$ represents the path length inside the crystal over which one TIR transmission, reabsorption, and remission takes place. The fraction of the initial TIR emission participating in radiative energy transfer (reabsorption - remission of 2.1 $\mu$m photons) over $d$ is therefore given by

$$I^+_{\text{rad}}(d,\lambda) = \kappa l_0^+(\lambda) \left[ \kappa (1 - e^{-\alpha(\lambda)d}) \right]$$

(5.2.1)

This quantity can then be transformed such that it is proportional to and has the same units as the radiative energy transfer rate:

$$I^+_{\text{rad}}(d,\lambda) = \text{energy} \div \left[ \text{(area) (time)} \right]$$

$$= \left( \text{energy} \div \# \text{ photon} \right) \left( \# \text{ photon} \div \text{time} \right) \left( 1 \div \text{area} \right)$$

$$= \left( \text{energy} \div \# \text{ photon} \right) \left( 1 \div \text{area} \right) W_{\text{rad}}$$

$$= \left( \frac{E'}{A} \right) W_{\text{rad}}$$

(5.2.2)

where $E' = C \left( 0.59 \text{ eV} \div 2.1 \mu\text{m photon} \right)$, and $C$ is a normalization constant.
A is the area of the portion of the sphere centered at the point of initial emission \((X, W/2, H/2)\) that is subtended by \(\mu_{\text{TIR}}\), the solid angle of TIR, and the sides of the slab. Given that the pump spot radius << the slab dimensions \(L, W,\) and \(H\), the following geometrical analysis was performed to calculate \(A\). The next figure shows the geometry of the slab length from side and top perspectives.

Fig. 5.3 Side view (a) and top view (b) of slab length geometry for determination of \(A\)
From Fig. 5.3 (a), the arclength $S_1$ was determined as follows:

$$r_1 = \frac{H}{2 \cos \phi_c} = \frac{2.62 \text{ mm}}{2 \cos 33.67^\circ} = 1.57 \text{ mm} \quad (5.2.3)$$

$$S_1 = \int_{\theta_1}^{\theta_2} \pi \cdot \phi_c \ r_1 \ d\theta = 3.09 \text{ mm} \quad (5.2.4)$$

Similarly, from Fig. 5.3 (b), the arclength $S_2$ was determined as follows:

$$r_2 = \frac{w}{2 \cos \phi_c} = \frac{2.10 \text{ mm}}{2 \cos 33.67^\circ} = 1.26 \text{ mm} \quad (5.2.5)$$

$$S_2 = \int_{\phi_1}^{\phi_2} \pi \cdot \phi_c \ r_2 \ d\phi = 2.48 \text{ mm} \quad (5.2.6)$$

Therefore,

$$A > or \sim S_1 S_2 = 7.66 \text{ mm}^2 > H w = 5.50 \text{ mm}^2 \quad , \quad (5.2.7)$$

or,

$$A \sim 8 \text{ mm}^2 = 0.08 \text{ cm}^2 .$$

Thus, $W_{\text{rad}}' (d, \lambda)$ can be determined as follows:

$$W_{\text{rad}}' (d, \lambda) = C^{-1} \ (0.59)^{-1} \ (0.08) \ \kappa^2 \ l_0^+ (\lambda) \ (1 - e^{-\alpha(\lambda)d}) . \quad (5.2.8)$$

The actual transfer rate of TIR remitted photons from initial pump cell to the next cell towards the detector (radiative energy transfer rate) when averaged over wavelength for the $^5l_7 \longleftrightarrow ^5l_8$ transitions is:

$$W_{\text{rad}} = (\lambda_2 - \lambda_1)^{-1} \int_{\lambda_1}^{\lambda_2} \lambda^2 \ W_{\text{rad}}' (\lambda) \ d\lambda . \quad (5.2.9)$$

where $\lambda_1 = 1.82 \ \mu m$, $\lambda_2 = 2.15 \ \mu m$, and $W_{\text{rad}}$ has units of $s^{-1}$. The following table and figure show the resulting temperature dependence of the Ho $^5l_7 \longleftrightarrow ^5l_8$ radiative energy transfer rate as calculated from this spectral model. Awaiting suitable normalization with respect to the radiative energy transfer rates calculated from the kinetic model, the normalization constant used in the following spectral model calculation was $C^{-1} = 1$. 

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TABLE 5.2

TEMPERATURE DEPENDENCE OF THE Ho$^{3+}$ $^{5I_7} \leftrightarrow ^{5I_8}$ RADIATIVE ENERGY TRANSFER RATE AS CALCULATED FROM THE SPECTRAL MODEL

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$W_{rad}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>1.760</td>
</tr>
<tr>
<td>120</td>
<td>2.391</td>
</tr>
<tr>
<td>160</td>
<td>3.143</td>
</tr>
<tr>
<td>200</td>
<td>3.302</td>
</tr>
<tr>
<td>295</td>
<td>5.404</td>
</tr>
<tr>
<td>350</td>
<td>6.022</td>
</tr>
<tr>
<td>400</td>
<td>6.533</td>
</tr>
<tr>
<td>450</td>
<td>6.629</td>
</tr>
<tr>
<td>500</td>
<td>6.746</td>
</tr>
</tbody>
</table>
Fig. 5.4 Temperature dependence of the Ho $^5l_7 \leftrightarrow ^5l_8$ radiative energy transfer rate calculated from the spectral model for YAG:Ho(3 %), $X = 4.3125$ mm.
5.3 KINETIC MODEL: ANALYSIS OF LIFETIME RESULTS

The Ho $^{5l_7}$ radiative energy transfer rate was calculated from the following model depicting the observed behavior of the corresponding lifetimes of 2.1 μm pulsed luminescence,

$$\frac{1}{\tau_{\text{meas}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}} - W_{\text{rad}},$$  \hspace{1cm} (5.3.1)

where $\tau_{\text{meas}}$ is the measured lifetime, $\tau_{\text{rad}}$ is the radiative transition lifetime, $W_{\text{rad}}$ is the radiative energy transfer rate, and $\frac{1}{\tau_{\text{non-rad}}}$ is the non-radiative transition rate. As a case study for this model, the measured lifetimes of the YAG:Ho(3 %) slab with $X = 4.3125$ mm as functions of temperature were used. The temperature dependence of the sum of the radiative and non-radiative transition rates was taken to be that of the measured fluorescence rates for the YAG:Ho(0.32 %) slab (when pumped at the nearest position from the detector). This hypothesis is reasonable since the radiative and non-radiative transition rates are associated with a single ion and therefore are not dependent on concentration and pump position, only temperature. The YAG:Ho(0.32 %) nearest pump position - rates were used since the conditions of minimal Ho$^{3+}$ concentration and minimal pump position yield minimal radiative energy transfer before detection. In other words, the sum of the radiative and non-radiative transition rates temperature dependence was approximated by solving (5.3.1) for $\frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}}$ under the assumption that $W_{\text{rad}}$ is zero.
Hence,
\[
\frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}} \sim \frac{1}{\tau_{\text{meas}}} + W_{\text{rad}}, \quad W_{\text{rad}} \sim 0
\]
\[
\sim \frac{1}{\tau_{\text{meas},c=0.32\%,X=0.96\text{mm}}} \quad (5.3.1.a)
\]
In this way, the temperature dependence of the Ho\textsuperscript{3+} radiative transition rate can be determined separately as follows. From (5.3.1.a) with \( W_{\text{rad}} \sim 0 \),
\[
\frac{1}{\tau_{\text{rad}}} \sim \frac{1}{\tau_{\text{meas},c=0.32\%,X=0.96\text{mm}}} - \frac{1}{\tau_{\text{non-rad}}} \quad (5.3.2)
\]
This calculation must be made with the knowledge of the temperature dependence of the non-radiative transition rates, which can be obtained from [21],
\[
\frac{1}{\tau_{\text{non-rad}}} = A (1 + n)^p e^{-\beta (p - 2.4)} , \quad (5.3.3)
\]
where \( A \sim 10^7 \text{s}^{-1} \) is the non-radiative transition rate at \( T = 0 \text{K} \), \( n \) is the thermal occupancy of phonons of energy \( \nu \text{v} \) given by
\[
n = [\exp(\nu / kT) - 1]^{-1} , \quad (5.3.4)
\]
the phonon energy \( \nu \text{v} \sim 500 \text{cm}^{-1} \) for YAG, \( p = E_g / \nu \text{v} = 9.6 \) is the smallest number of highest energy (\( \nu \text{v} \) ) phonons required to bridge the energy gap \( E_g = 9.5 \times 10^{-20} \text{J} \) (for \( \lambda_g = 2.1 \mu\text{m} \)), and \( \beta \sim 2 \) for YAG-type hosts. The following table shows the resulting non-radiative transition rates and lifetimes as functions of temperature.
<table>
<thead>
<tr>
<th>T (K)</th>
<th>$1 / \tau_{\text{non-rad}} \text{ (s}^{-1}\text{)}$</th>
<th>$\tau_{\text{non-rad}} \text{ (ms)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>5.5784</td>
<td>179.3</td>
</tr>
<tr>
<td>120</td>
<td>5.7093</td>
<td>175.2</td>
</tr>
<tr>
<td>160</td>
<td>6.2088</td>
<td>161.1</td>
</tr>
<tr>
<td>200</td>
<td>7.2795</td>
<td>137.4</td>
</tr>
<tr>
<td>295</td>
<td>13.4030</td>
<td>74.61</td>
</tr>
<tr>
<td>350</td>
<td>20.7957</td>
<td>48.09</td>
</tr>
<tr>
<td>400</td>
<td>31.5750</td>
<td>31.67</td>
</tr>
<tr>
<td>450</td>
<td>48.5838</td>
<td>20.58</td>
</tr>
<tr>
<td>500</td>
<td>75.0147</td>
<td>13.33</td>
</tr>
</tbody>
</table>
The calculation of this radiative transition rate temperature dependence, shown in segments in the following two tables, is thus determined from both experimental and theoretical values.

### TABLE 5.4

TEMPERATURE DEPENDENCE OF THE MEASURED FLUORESCENCE RATE

WHEN $W_{rad} \sim 0$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$1 / \tau_{meas,c=0.32%,X=0.96mm\ (s^{-1})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>137.276</td>
</tr>
<tr>
<td>120</td>
<td>133.871</td>
</tr>
<tr>
<td>160</td>
<td>131.667</td>
</tr>
<tr>
<td>200</td>
<td>127.672</td>
</tr>
<tr>
<td>295</td>
<td>130.494</td>
</tr>
<tr>
<td>350</td>
<td>*</td>
</tr>
<tr>
<td>400</td>
<td>134.842</td>
</tr>
<tr>
<td>450</td>
<td>*</td>
</tr>
<tr>
<td>500</td>
<td>149.701</td>
</tr>
</tbody>
</table>

* data was not available at these temperatures
TABLE 5.5
TEMPERATURE DEPENDENCE OF THE CALCULATED RADATIVE TRANSITION RATES

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$1 / \tau_{\text{rad}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>131.696</td>
</tr>
<tr>
<td>120</td>
<td>128.161</td>
</tr>
<tr>
<td>160</td>
<td>125.457</td>
</tr>
<tr>
<td>200</td>
<td>120.392</td>
</tr>
<tr>
<td>295</td>
<td>117.094</td>
</tr>
<tr>
<td>350</td>
<td>112. *</td>
</tr>
<tr>
<td>400</td>
<td>103.262</td>
</tr>
<tr>
<td>450</td>
<td>92. *</td>
</tr>
<tr>
<td>500</td>
<td>74.691</td>
</tr>
</tbody>
</table>

* these values were interpolated
We now return to the main objective, the calculation of the temperature dependence of the radiative energy transfer rates for \( c = 3\% \) and \( X = 4.3125 \) mm. From (5.3.1),

\[
W_{\text{rad}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}} - \frac{1}{\tau_{\text{meas},c=3\%,X=4.3125\text{mm}}} \quad (5.3.5)
\]

\[
= \frac{1}{\tau_{\text{meas},c=0.32\%,X=0.96\text{mm}}} - \frac{1}{\tau_{\text{meas},c=3\%,X=4.3125\text{mm}}}.
\]

The temperature dependence of the measured fluorescence rate for \( c = 3\% \) and \( X = 4.3125 \) mm is shown in the following table.
Thus, the radiative energy transfer rate temperature dependence was calculated using the model from the previously listed totally experimental temperature dependencies of the non-radiative transition, measured fluorescence, and radiative transition rates, and is shown in the following table.

### TABLE 5.6
TEMPERATURE DEPENDENCE OF THE MEASURED FLUORESCENCE RATE

<table>
<thead>
<tr>
<th>T (K)</th>
<th>(1 / \tau_{\text{meas},c=3%,X=4.3\text{mm}}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>132.487</td>
</tr>
<tr>
<td>120</td>
<td>121.542</td>
</tr>
<tr>
<td>160</td>
<td>112.170</td>
</tr>
<tr>
<td>200</td>
<td>105.647</td>
</tr>
<tr>
<td>295</td>
<td>101.149</td>
</tr>
<tr>
<td>350</td>
<td>104.982</td>
</tr>
<tr>
<td>400</td>
<td>110.340</td>
</tr>
<tr>
<td>450</td>
<td>115.919</td>
</tr>
<tr>
<td>500</td>
<td>124.324</td>
</tr>
</tbody>
</table>
TABLE 5.7

TEMPERATURE DEPENDENCE OF THE Ho$^{3+}$ $^{5}I_{7}$ $\leftrightarrow$ $^{5}I_{8}$ RADIATIVE ENERGY TRANSFER RATE AS CALCULATED FROM THE KINETIC MODEL

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$W_{\text{rad}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>4.788</td>
</tr>
<tr>
<td>120</td>
<td>12.330</td>
</tr>
<tr>
<td>160</td>
<td>19.496</td>
</tr>
<tr>
<td>200</td>
<td>22.025</td>
</tr>
<tr>
<td>295</td>
<td>29.345</td>
</tr>
<tr>
<td>350</td>
<td>27.818</td>
</tr>
<tr>
<td>400</td>
<td>24.502</td>
</tr>
<tr>
<td>450</td>
<td>24.661</td>
</tr>
<tr>
<td>500</td>
<td>25.377</td>
</tr>
</tbody>
</table>

The next two figures display graphically the calculation of this temperature dependence of the radiative energy transfer rate from the kinetic model.
Fig. 5.5 Temperature dependence of the sum of the radiative and non-radiative transition rates and of the measured fluorescence rate for YAG:Ho(3%), X = 4.3125 mm.
Fig. 5.6  Temperature dependence of the Ho $^{5}I_{7} \leftrightarrow ^{5}I_{8}$ radiative energy transfer rate as calculated from the kinetic model for YAG:Ho(3%), $X = 4.3125$ mm.
5.4  CORRELATION OF SPECTRAL AND KINETIC MEASUREMENTS

The spectral measurements (absorption and luminescence) were correlated with the kinetic measurements (lifetimes) because of the close agreement in the temperature dependence of the Ho $^{5}I_7 <--> ^{5}I_8$ radiative energy transfer rates calculated from the corresponding spectral and kinetic models. If the spectral model rates from Table 5.2 are all multiplied by the normalization constant $C^{-1} = 4.569$ (already accounted for in equation 5.2.8), then the spectral - and kinetic - determined rates are quite comparative as shown in the table and figure below.
TABLE 5.8
COMPARISON OF TEMPERATURE DEPENDENCE OF SPECTRAL AND
KINETIC MODEL RADIATIVE ENERGY TRANSFER RATES

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$W_{\text{rad,spectral}}$ (s$^{-1}$)</th>
<th>$W_{\text{rad,kinetic}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>8.042</td>
<td>4.788</td>
</tr>
<tr>
<td>120</td>
<td>10.926</td>
<td>12.330</td>
</tr>
<tr>
<td>160</td>
<td>14.359</td>
<td>19.496</td>
</tr>
<tr>
<td>200</td>
<td>15.088</td>
<td>22.025</td>
</tr>
<tr>
<td>295</td>
<td>24.691</td>
<td>29.345</td>
</tr>
<tr>
<td>350</td>
<td>27.516</td>
<td>27.818</td>
</tr>
<tr>
<td>400</td>
<td>29.849</td>
<td>24.502</td>
</tr>
<tr>
<td>450</td>
<td>30.286</td>
<td>24.661</td>
</tr>
<tr>
<td>500</td>
<td>30.824</td>
<td>25.377</td>
</tr>
</tbody>
</table>

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Fig. 5.7 Temperature dependence of the Ho $^5I_7 \leftrightarrow ^5I_8$ radiative energy transfer rate as calculated from both the spectral and kinetic models for YAG:Ho(3 %), $X = 4.3125$ mm.
An extensive characterization of the Ho$^{3+} \ 5_{17}$ manifold in YAG ($Y_3Al_5O_{12}$) has been the goal of this research, since the 2.1 $\mu$m laser emission from this manifold is of significant interest in the field of solid-state laser development for the purposes of atmospheric studies (e.g., detection of wind shear). This research included cw absorption and luminescence emission (spectral) studies and lifetime of pulsed emission (kinetic) studies using a wide range of Ho concentrations (from 0.32 to 8.5 %), temperatures (from 30 to 500 K), and emission path lengths within the crystal (taking advantage of the rectangular cross section fiber geometry of each of the slabs).

In the absorption measurements, as the temperature was decreased, the absorption peaks decreased in intensity and structural definition for the higher wavelengths (centered around 2.05 $\mu$m) in the $5_{18} \rightarrow 5_{17}$ transition and remained approximately the same for the lower wavelengths (centered around 1.9 $\mu$m). In general, the absorption cross section decreased with decreasing temperature. These observed spectral behavior of Ho is typical in the sense that at lower temperatures electrons occupy lower Stark levels within the $5_{18}$ ground manifold. Thus, excitation of these electrons to Stark levels in the $5_{17}$ manifold is achieved through absorption of photons of higher energies or lower
wavelengths.

In the luminescence measurements, the $^5I_7$ emission intensity and structure definition decreased (in the neighborhood of 1.9 μm) as the concentration or the pump position was increased. This observed behavior is attributed to the higher absorption in the 1.9 μm region. That is, the number of Ho ions present per unit volume or emission path length for reabsorption of the initial 2 μm emission (occurring after absorption of pump radiation) increases as the concentration or pump position increases. These effects are seen more distinctly in the decrease of integrated luminescent intensity with increasing pump position for a given concentration or slab as well as in the overall reduction in integrated luminescent intensity for all pump positions with increased concentration. In fact, these luminescence spectra were normalized in order to provide the emission that would result if each slab or concentration absorbed the same quantity of pump radiation. Even so, as the pump position was increased, the integrated intensity decreased more rapidly for higher concentrations.

In the kinetic measurements, the lifetime of the Ho $^5I_7$ emission was found to increase continuously with concentration up to 3 %. The lifetime then decreased when the concentration was increased further to 8.5 %. The lifetime increased with pump position for concentrations above 0.32 % (at 0.32 % the lifetime was essentially constant with pump position.). For each concentration, the temperature dependence of the lifetimes was maximal around 295 K. In fact, lifetimes as high as about 11 ms were measured using high concentrations at 295 K. This Ho $^5I_7$ increase in lifetime with concentration and decrease in lifetime as temperature is decreased below 295 K is in contrast with the
corresponding behavior of most other Lanthanide series elements. For Ho:LiYF$_4$, it has been suggested that the increase observed in this lifetime with increasing concentration is the result of radiative energy transfer among Ho ions [22].

A comprehensive spectral model was developed which closely predicted the Ho $5\ell_7$ luminescence spectrum for a given concentration, pump position, and temperature, thus achieving correlation between the absorption and luminescence results. In addition, this model produced the temperature dependence of the radiative energy transfer rate among Ho ions for a given concentration and pump position from these spectral measurements. Independently, a kinetic model was devised which also calculated the radiative energy transfer rate temperature dependence using, instead, measured lifetimes and calculated radiative and non-radiative lifetimes. The overall temperature dependencies of these transfer rates determined from both the spectral and kinetic models were in close agreement, which suggests that strong radiative energy transfer among excited Ho ions in the $5\ell_7$ manifold is responsible for the unusual observed behavior of Ho lifetimes.

Thus, through the systematic measurement, modeling, and correlation of the spectral and kinetic behavior of the YAG:Ho$^{3+}$ $5\ell_7$ emission, the radiative energy transfer process among Ho ions, as a loss to the desired 2.1 μm laser emission from this manifold, has been characterized macroscopically in terms of Ho concentration as well as slab pump position and temperature.
Some suggestions for future related research are as follows.

Generalize this research to include other:

(i) emission manifolds
(ii) single dopants
(iii) host crystals
(iv) slab geometries.
NOTES TO THE TEXT


VITA

Terri Lynn Lazarus


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