Two-photon absorption and two-photon-resonant four-wave mixing for the Tb^3+ ion in insulators by Jin Huang

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
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Abstract:
Resonant enhancement of over two orders of magnitude of direct two-photon absorption from the ground state 7F6 to the excited state 5G6 of the 4f8 configuration of Tb^3+ at 40,200 cm^-1 has been observed in time resolved experiments with two separate lasers. The results provide clear evidence for resonant enhancement of two-photon absorption in rare earth compounds and imply the same for Raman scattering. Two separate transition mechanisms have been observed. When a single laser frequency was used, the intermediate states making the largest contribution were from excited configurations of opposite parity which were far from resonance. Detailed two-frequency experiments showed, however, that near the single photon resonance, there was a much stronger contribution from the 4f8 configuration 3D4 intermediate state.

The phase-matching-induced frequency selectivity in the single-photon-resonant four-wave mixing has been observed in further rare earth compounds. These observations provide additional evidence that the phase matching effects, resulting from anomalous dispersion associated with the single-photon resonance, play a major role in determining both the intensity and the line narrowing of the mixing signal, and that similar effects will be observable in any rare earth compound.

An effect of two-photon-resonant four-wave mixing has been observed for a transition to the 4F8 configuration 5K8 state of the Tm^3+ ion in LiYF4. The strength of the resonance is comparable to that of single-photon resonances. This technique holds promise as a new spectroscopic tool, especially for studies of two-photon transitions in non-fluorescent materials.
TWO-PHOTON ABSORPTION AND TWO-PHOTON-RESONANT
FOUR-WAVE MIXING FOR THE Tb$^{3+}$ ION IN INSULATORS

by

Jin Huang

A thesis submitted in partial fulfillment
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of
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Bozeman, Montana

August 1987
APPROVAL

of a thesis submitted by

Jin Huang

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

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ABSTRACT

Resonant enhancement of over two orders of magnitude of direct two-photon absorption from the ground state $^7F_\text{g}$ to the excited state $^3G_4$ of the $4f^8$ configuration of Tb$^{3+}$ at 40,200 cm$^{-1}$ has been observed in time resolved experiments with two separate lasers. The results provide clear evidence for resonant enhancement of two-photon absorption in rare earth compounds and imply the same for Raman scattering. Two separate transition mechanisms have been observed. When a single laser frequency was used, the intermediate states making the largest contribution were from excited configurations of opposite parity which were far from resonance. Detailed two-frequency experiments showed, however, that near the single photon resonance, there was a much stronger contribution from the $4f^8$ configuration $^3D_4$ intermediate state.

The phase-matching-induced frequency selectivity in the single-photon-resonant four-wave mixing has been observed in further rare earth compounds. These observations provide additional evidence that the phase matching effects, resulting from anomalous dispersion associated with the single-photon resonance, play a major role in determining both the intensity and the line narrowing of the mixing signal, and that similar effects will be observable in any rare earth compound.

An effect of two-photon-resonant four-wave mixing has been observed for a transition to the $4f^8$ configuration $^3K_4$ state of the Tb$^{3+}$ ion in LiYF$_4$. The strength of the resonance is comparable to that of single-photon resonances. This technique holds promise as a new spectroscopic tool, especially for studies of two-photon transitions in non-fluorescent materials.
CHAPTER I

INTRODUCTION

Nonlinear spectroscopy has gained importance in many sub-fields of physics.\(^1\)\(^2\) It was developed at the advent of laser light with high intensity and pure frequency. The development of powerful and convenient tunable lasers has made studies possible throughout the visible region of the spectrum. Nonlinear techniques, such as stimulated Raman scattering (SRS),\(^3\)\(^-\)\(^6\) coherent anti-Stokes Raman scattering (CARS),\(^7\)\(^-\)\(^9\) multi-quantum absorption,\(^10\)\(^-\)\(^12\) four-wave mixing\(^13\)\(^,\)\(^14\) etc., however, have extended this study range to far infrared\(^13\)\(^,\)\(^16\) and vacuum ultraviolet.\(^17\)\(^,\)\(^18\) The field of nonlinear spectroscopy has matured rapidly but still has much potential for further exploration and for application. Also, nonlinear laser spectroscopy has proven to be a fruitful area of research to investigate the optical behavior of rare earth ions in crystalline materials.\(^19\)\(^-\)\(^21\)

This thesis consists of two separate but interdependent efforts to study the optical transitions in rare earth compounds. One of them deals with direct two-
photon absorption and particularly with a resonant enhancement of this transition process. The other deals with resonant four-wave mixing processes, with particular attention on the effect of two-photon-resonant four-wave mixing. The whole thesis will describe using these two techniques to study rare earth compounds and the connection between them.

In a two-photon absorption process, two photons are simultaneously absorbed to excite a material system. One-photon and two-photon transitions obey different selection rules, so they are complementary to each other as spectroscopic tools. Thus, two-photon absorption not only extends the observable range for the spectrum, but also provides information which cannot be obtained by linear absorption.

The basic theory of two-photon absorption was given, more than fifty years ago, in 1931 by Göppert-Mayer. Since that time there has been considerable work on the theory of two-photon absorption in solids. Particularly, Axe had developed such a theory of allowed two-photon transitions for rare earth ions in 1964 by extending the Judd-Ofelt formalism using second-order perturbation theory.

It is interesting that the first observation of a two-photon absorption transition was obtained in a rare earth compound. In 1961, Kaiser and Garrett used the red light
from a pulsed ruby laser to excite Eu\(^{2+}\) to a broad ultraviolet band arising from a 4f\(^7\)-4f\(^6\)5d transition, and recorded the blue fluorescence which resulted from the two-photon resonance. At that time, they had to use the broad band absorption feature of Eu\(^{2+}\), because no tunable lasers were available. With the development of tunable dye lasers, the sharp parity-allowed 4f\(^N\)-4f\(^N\) transitions of rare earth ions in solids became observable by direct two-photon absorption. Since then, transitions have been observed for the 4f\(^7\) configuration \(^{29,30}\) of Eu\(^{2+}\) in CaF\(_2\) and Gd\(^{3+}\) in LaF\(_3\) \(^{31-33}\) and for Pr\(^{3+}\) in LaF\(_3\). \(^{34}\) This thesis will present the observation of direct two-photon transitions for Tb\(^{3+}\) in LiYF\(_4\). \(^{35}\) In all previous cases, however, only the two-photon resonance was important.

Attention was given earlier by others to a demonstration of the resonant enhancement of two-photon transitions by a real intermediate state in a gas. As predicted by the theory, the two-photon absorption process should present a strongly enhanced behavior whenever a single photon energy approaches an allowed transition. Such an experiment was performed by Bjorkholm and Liao in 1974. \(^{36}\) Dramatic resonant enhancement, up to seven orders of magnitude, of two-photon absorption was observed in sodium vapor. The real intermediate states \(^3P_{3/2}\) and \(^3P_{1/2}\) played important roles in this enhancement of the 3S-4D two-photon transition. This result has important
implications for potential applications of two-photon spectroscopy.

There was no report of such resonant enhancement effect of direct two-photon absorption for rare earth compounds prior to this thesis work. Related processes in rare earth compounds, such as resonant electronic Raman scattering, had been reported for Tb$^{3+}$ in terbium aluminum garnet (TbAlG) by Nicollin and Konigstein in 1980. In their experiments resonant enhancement of Raman scattering due to the $^7F_4 - ^3D_4$ transition was observed. Also, resonance Raman effects were studied for Er$^{3+}$ and Pr$^{3+}$ in several phosphate crystal by Becker and coworkers, and multiply enhanced site selective CARS spectroscopy has been studied by Steehler and Wright for pentacene:p-terphenyl crystal. Resonance Raman scattering from parity-allowed transitions of Tb$^{3+}$ in Tb$^{3+}$:LiYF$_4$, and Tb(OH)$_3$ has been studied by Cone et al. For the Raman experiments, fluorescence raises a considerable ambiguity in the interpretation, since the scattered light cannot be clearly separated from fluorescence when the resonance occurs. The results obtained from this thesis work, however, show much clearer evidence of these resonant enhancement effects in the rare earths.

Another effort involved in this thesis work was the study of resonant behavior of the four-wave mixing process in the rare earth ions. The observation of two-photon-
resonant four-wave mixing was particularly interesting. This study is directly related to the study of the two-photon absorption for the following reasons: (1) As nonlinear processes, both the two-photon absorption and the four-wave mixing are described by the third order nonlinear susceptibility. Generally speaking, since the direct two-photon absorption process has already been observed, the four-wave mixing process is expected to present some resonant effect when the exciting laser frequency \( \Omega_1 + \Omega_2 \) reaches to the two-photon transition. Similar effects have been widely observed in the metallic gases and have been used to generate coherent tunable UV and VUV radiations. (2) Weak beam attenuation due to two-photon absorption is generally difficult to measure. Because anti-Stokes fluorescence from excited states is easily detectable, it provides a means to monitor two-photon absorption with sensitivity many orders of magnitude higher than the beam attenuation measurement. In fact, all the observed two-photon absorption spectra for rare earth compounds were obtained as excitation spectra by monitoring the appropriate fluorescence cascading from excited states. The disadvantage of this method is that it is not applicable with some non-fluorescent materials. The four-wave mixing can potentially solve that problem. It may provide a different approach to detect the two-photon transitions by monitoring the resonant behavior of the
generated coherent radiation, since such processes are generally allowed in all media.

The initial observation of this resonant four-wave mixing process in rare earth compounds was obtained by Rufus Cone and Joel Friedman at AT&T Bell laboratories. Dave Ender and Mike Otteson have contributed to the study of phase matching selectivity in the single-resonance four-wave mixing\(^2\),\(^4\),\(^5\) and gave an observation of the effect of double-resonance four-wave mixing in the broad 4f\(^7\)5d absorption band for Tb(OH)\(_3\) crystal. Their contribution formed the basis for the present studies in this thesis work. Related coherent four-wave mixing experiments have been reported for rare earth compounds by Lee et al.,\(^4\) who studied Rayleigh type resonances where \(\Omega_1\approx\Omega_2\approx\Omega_3\approx\Omega_4\) in Sm\(^2^+\):CaF\(_2\), and by Shand,\(^4\) who studied electronic Raman resonances in terbium garnet.

Four-wave mixing phenomena were first observed in 1963 and have presented many interesting applications in physics. In particular, four-wave mixing has been used to create a grating useful in real-time image reconstruction.\(^4\)\(^8\),\(^4\)\(^9\) The generation of new frequencies in the four-wave mixing permits the extension of coherent light sources to new frequency ranges.\(^5\)\(^0\),\(^5\)\(^1\) Also, four-wave mixing allows one to study material excitations and mechanisms, as illustrated in this thesis work. Reviews of four-wave mixing spectroscopy have been given by
Bloembergen, \(^{52, 53}\) Levenson and Song, \(^{54}\) Levenson, \(^{55}\) and Y. R. Shen. \(^{56}\)

In summary, this thesis is organized as follows: Chapter II gives the basic theory of the two-photon absorption and the four-wave mixing. The experimental apparatus is described in Chapter III. The observed experimental results are presented and discussed in Chapter IV. That includes the results of direct two-photon absorption in a dilute crystal \(\text{Tb}^{3+}:\text{LiYF}_4\) and the resonant enhancement of this transition, and the results of the two-photon-resonant four-wave mixing experiment in the concentrated crystal \(\text{LiTbF}_4\). New results on the phase matching induced frequency selectivity in the single-resonance four-wave mixing are also presented as a continuation of previous studies in this laboratory.
CHAPTER II

THEORY OF NONLINEAR OPTICAL PHENOMENA

The large variety of nonlinear optical phenomena arises from higher order terms of the induced polarization of a medium. These nonlinear properties are described by expanding the macroscopic polarization in a power series in the optical electric field as follows:

\[ P = \chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(3)} : EEE \]  

where the first term defines a linear electric susceptibility, the second term defines a second order susceptibility, the lowest order nonlinear susceptibility, and so on. In media with inversion symmetry the even-order nonlinear susceptibilities must vanish, thus third order nonlinear susceptibility is often the lowest order nonlinear electromagnetic response.\textsuperscript{57}

It is now well-known that the coupling between four light waves is described by the third order nonlinear susceptibility.\textsuperscript{57-59} The two-photon absorption formulation, which was first derived by second-order perturbation theory, can be also described by the imaginary
part of the third order nonlinear susceptibility.\textsuperscript{42}

The theory of two-photon absorption and four-wave mixing presented in this chapter is restricted to provide a framework for understanding the experimental results obtained in this thesis work. Since the phase matching induced line narrowing selectivity has already been proved to be important for all resonant mixing processes in condensed materials,\textsuperscript{43} the model calculation related to the dispersion of the index of refraction will also be given in this chapter.

Most of this chapter is taken from various references, since all these theories are well developed.

**Nonlinear Susceptibilities**

Nonlinear susceptibilities\textsuperscript{32,39} are characteristic properties of a medium which depend on the atomic and crystalline structure of the medium. To find the microscopic expression for nonlinear susceptibilities, a density matrix formalism is the most convenient method for the calculation. The density matrix operator is defined as the ensemble average over the outer product of the state vectors,

\[
\rho = |\phi>|\phi| (II-2)
\]

where \(|\phi>| is the wave function of the material system under the influence of the electromagnetic field. The ensemble
average of the electric polarization is given by,

\[ \langle \mathbf{P} \rangle = \langle \hat{\mathbf{P}} \rangle = \text{Tr}(\rho \mathbf{P}) \]  

(II-3)

The density matrix satisfies the equation of motion,

\[ \frac{d\rho}{dt} = \frac{i}{\hbar} [H, \rho] \]  

(II-4)

which is known as the Liouville equation. The Hamiltonian \( H \) consists of three parts,

\[ H = H_0 + H_1 + H_{\text{dipole}} \]  

(II-5)

Here \( H_0 \) is the Hamiltonian of the material system with the set of energy eigenstates \( \{ n \} \). The Hamiltonian for interaction of the system with the radiation field contains three contributions,

\[ H_1 = H_{\text{dipole}} + H_{\text{quadrupole}} + H_{\text{magnetic}} \]  

(II-6)

where the electric-dipole interaction is

\[ H_{\text{dipole}} = e \sum r_j \mathbf{E} \]  

(II-7)

the electric-quadrupole interaction is

\[ H_{\text{quadrupole}} = (1/2) e \sum (r_j \cdot \mathbf{v})(r_j \cdot \mathbf{E}) \]  

(II-8)

and the magnetic-dipole interaction is

\[ H_{\text{magnetic}} = (e\mu_0/2m) \mathbf{H} \cdot \mathbf{\mu} \]  

(II-9)
Since the terms $H_{eq}$ and $H_{ho}$ have much smaller contributions to optical transitions than the term $H_{ed}$ for rare earth compounds, the interaction Hamiltonian may be considered, under the electric-dipole approximation, as

$$H_I = H_{eq} = e\mathbf{D} \cdot \mathbf{E} \quad (II-10)$$

The damping Hamiltonian refers to relaxations of material excitations. Thus the expression (II-4) becomes

$$\frac{\delta \rho}{\delta t} = \frac{1}{i\hbar} [H_0 + H_I, \rho] + \left( \frac{\delta \rho}{\delta t} \right)_{relax} \quad (II-11)$$

with

$$\left( \frac{\delta \rho}{\delta t} \right)_{relax} = \frac{1}{i\hbar} [H_{damping}, \rho] \quad (II-12)$$

The relaxation of the diagonal elements is given by

$$\frac{\delta}{\delta t} (\rho_{nn} - \rho_0 n)_{relax} = -1/(T_1)_{nn} (\rho_{nn} - \rho_0 n) \quad (II-13)$$

where the parameter $T_1$ is called the longitudinal relaxation time. The relaxation of the off-diagonal elements can be written as

$$\left( \frac{\delta \rho_{nn'}}{\delta t} \right)_{relax} = -\Gamma_{nn'} \rho_{nn'} \quad (II-14)$$

with $\Gamma_{nn'} = 1/(T_2)_{nn'}$, being a characteristic relaxation time for $\rho_{nn'}$ between the states $|n\rangle$ and $|n'\rangle$. The parameter $T_2$ is called the transverse relaxation time.
To find the nonlinear polarization and nonlinear susceptibility for the steady-state response, one can use the perturbation expansion as follow

$$\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \rho^{(3)} + \cdots$$  \hspace{1cm} (II-15)

and

$$\langle P \rangle = \langle P^{(1)} \rangle + \langle P^{(2)} \rangle + \langle P^{(3)} \rangle + \cdots$$  \hspace{1cm} (II-16)

with

$$\langle P^{(n)} \rangle = \text{Tr}(\rho^{(n)} P)$$  \hspace{1cm} (II-17)

Inserting the expansion of into (II-11), and collecting terms of the same order with $H_1$, one obtains:

$$\frac{\delta \rho^{(1)}}{\delta t} = \frac{1}{i \hbar} \left[ (H_0, \rho^{(1)}) + (H_1, \rho^{(0)}) \right] + \frac{\delta \rho^{(1)}}{\delta t}_{\text{relax}}$$  \hspace{1cm} (II-18)

$$\frac{\delta \rho^{(2)}}{\delta t} = \frac{1}{i \hbar} \left[ (H_0, \rho^{(2)}) + (H_1, \rho^{(1)}) \right] + \frac{\delta \rho^{(2)}}{\delta t}_{\text{relax}}$$  \hspace{1cm} (II-18)

$$\frac{\delta \rho^{(3)}}{\delta t} = \frac{1}{i \hbar} \left[ (H_0, \rho^{(3)}) + (H_1, \rho^{(2)}) \right] + \frac{\delta \rho^{(3)}}{\delta t}_{\text{relax}}$$  \hspace{1cm} (II-18)

and so on. The full expressions of the nonlinear polarization $\langle P^{(n)} \rangle$ and the nonlinear susceptibilities $\langle \chi^{(n)} \rangle$ follow immediately from the expressions for $\rho^{(n)}$ by solving these equations. The third order nonlinear susceptibility is defined as

$$\chi^{(3)} \equiv \frac{\langle P^{(3)}(\Omega) \rangle}{E_1(\Omega_1)E_2(\Omega_2)E_3(\Omega_3)}$$  \hspace{1cm} (II-19)
The complete expression for $\chi^{(3)}$ has a total of 48 terms. It can be written as the sum of a resonant part $\chi^{(3)R}$ and a nonresonant part $\chi^{(3)NR}$ for different physical processes. More explicit expressions for the two-photon absorption and four-wave mixing processes will be given in later sections.

**Two-Photon Absorption**

The calculation of the two-photon absorption rate is parallel to the calculation of the light scattering process. Both processes result from the interaction of two distinct photons with a single atom or ion. In the case of scattering, one photon is absorbed and one is emitted, whereas both are absorbed in the two-photon absorption process. The transition rate from the state $\langle g |$ to the state $\langle f |$ for two-photon absorption is given by

$$\frac{1}{\tau} = \frac{d}{dt} \left| \frac{\langle f | \exp\{-iH(t-t_0)/\hbar\} | g \rangle}{\hbar}\right|^2$$

where $H=H_0+H_I$ is the total time-independent Hamiltonian.

By expanding the $\exp\{-iH(t-t_0)/\hbar\}$ in powers of $H_I$ and using time-dependent perturbation theory, the expression (II-20) can be written, up to second order, as

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_i \left| \langle f | H_I | g \rangle + \frac{1}{\hbar} \sum_i \frac{\langle f | H_I | i \rangle \langle i | H_I | g \rangle}{\Omega_i - \Omega_f} \right|^2 \delta(\Omega_0 - \Omega_f)$$

considering that the absorbed photons have different
frequencies $\Omega_1$ and $\Omega_2$ corresponding to two single-mode light beams, the transition rate for two-photon absorption, for the second-order contribution, can be written as

$$1 = \sum_i \frac{\langle f \mid E \cdot D \mid i \rangle \langle i \mid E \cdot D \mid g \rangle}{\hbar \Omega_i - \hbar \Omega_f} + \frac{\langle f \mid E \cdot D \mid i \rangle \langle i \mid E \cdot D \mid g \rangle}{\hbar \Omega_f - \hbar \Omega_i} \frac{1}{\delta(\Omega_f - \Omega_i - \Omega_2)}$$

where $C$ is a constant, $\langle f \rangle$ and $\langle g \rangle$ refer to the final and initial states, and $\langle i \rangle$ is the intermediate state. The electric-dipole approximation was used to get that formula. This expression was obtained from Fermi's golden rule by Mayer in 1931. The same expression was also obtained from the third order nonlinear electric susceptibility by Bloembergen. Considering an expression:

$$\chi^{(3)} = \sum_{n,n',n''} \frac{\langle g \mid E \cdot D \mid n \rangle \langle n \mid E \cdot D \mid n' \rangle \langle n' \mid E \cdot D \mid g \rangle}{(\Omega_{n,g} - \Omega_1 - i\Gamma_{n,g})(\Omega_{n',g} - \Omega_1 - i\Gamma_{n',g})(\Omega_{n'',g} - \Omega_4 - i\Gamma_{n'',g})}$$

one can take $\Omega_4 = \Omega_1$, $\Omega_2 = -\Omega_3$ for the situation of two-photon absorption. Furthermore, the resonant condition $\Omega_{n',g} = \Omega_1 + \Omega_2$ can be satisfied for $\langle n' \rangle = \langle f \rangle$ as the final state for the two-photon absorption. Since there are only two such resonant terms, depending on the order of $\Omega_1$ and $\Omega_2$, such that the summation over $n'$ is reduced to a single final state $\langle f \rangle$, the double summation over $n$ and $n''$ may written
as the square of a single summation. For two-photon absorption \(^4\),

\[ \text{Im} \chi^{(3)}(-\Omega_1, \Omega_1, \Omega_2, -\Omega_2) \propto \]

\[ \sum_i \frac{\langle f | E \cdot D_i | i \rangle \langle i | E \cdot D_i | q \rangle}{\hbar \Omega_i} + \frac{\langle f | E \cdot D_i | i \rangle \langle i | E \cdot D_i | q \rangle}{\hbar \Omega_i} \delta(\Omega_1, -\Omega_1 - \Omega_2) \]

\[ (\text{II}-24) \]

The power absorbed from the beams at \( \Omega_1 \) or \( \Omega_2 \) is proportional to \( |E_1|^2 |E_2|^2 \) and the imaginary part of the third order susceptibility. Thus the total power absorbed by the material in two-photon absorption is proportional to \( 1/(2(\Omega_1 + \Omega_2)) \text{Im} \chi^{(3)} |E_1|^2 |E_2|^2 \). Dividing this expression by the energy \( \hbar(\Omega_1 + \Omega_2) \) involved in this transition, one arrives at the same expression as (II-22) for the transition rate for two-photon absorption.

When one of the photon frequencies approaches a real intermediate state in the expression (II-22), resonant enhancement of the two-photon absorption is expected.\(^{10,36,42}\) This phenomenon will be presented in Chapter IV. The selection rules for two-photon absorption for the \( S_4 \) symmetry \( \text{Tb}^{3+} : \text{LiYF}_4 \) crystal will also be discussed in Chapter IV.
Four-Wave Mixing

Four-wave mixing refers to the process in which three input beams in a medium generate a fourth wave. Physically, this process can be understood as follows. Considering the material excitations explicitly as an intermediate step, two of the three input waves can beat and drive a material excitation. In general, this process can occur even in the nonresonant case. If one of the three frequencies or any combination of them matches a transition of the material, resonance can occur. In any case, the material excitation wave can mix with the third input frequency to yield a nonlinear polarization at the resultant beat frequency. That polarization gives a coherent output at, for example, \( \Omega_4 = \Omega_1 + \Omega_2 - \Omega_3 \). This generated beam is both spatially and spectrally distinct from the three input beams. The phase matching diagram is shown in the Fig. 1 (b) and (c).

In four-wave mixing, the observed signal is proportional to the product of the square of the third order nonlinear susceptibility and a phase matching factor \( G \),

\[
I(\Omega_4) \propto | \chi^{(3)}(\Omega_4, \Omega_1, \Omega_2, -\Omega_3) |^2 \cdot G \quad (II-25)
\]

where \( \Omega_1, \Omega_2, \) and \( \Omega_3 \) are the input frequencies, \( \Omega_4 \) is the generated frequency, and \( I(\Omega_4) \) refers to the intensity of the mixing signal. The third order nonlinear susceptibility which is relevant to the present experiments
Figure 1. (a) Schematic diagram of four-wave mixing experiment. (b) General three-beam phase matching diagram. (c) Two-beam phase matching with beam crossing angle $\theta_{1,3}$.
is given as

\[ \chi'^3(-\Omega_4, \Omega_1, \Omega_2, -\Omega_3) \propto \]

\[ \frac{\mu_{ab}}{[\Omega_{ba} - \Omega_1 - i\Gamma_{ab}]} \frac{\mu_{bc}}{[\Omega_{ca} - (\Omega_1 + \Omega_2) - i\Gamma_{ac}]} \frac{\mu_{cd}}{[\Omega_{da} - (\Omega_1 + \Omega_2 - \Omega_3) - i\Gamma_{ad}]} \]

\[ + \frac{\mu_{ab}}{[\Omega_{ba} - \Omega_1 - i\Gamma_{ab}]} \frac{\mu_{bc}}{[\Omega_{ca} - (\Omega_1 + \Omega_2 - \Omega_3) - i\Gamma_{ac}]} \frac{\mu_{cd}}{[\Omega_{da} - (\Omega_1 + \Omega_2 - \Omega_3) - i\Gamma_{ad}]} \]

(II-26)

where the \( \mu \) factors are dipole transition moments between the states indicated by the subscripts and the \( \Gamma \) factors are phase relaxation rates. The energy levels of the material are labeled as a, b, c, and d which are shown in Fig. 1 (a).

The resonant behavior of the four-wave mixing is clearly shown in the expression (II-26) and the energy level diagram. When the \( \Omega_1 \) beam frequency approaches a transition from the state a to the state b, a single-photon resonance occurs. Multiple resonance could happen when the additional condition, for example \( \Omega_1 + \Omega_2 = \Omega_{ca} \), is satisfied. This doubly resonant mixing process has shown interesting properties which will be discussed in a later chapter.

The phase matching factor for our circumstances can be written as

\[ G(\delta k) = \]

\[ \frac{1 + \exp[-(\alpha_1 + \alpha_2 + \alpha_3 - \alpha_4) L]}{[\delta k]^2 + [\alpha_1 + \alpha_2 + \alpha_3 - \alpha_4]^2 / 4} - \frac{2 \exp[-(\alpha_1 + \alpha_2 + \alpha_3 - \alpha_4) L]}{[\delta k]^2 + [\alpha_1 + \alpha_2 + \alpha_3 - \alpha_4]^2 / 4} \cos(\delta k L) \]

(II-27)
where the $\alpha's$ refer to the frequency dependent absorption coefficients, $L$ is the thickness of the crystal sample, and $\delta k = k_4 - k_1 - k_2 + k_3$ is the wave vector mismatch. Both experimental observation and calculation, which were done by D. Ender, R. Cone and M. Otteson in our laboratory, have shown that phase matching induced frequency selectivity plays a major role in the interpretation of nonlinear mixing processes in condensed materials.\textsuperscript{43, 68, 69} The experimental results\textsuperscript{43} for the LiTbF$_4$ crystal are shown in Fig. 2. The line narrowing, which is due to the phase matching conditions related to the anomalous dispersion of the index of refraction, is well demonstrated in these results.

The experimental results may be qualitatively understood by the simpler phase matching factor:

$$G = \sin^2\left(\frac{\delta k L}{2}\right) + \left(\frac{\delta k L}{2}\right)^2$$

(II-28)

where $G$ reaches its maximum value when $\delta k$ goes to zero.

Note that changing the frequency $\Omega_1$ causes an individual wave vector $k_1 = n_1 \Omega_1 / c$ to be changed as follows,

$$\frac{\delta k_1}{k_1} = \frac{\delta \Omega_1}{\Omega_1} + \frac{\delta n_1}{n_1}.$$ 

(II-29)

When $\Omega_1$ is scanned over a small range of frequencies, which is the case in the experiment, $\delta \Omega_1$ gives a negligible change in $k_1$. But the change in $n_1$ due to the anomalous linear dispersion associated with a resonance of a real
Figure 2. (a) Four-wave mixing signal in LiTbF₄ for several internal beam crossing angles. (b) Absorption coefficient for \( ^3D_4 \) \((\Gamma_4)\) state of LiTbF₄. (c) Index of refraction of same state.
transition in the material causes a larger amount of change in $k_1$ than for the case of nonresonance.

Knowing the shape of the anomalous dispersion of $n_1$ around the resonance allows one to predict the angular behavior of the phase matching. The angle $\theta_{1,3}$ between the $\Omega_1$ and $\Omega_3$ beams determines the $\Omega_1$ value where the peak mixing signal, determined by $\delta k = 0$, occurs. The slope $dn_1/d\Omega_1$ then determines the degree of the line narrowing due to $G$.

More complicated model calculations of this effect which take into account the $\Omega_1$ resonance in the four-wave mixing provide the intensity of the mixing signal as

$$I_{\text{mix}}(\Omega_1) \propto \chi^{(3)} \frac{1 + \exp(-2\pi(\Omega_1)L) - 2\exp(-\pi(\Omega_1)L) \cos(\delta k L)}{[\delta k]^2 + [\pi(\Omega_1)]^2},$$

(II-30)

where

$$\delta k = -(2\Omega_1/c)\delta n_1,$$

$k_1 = k_2$, $\alpha_1 = \alpha_2$, and $\Omega_3$, $\Omega_4$ are off resonance with any transition. The generality of this effect in the rare earth compounds has been proved by providing additional evidence from this thesis work. Details are presented in Chapter IV.
CHAPTER III

EXPERIMENTAL APPARATUS AND TECHNIQUES

The two-photon absorption and the four-wave mixing experiments reported in this thesis were performed on several different rare earth samples whose properties were chosen for different purposes. The experimental setup utilized in these studies consists of laser sources, optical system, dewar, detection and recording system, electronics, and computer control system.

In this chapter, a short description of the samples is followed by sections which describe the lasers, dewar and dewar optics, and the particular system used in the two-photon absorption and the four-wave mixing experiments. The electronics and computer control system are presented in the last section.

Samples

The two-step excitation experiment was performed on Tb$^{3+}$:LiYF$_4$ and LiTbF$_4$ samples. The Tb$^{3+}$:LiYF$_4$ sample was also used to study direct two-photon absorption and the resonant enhancement process. The four-wave mixing study
was focused on the LiTbF₄ sample, although similar results were also observed in TbF₃ and ErPO₄ samples. All of these single crystals are hard and transparent and exhibit excellent optical quality.

The Tb³⁺:LiYF₄ crystal was obtained from H. J. Guggenheim of AT&T Bell Laboratories. The rectangular sample has dimensions 3.0x3.0x5.5 mm with the longest dimension perpendicular to the c axis. The Tb³⁺:LiYF₄ has S₄ point symmetry.⁷⁰,⁷¹

The LiTbF₄ crystal also was provided by H. J. Guggenheim. Two of these samples with thicknesses of 0.300 mm and 0.078 mm were prepared for the experiments by D. Ender, Mark Ritter and M. Otteson. This LiTbF₄ crystal also has S₄ point symmetry.⁶⁰

The TbF₃ single crystal was grown in Hughes Laboratory by the Czochralski method and was provided by B. Jacquier of Université de Lyon I. The dimensions of this sample are 0.625x1.53x1.36 mm, with the thickness 1.36 mm along the c axis. The point symmetry of TbF₃ is C₅.⁷²

The ErPO₄ crystal⁶⁵ was obtained from N. Endelstein of Berkeley. It was grown by M. M. Abraham and L. A. Boatner at Oak Ridge National Laboratory. This crystal is slightly pink and unpolished. Naturally cleaved faces were of suitable optical quality for the experiment.
Lasers

Three dye lasers were pumped by two pulsed nitrogen lasers which were operated at 337.1 nm with a repetition rate of 6 Hz. The peak power of the nitrogen lasers was 400-500 kw and the pulse width was 10 nsec.

The dye lasers were of the Hänisch type with an output pulse width of 5 nsec and peak power 20-40 kw. One of the three dye lasers was operated in the etalon-narrowed high resolution mode with line width < 0.05 cm⁻¹. The frequency of this laser was scanned by computer-controlled pressure in a range of over 10 cm⁻¹. This laser was used as the Ω₁ laser in the two-photon absorption and four-wave mixing experiments.

Both of the other lasers were pumped by a separate nitrogen laser from the Ω₁ laser and could be scanned by computer-controlled stepper motors. One of them was used as the Ω₂ laser in the two-photon excitation and four-wave mixing experiments, and the other as the Ω₃ laser in the four-wave mixing experiments. All three dye lasers were located on a 4'x8' NRC table.

An important feature of this laser system is that the time relationship between the Ω₁ laser and the other two lasers could be adjusted manually or could be scanned by computer-control as will be seen in a later section. Moreover, the lasers could be synchronized with 1 nsec accuracy and < 1 nsec jitter.
Dewar and Dewar Optics

A glass dewar, with three flat windows spaced at 90 degrees, was mounted on a 3'x4' NRC table as shown in Fig. 3.

The incident laser beams were sent into the dewar from the front window. The absorption spectrum could be detected from the back window along with the four-wave mixing signal, while the excitation spectrum could be taken from the side window. This arrangement was very useful in the four-wave mixing experiments.

To locate the beam waist position in the sample inside the dewar and to ensure that all the beams crossed at the waist position, a pair of orthogonal razor blades was mounted at a conjugate sample position outside the dewar. This setup was used to make quite accurate adjustments. The laser induced thermal effect on the surface of the crystal provided an additional method to adjust the beam focusing and overlapping.

Experimental Setup

The experimental setup was designed to record simultaneously three different spectra: the absorption spectrum of $\Omega_1$ or $\Omega_2$, the four-wave mixing spectrum, and the two-photon excitation spectrum. A schematic diagram of the entire spectroscopic system is shown in Fig. 3. The
Figure 3. Experimental setup for two-photon excitation and four-wave mixing.
following description will use the notations which are used in this figure.

Three dye lasers (DL1, DL2, DL3) at different frequencies \( Q_1, Q_2, \) and \( Q_3 \) passed through three separate lenses to give a similar waist for each beam. A 25 cm focal-length lens (L4) defined the final waist size (about 0.070 mm) and the proper position in the crystal.

The polarizations of the laser beams were purified by three polarizing prisms (P1, P2, P3). The half-wave plate (W) could be inserted into the laser beams when the different polarization directions were needed.

To record the fluctuation of laser power during the experiments, the three reference beams could be picked up by three beam splitters. Most of the time, however, the beam splitters introduced spurious Fabry-Perot behavior due to parallel surfaces. To avoid this unwanted effect, reflected laser beams from the surfaces of some of the optical devices, such as lenses, dewar window, etc., were used as the reference beams.

The absorption spectra were detected by two photodiodes (PD1, PD4). One was used for the reference beam (as mentioned earlier), the other for the absorbed laser beam which passed through the crystal. The intensity of the laser beam after the sample divided by the intensity of its reference beam gave the absorption spectra when the frequency scan was made.
The four-wave mixing signal was spatially separated by a diaphragm and a mirror and spectrally detected by a SPEX #14018 0.85 meter Czerny-Turner double monochromator (M2) with two 1800 groove/mm holographic gratings as shown in Fig. 3. Also, three reference beams had to be recorded simultaneously to calibrate the intensity of the four-wave mixing signal. The resultant intensity is the following:

\[ \text{Intensity of FWM} = \frac{\text{Detected Intensity of FWM}}{(I_1 \times I_2 \times I_3)} \]

where \( I_1, I_2 \) and \( I_3 \) are the intensities of the three reference beams, respectively.

The ultraviolet fluorescence from the two-photon excitation process was collected at an angle of 90 degrees from the laser beams. A two-lens system (L6, L7) ensured that the observation of fluorescence used the largest possible solid angle from the side window of the dewar. Glass filters and the photomultiplier or a combination of glass filters and a McPherson Model-218 0.3 meter monochromator (M1) were used to spectrally filter the signal.

In the direct two-photon absorption experiment, a longer sample (5.5 mm) was used to increase the intensity of the signal. To be able to collect more fluorescence, the McPherson monochromator was oriented 90 degrees away from its normal position; thus, the slits on the
monochromator were parallel to the laser beam in the sample.

**Electronics and computer-control**

The electronics and computer control systems played an important role in operating all these experiments. Triggering of the two nitrogen lasers was controlled by an electronic laser delay module. The manual control in this unit allowed one to fire the two nitrogen lasers at the same time or at variable delay times. The time scanning between two lasers, for example in the direct two-photon absorption experiment, was done by using the computer-control function in this unit.

The time relationship between the laser pulses was monitored by the scattered light from the front window of the dewar. The scattered light was detected by a fast photo-diode (HP 4220), and the resulting signal was displayed by a Tektronix 7912AD transient digitizer with a wave-form monitor.

The pulse jitter of the nitrogen lasers was about one nanosecond. The time drift of the laser pulses was controlled by a 'Timing Stabilization' unit built by P. Fisher. Feedback signals derived from the nitrogen laser pulses allowed this unit to stabilize the laser firing time.

In the four-wave mixing experiment, the three
reference laser beams and the absorbed laser beam were
detected by photo-diodes (HP 4220) and sample-hold
circuits. The four-wave mixing signal was detected by a
EMI 9558QB photomultiplier and sent to the computer via a
sample-hold circuit (or a boxcar averager).

All these five signals were read into the computer
through an A/D converter as shown in Fig. 4. The sample-
hold circuits and the A/D converter were synchronized by
the trigger signal from the dye laser pulses.

In the two-step excitation experiment, the signal from
the photomultiplier tube was sent into a PARC 162 boxcar
averager and then to a Northern Scientific 575 multichannel
analyzer. The data were temporarily stored in the latter
unit then transferred and stored on computer disks.

In the direct two-photon absorption experiment, a
sensitive photon-counting system was used to collect the
very weak signal. A block-diagram of this system used in
the experiment is shown in Fig. 5. The signal from the
cooled photomultiplier (RCA C31034A-02) passed the
preamplifier and discriminator and then triggered the pulse
generator. The gated 150 nsec wide signal pulses were sent
to the MCS input of the multichannel analyzer to record the
counts.

The dark current of the cooled photomultiplier was
1.0x10^{-11} A with the tube at 1450 volts. The dark counts
were reduced to less than one count per second with a
Figure 4. Computer control system for the experiments.
Figure 5. Photon counting system in the direct two-photon absorption experiment.
variable gate.

A DEC PDP-11 (LSI-11/2) computer was used to control all the experiments. The computer was interfaced to the experimental apparatus as shown in Fig. 4. The software was based on the C programming language from AT&T Bell Laboratories.

The computer program which drove the DL1 pressure scan laser and simultaneously recorded and plotted both the four-wave mixing and the absorption data in the four-wave mixing experiment is given in Appendix (Fig. 30) and was used for high resolution scans. Another program for driving the DL2 stepper motor scan laser in the four-wave mixing experiment is given in Appendix (Fig. 31), it was used for wider scan in the two-photon resonance experiment. The program for scanning the laser timing is given in Appendix (Fig. 32), and the program for synchronizing the stepper motor and the NS575 digital signal analyzer in the two-photon absorption experiments is given in Appendix (Fig. 33).
CHAPTER IV

EXPERIMENTS AND DISCUSSION

This chapter presents the major experimental results and interpretations for the direct two-photon absorption, the resonant enhancement of the direct two-photon absorption and the four-wave mixing in the various Tb$^{3+}$ and Er$^{3+}$ samples.

As a preliminary experiment, the two-step excitation in the Tb$^{3+}$:LiYF$_4$ and the LiTbF$_4$ will be briefly discussed. That discussion is followed by the experimental results for direct two-photon absorption in Tb$^{3+}$:LiYF$_4$ and the results for the resonant enhancement of this process. The results of the four-wave mixing experiments are presented and discussed in the latter part of this chapter and include the single-resonance results in the LiTbF$_4$, TbF$_3$, and ErPO$_4$ samples and the double-resonance results in the LiTbF$_4$ sample.
Two-Step Excitation in Tb:LiYF₄ and LiTbF₄

The Tb³⁺:LiYF₄ and LiTbF₄ crystals have been widely studied. Using the two-step excitation method to study the high excited energy levels in the Tb³⁺:LiYF₄ and LiTbF₄ samples provided useful information, such as the accurate energy levels, the strength of the transitions, and the polarizations, for the direct two-photon absorption and the four-wave mixing experiments.

This study was based on the results obtained by Cone at Bell Laboratories. In those investigations, the excited states of the Tb³⁺ ranging from the ⁵D₄ manifold at 20,568.8 cm⁻¹ up to 45,000 cm⁻¹ in the 1% Tb³⁺:LiYF₄ were studied. The same sample was used in the present study. The results presented in this section are focused on the energy levels involved in the direct two-photon absorption and four-wave mixing experiments.

Tb³⁺:LiYF₄

The ground state of the Tb³⁺ ion is the ⁴f⁸ configuration ⁷F₆(Γ₂) state. The ⁵D₄(Γ₁) state of this configuration at 20,568.8 cm⁻¹ played the role of a real intermediate state in the two-step excitation process. In the experiment, the Q₁ laser frequency was fixed at the transition from the ground state to the ⁵D₄ state to excite the Tb³⁺ ion up to this real intermediate state. The strong yellow fluorescence from the ⁵D₄ energy level could
be seen visually when the $\Omega_1$ laser was tuned to the resonant frequency. The second laser frequency $\Omega_2$ was scanned over a wide range to match the transitions from $^5D_4$ to the much higher excited energy levels. This is the so-called two-step excitation process or the stepwise two-photon absorption process.

The highly structured two-step excitation spectrum in the Tb$^{3+}$:LiYF$_4$ was obtained by monitoring the anti-Stokes ultraviolet fluorescence cascading from the excited state $^5D_3$ to other components $^7F_3$ and $^7F_4$ of the ground term. The unpolarized fluorescence spectrum corresponding to the observed emission is shown in Fig. 6. This fluorescence was spectrally separated from the scattered laser light by two bandpass glass filters, CS 5-58 and CS 7-54, then recorded by the McPherson monochromator.

The strong fluorescence signal could be observed by an oscilloscope with an input impedance of 1 M$\Omega$ when the $\Omega_2$ laser frequency was matched to a transition from $^5D_4$ to the higher excited state. In order to check whether the two-step excitation of Tb$^{3+}$ was achieved by the two dye laser pulses the following tests were made. First, when any one of the dye laser beams was blocked, the fluorescence signal was observed to vanish. The second test consisted of delaying the $\Omega_2$ laser pulse with respect to the $\Omega_1$ laser pulse. When the $\Omega_1$ laser was fired before or at the same time as the $\Omega_2$ laser, then the signal was observed. No
Figure 6. Fluorescence spectrum at 1.3K of Tb$^{3+}$ from $^5D_1$ to $^7F_2$ and $^7F_4$. 
signal was detected when the delay between the two laser pulses was reversed.

Further checking and adjustment was done by changing the location of one of the laser beams in the sample. Failure of the two laser beams to overlap caused the signal to vanish. Fine adjustment of the overlapping of the two laser beams was necessary before taking any data.

Since the lifetime of the $^5D_4(\Gamma_4)$ state is larger than 1 msec, the $\Omega_1$ laser firing was normally set about 20-50 nsec earlier than the $\Omega_2$ laser firing to avoid potential time jitter and drift problems.

Overall, when the two dye lasers were superimposed in the sample and the $\Omega_2$ laser frequency was scanned, the excitation spectrum was obtained by recording the intensity of the ultraviolet fluorescence. The excitation spectra of the $^7F_6-^5G_4$ transitions, obtained by varying the $\Omega_2$ laser frequency, are shown in Fig. 7, 8. The center of gravity of the $^5G_4$ manifold is in a good agreement with the result calculated by Crosswhite et al. in an unpublished study. The noise background in the experiment was negligible as can be seen in the figures.

These excitation spectra can be understood by considering the crystal-field splittings and the single photon selection rules. For the $S_4$ symmetry of the Tb$^{3+}$:LiYF$_4$ crystal the $J$ multiplet splittings in the crystal-field are shown in Table 1, where $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ and $\Gamma_4$
Figure 7. Two-step excitation spectrum ($^7F_6 - ^3D_4 - ^3G_6$) in Tb$^{3+}$:LiYF$_4$. 
Figure 8. Two-step excitation spectrum ($^7F_6 - ^3D_4 - ^5G_6$) πσ in Tb$^{3+}$:LiYF$_4$. 
refer to the notation of Koster et al. \textsuperscript{71} The $\Gamma_3, \Gamma_4$ are referred to as $\Gamma_{3,4}$, since they are related by time-reversal symmetry and are degenerate.

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\Gamma_1$</th>
<th>$\Gamma_2$</th>
<th>$\Gamma_{3,4}$</th>
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<tr>
<td>0</td>
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<td>0</td>
<td>1</td>
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<tr>
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<td>5</td>
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</tr>
<tr>
<td>6</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

With the applied electromagnetic radiation field, the most significant contributions to the transitions between levels are the electric dipole and magnetic dipole interaction. For the rare earths, in general, the electric dipole transitions are stronger than the magnetic dipole transitions. The electric dipole transitions are parity forbidden within a single configuration, so they occur only as a result of the configuration mixing. The selection rules for the electric dipole transition in $S_4$ symmetry are given in Table 2.
The $\Omega_1$ laser beam was $\pi$ polarized in the experiment to match the allowed electric dipole transition from the ground state $^7F_6(\Gamma_2)$ to the excited state $^5D_4(\Gamma_1)$. The polarization of the $\Omega_2$ laser beam was set in either $\pi$ or $\sigma$ orientation to match the $^5D_4(\Gamma_1)-^5G_6(\Gamma_2)$ and the $^5D_4(\Gamma_1)-^5G_6(\Gamma_{3,4})$ transitions. The spectra for the $\pi$ and the $\sigma$ polarized $\Omega_2$ laser are shown in Fig. 7 and Fig. 8 respectively. The observed energy levels of the $^5G_6$ manifold will be given in Table 4.

The four $\Gamma_2$ states and the three $\Gamma_{3,4}$ states of the $^5G_6$ manifold have been found in these $\pi\pi$ and $\pi\sigma$ two-step excitation spectra, but there also are a few unexpected weak peaks. Some of the latter were due to the impure polarization of the laser beams. A clear direct two-photon absorption spectrum corresponding to the same spectral range which exactly obeys the selection rules will be presented in the latter part of this chapter. Also a
comparison of those two spectra will be given there.

LiTbF₄

In order to study the two-photon resonance in the third order susceptibility with the four-wave mixing process in LiTbF₄, knowing the accurate excited energy levels in this crystal was required. Although the two-step excitation experiment provided the high excited energy levels for the Tb³⁺ ion in Tb³⁺:LiYF₄, it was necessary to do the same experiment in this sample since the energy levels are slightly different.

It was much more difficult to run the experiment in this concentrated crystal than in the case of the dilute crystal: Tb³⁺:LiYF₄. For LiTbF₄, unlike Tb³⁺:LiYF₄, there is a two-center non-radiative relaxation process which partially quenches the fluorescence used to monitor the two-step excitation process. In fact this ultraviolet fluorescence found in LiTbF₄ is much weaker than in Tb³⁺:LiYF₄.

Raising the voltage on the photomultiplier to detect the weak signals caused a laser background which could not be completely ignored. A time resolved technique was used to separate the fluorescence from the background of the lasers. Figure 9 shows the fluorescence signal observed by an oscilloscope with 50 Ω input impedance. The time scale is 20 nsec per division.

The first two narrow peaks in this figure are the
Figure 9. Fluorescence signal of the two-step excitation in LiTbF$_4$ (20 nsec/div.).
leaked laser beams. The broad peak is the fluorescence due to the two-step excitation. This was checked by the timing of two laser pulses. When the Q₁ and Q₂ laser pulses were reversed in time the broad peak vanished.

The real-time fluorescence decay shown in Fig. 9 is about 50 nsec for the two-step excitation. A gate of about 50 nsec on a boxcar averager was used to cut off the laser background.

The observed two-step excitation spectrum for the ⁷F₆-⁵K₈ transition in LiTbF₄ is given in Fig. 10, and the corresponding energy levels are listed in Table 3. Both laser beams were π polarized in this experiment.

<table>
<thead>
<tr>
<th>²Ω₂ (cm⁻¹)</th>
<th>²Ω₁+²Ω₂ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20,291.4</td>
<td>40,859.2</td>
</tr>
<tr>
<td>20,314.6</td>
<td>40,882.7</td>
</tr>
<tr>
<td>20,419.5</td>
<td>40,987.6</td>
</tr>
<tr>
<td>20,424.3</td>
<td>40,992.4</td>
</tr>
<tr>
<td>20,472.4</td>
<td>41,040.5</td>
</tr>
<tr>
<td>20,481.2</td>
<td>41,049.3</td>
</tr>
<tr>
<td>20,493.9</td>
<td>41,062.0</td>
</tr>
</tbody>
</table>
Figure 10. Two-step excitation spectrum ($^7F_6 - ^3D_4 - ^3K_2$) ππ in LiTbF₄.
This spectrum, however, was not normalized with respect to the dye-emission profile. The strongest transition at 40,987.6 cm\(^{-1}\) in this \(^5\)K\(_a\) manifold is about 18.3 cm\(^{-1}\) higher than the same one found in the dilute crystal Tb\(^{3+}\):LiYF\(_4\). This transition was used to study the \(Q_1 + Q_2\) resonance in the four-wave mixing experiment as will be seen below.

**Direct Two-Photon Absorption in Tb\(^{3+}\):LiYF\(_4\)**

Direct two-photon absorption from the Tb\(^{3+}\) ground state \(^7\)F\(_6\) to the excited state components of \(^5\)G\(_6\) at 40,200 cm\(^{-1}\) has been observed for the Tb\(^{3+}\) in LiYF\(_4\).

The partial energy level diagram for the 4f\(^8\) configuration of the Tb\(^{3+}\) ion presented in Fig.11 was provided by the previous studies of two-step excitation spectra for Tb\(^{3+}\):LiYF\(_4\).

The Tb\(^{3+}\) ion is ideal for studies of direct two-photon absorption and resonant enhancement of this transition, since there are large energy gaps on both the higher and lower energy sides of the \(^5\)D\(_a\) energy levels at 20,554.0 cm\(^{-1}\).

For this single-beam two-photon absorption experiment, the laser frequency \(Q_L\) was tuned so that 2\(Q_L\) matched the \(^7\)F\(_6\)–\(^5\)G\(_6\) transition energy. The 410 nm anti-Stokes ultraviolet fluorescence cascading from \(^5\)D\(_3\) to \(^7\)F\(_5\) was used to sensitively monitor this direct two-photon absorption
Figure 11. Partial energy level diagram of the Tb$^{3+}$ ion for direct two-photon absorption experiment.
transition as shown in Fig. 11, just as in the two-step excitation experiment. Care was taken to differentiate the direct and two-step processes in all the experiments.

The laser powers were typically 12 kW, and the pulse duration was 5 nsec. The laser beam was focused to approximately 75 μm diameter such that the maximum light intensity was about 300 MW/cm² for the laser, which was well below the damage threshold for the material.

The ultraviolet fluorescence was detected by using a McPherson Model-218 0.3 meter monochromator, whose slits were oriented parallel to the laser beam in the crystal, and an RCA C31034A-02 cooled photomultiplier. Gated photon counting with negligible dark counts was used to record the signal. To limit the laser background, a bandpass glass filter CS 5-58 was placed between the sample and the monochromator. All experiments were performed under cryogenic conditions (1.3 K).

Figure 12 gives the direct two-photon absorption spectra from the ground state \( ^7F_6 \) (\( \Gamma_2 \)) to \( ^5G_6 \) (\( \Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4 \)) and shows the excellent signal-to-noise ratio obtained. All the energy levels of \( ^5G_6 \) shown in these spectra are in good agreement with the earlier two-step excitation results as shown in Table 4.

Since the laser frequency \( Q_L \) was about 400 cm\(^{-1} \) below the \( ^3D_4 \) energy level, there are no one-photon processes which are possible in this one-beam experiment. In
Figure 12. Direct two-photon absorption spectra of Tb$^{3+}$ ion from ground state $^7F_6$ ($\Gamma_2$) to $^3G_6$ in Tb$^{3+}$:LiYF$_4$ crystal.
addition the nature of this single-beam direct two-photon absorption transition has been carefully checked by measuring the power dependence of the signal strength. The observed quadratic dependence for laser power is shown in Fig. 13. These factors leave no room for any ambiguity that the signal found is from the direct two-photon transitions.

Table 4. Comparison of the energy levels observed from TPA and TSE in Tb$^{3+}$:LiYF$_4$

<table>
<thead>
<tr>
<th>$^5$G$_4$</th>
<th>TPA$^*$ (cm$^{-1}$)</th>
<th>TSE$^{**}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ₁</td>
<td>40,340.5</td>
<td></td>
</tr>
<tr>
<td>Γ₁</td>
<td>40,344.2</td>
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<tr>
<td>Γ₁</td>
<td>40,402.2</td>
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<td>Γ₂</td>
<td>40,272.0</td>
<td>40,272.4***</td>
</tr>
<tr>
<td>Γ₂</td>
<td>40,273.2</td>
<td>40,272.4***</td>
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<td>Γ₂</td>
<td>40,323.1</td>
<td>40,322.6</td>
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<tr>
<td>Γ₂</td>
<td>40,387.0</td>
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<td>Γ₃,₄</td>
<td>40,318.4</td>
<td>40,318.0</td>
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<tr>
<td>Γ₃,₄</td>
<td>40,352.0</td>
<td>40,352.3</td>
</tr>
<tr>
<td>Γ₃,₄</td>
<td></td>
<td>40,394.8</td>
</tr>
</tbody>
</table>

$^*$ TPA: Direct Two-Photon Absorption

$^{**}$ TSE: Two-Step Excitation

$^{***}$ Not resolved by TSE
Figure 13. Power dependence of direct two-photon absorption signal.
The crystal-field levels of the $^5G_6$ level for the Tb$^{3+}$ ion in the LiYF$_4$ crystal ($S_4$ symmetry) are three $\Gamma_1$ states, four $\Gamma_2$ states and three $\Gamma_3$, $\Gamma_4$ states as shown in Table 1.

The selection rules for electric dipole transitions in $S_4$ symmetry are given in Table 2. It is clear that the $\Gamma_2$ levels of $^5G_6$ of the Tb$^{3+}$ ion cannot be detected by one-photon ultraviolet absorption, since the ground state is $^7F_6(\Gamma_2)$. If one considers the two-step excitation process which uses $^5D_4(\Gamma_1)$ as an intermediate state, then the $^5D_4(\Gamma_1)$ to $^5G_6(\Gamma_1)$ transition is also forbidden for electric dipole transitions. In short, neither one-photon ultraviolet absorption nor two-step excitation could be used to identify all the $^5G_6$ energy levels.

For the direct two-photon absorption process, however, the selection rules$^{84-86}$ are different. Table 5 shows that all two-photon transitions from the ground state $^7F_6(\Gamma_2)$ to the $^5G_6(\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4)$ are allowed.

Table 5. Selection rules for two-photon absorption from $^7F_6(\Gamma_2)$ to $^5G_6$

<table>
<thead>
<tr>
<th>$\Gamma_1$</th>
<th>$\Gamma_2$</th>
<th>$\Gamma_3, \Gamma_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_2$</td>
<td>$\sigma, \pi \sigma, \sigma \pi$</td>
<td>$\pi \pi, \sigma \sigma, \pi \sigma, \sigma \pi$</td>
</tr>
</tbody>
</table>
In the experiments, the light propagation vector $k$ was perpendicular to the $c$ axis, and the following polarization configurations were used: ($\pi\pi$) the laser linearly polarized $E \parallel C$, ($\sigma\sigma$) the laser linearly polarized $E \perp C$, and ($\pi\sigma/\sigma\pi$) combinations of polarizations (circular polarization was used in the present experiments).

In Fig. 12 (a), four $\Gamma_2-\Gamma_2$ transitions from $^7F_6$ to $^5G_4$ have been clearly identified by the two-photon absorption using pure $\pi\pi$ polarization. The $^7F_6(\Gamma_2)-^5G_6(\Gamma_1)$ and $^7F_6(\Gamma_2)-^5G_6(\Gamma_2)$ transitions are shown in (b) with the laser beam $\sigma\sigma$ linearly polarized. Since $\Gamma_2-\Gamma_2$ transitions had been identified in the spectrum (a), one could easily find the three $\Gamma_2-\Gamma_1$ transitions. The $^7F_6(\Gamma_2)-^5G_6(\Gamma_3,4)$ transitions appeared in Fig. 12 (c) when the ($\pi\sigma/\sigma\pi$) combination of polarizations was used. One of the $\Gamma_3,4$ lines could not be found in the present experiment, but nine out of the total ten lines of the $^7F_6(\Gamma_2)-^5G_6(\Gamma_1,\Gamma_2,\Gamma_3,4)$ transitions have been clearly identified. This provides a good illustration that two-photon absorption is complementary to one-photon absorption spectroscopy in $\text{Tb}^{3+}$ compounds.
Resonant Enhancement of Two-Photon Absorption in Tb$^{3+}$: LiYF$_4$

A resonant enhancement of over two orders of magnitude of this direct two-photon absorption for the $^7$F$_{5/2}$-$^5$G$_{5/2}$ transition in LiTbY$_4$ has been observed when the laser frequency $\Omega_1$ was tuned near the $^5$D$_{5/2}$ real intermediate state. These results are in good agreement with a theoretical calculation shown below. A time-resolved excitation technique was used to study the strength of this direct two-photon absorption as a function of intermediate state detuning.

This resonant enhancement effect was studied by Bjorkholm and Liao in sodium vapor$^{36}$ where a strong enhancement of over seven orders of magnitude and a destructive-interference effect were observed.

The intensity of a two-photon transition, in general, is proportional to

$$I = \sum_{i} \left| \frac{\langle f| E\cdot D| i \rangle \langle i| E\cdot D| g \rangle}{\hbar\Omega_1 - \hbar\Omega_2} \right|^2$$

where $|g\rangle$ is the ground state, $|f\rangle$ is the final state, $|i\rangle$ is an intermediate state, and $\hbar\Omega_1$ is the energy of the intermediate states $|i\rangle$. Summation is carried out over all intermediate states. For the present experiment, the 4f$^7$5d and 4f$^7$5g configurations of the Tb$^{3+}$ ion are very far from the resonance so that they give constant contributions.
to this summation. The $^3D_4$ energy level, however, acts as the dominant intermediate state only when the laser frequency $Q_i$ is near this energy level.

To demonstrate the resonant enhancement of the direct two-photon absorption from $^7F_6$ to $^5G_6$ by the real intermediate state $^3D_4$, unlike the single-beam case, two different frequencies had to be used and a series of spectra had to be recorded for different $Q_i$ settings.

In this experiment, some weak laser dye fluorescence was present even after filtering the laser beam with a prism monochromator. The spectra for the $Q_1$ and $Q_2$ laser beams are shown in Fig. 14, 15. The intensity of the center frequency was attenuated by a 3.0 neutral density filter for all of these spectra. Part (a) in Fig. 14 and Fig. 15 shows the laser spectra without any filtering. The broad band fluorescence can only be cut beyond 30 cm$^{-1}$ around the center frequency by the prism monochromator with a pin hole (50 micron) as shown in Fig. 14 (c) and Fig. 15 (b). When the laser frequency $Q_i$ was tuned near the $^3D_4$ energy level, this broad dye fluorescence weakly populated this intermediate energy level, thus the two-step excitation could not be completely avoided. This small population could also contribute weak ultraviolet fluorescence to the signal by the two-ion process involving up-converted energy transfer.

Since the ultraviolet fluorescence from all these
Figure 14. Spectra of the $\Omega_1$ laser (etalon-narrowed) beam: 
(a) without filtering (b) with the filtering of 
the prism monochromator (c) with filtering of 
prism monochromator and 50$\mu$m pin hole.
Figure 15. Spectra of the Ω2 laser beam: (a) without any filtering (b) with filtering of the prism monochromator and 50μ pin hole.
processes has a one msec lifetime, it provides no means for
discriminating the origin. In order to classify the
different contributions and to detect the real direct two-
photon transition signal, the following time resolved
excitation technique has been developed in the experiment.

The data were taken in several steps. First, a
spectrum was recorded by scanning the frequency $Q_2$ across
the direct two-photon transition to $^5G_4$ with the timing of
the two beams $Q_1$ and $Q_2$ kept exactly coincident and a given
laser frequency $Q_1$ fixed below the $^5D_4$ energy level by $Q$.
A typical spectrum for $Q_1$ 3 cm$^{-1}$ below the $^5D_4(\Gamma_4)$ state is
given in Fig. 16. The two small peaks separated by 0.9 cm$^{-1}$
arose from the direct two-photon absorptions of the two $\Gamma_2$
components of the ground state of $^7F_6$ which will be
discussed below. The strong signal on the low frequency
side of this spectrum resulted from the two-step excitation
due to the weakly populated $^5D_4$ state.

The second step consists of fixing $Q_1$ at each observed
peak frequency, then scanning the delay time of the $Q_2$
laser to isolate the direct two-photon absorption signal
from the various background signals. A typical result
given in Fig. 17 shows the signal versus the time separation
between the two lasers. Each laser pulse duration was 5
nsec, and the line width of the signal was 10 nsec which
was just the pulse overlap time as expected for the direct
two-photon absorption. Since the population lifetime of
Figure 16. Excitation spectrum for two-photon absorption in Tb$^{3+}$:LiYF$_4$. 
Figure 17. Time resolved excitation spectrum for two-photon absorption in Tb$^{3+}$:LiYF$_4$. 
the \( ^5D_4(\Gamma_1) \) intermediate state is about 1 msec, the strength of the two-step excitation contribution appears as a long "flat" background to the right of the peak when \( \Omega_1 \) is ahead of \( \Omega_2 \) in time. This result clearly shows the transient property of the direct two-photon absorption and provides a means to classify the different transition mechanisms. The real strength of the two-photon absorption was obtained by subtracting this background from the peak.

Furthermore, to correct the data from the many runs, the fluctuations of the laser powers were monitored by two photodiodes and recorded by the computer for each laser pulse. The final results were normalized to the recorded intensities of the laser power.

One of the results for the resonant enhanced direct two-photon absorption is given in Fig. 18. The horizontal axis shows the \( \Omega_1 \) laser frequency detuning below the \( ^5D_4(\Gamma_1) \) energy level at 20,554.0 cm\(^{-1} \) (the lowest component of \( ^5D_4 \) levels). The vertical axis shows the strength of the direct two-photon transition obtained from series of spectra described above.

This typical result is for the \( ^7F_6(\Gamma_2) - ^3G_6(\Gamma_2) \) transition with both laser beams \( \pi \) polarized. From Table 2, it may be seen that both single-photon transitions, from the ground state \( ^7F_6(\Gamma_2) \) to the intermediate state \( ^5D_4 \) and from the intermediate state \( ^5D_4(\Gamma_1) \) to the final state \( ^5G_6(\Gamma_2) \) are allowed. Resonant enhancement of over two
Figure 18. Resonant enhancement of direct two-photon absorption in Tb$^{3+}$: LiYF$_4$: dots show the experimental results, solid line shows the calculation result.
orders of magnitude of this transition was found when $Q$ was $2 \text{ cm}^{-1}$ from the resonance with $^5\text{D}_4(\Gamma_1)$.

Similar results were also obtained for the $^7\text{F}_6(\Gamma_2)-^5\text{G}_6(\Gamma_{3,4})$ transition, when the $Q_1$ laser beam was $\pi$ polarized and the $Q_2$ laser beam was $\sigma$ polarized. As expected, no resonant enhancement was observed at the $Q_1+Q_2$ frequency corresponding to $^7\text{F}_6(\Gamma_2)-^5\text{G}_6(\Gamma_1)$ ($\sigma\sigma$) transition since both the $^7\text{F}_6(\Gamma_2)-^3\text{D}_4(\Gamma_1)$ and the $^5\text{D}_4(\Gamma_1)-^5\text{G}_6(\Gamma_1)$ single photon transitions are forbidden in that case, as seen in Table 2.

Thus, the conclusion is that the $^5\text{D}_4(\Gamma_1)$ level acts as a real intermediate state for this resonant enhancement of the two-photon transition from $^7\text{F}_6(\Gamma_2)$ to $^5\text{G}_6(\Gamma_2, \Gamma_{3,4})$.

The nonresonant part of the direct two-photon transition rate is due to the contribution of the $4f^75d$ and $4f^75g$ intermediate states. Since changing the $Q_1$ frequency does not significantly change the energy denominator for this contribution, the strength of the nonresonant part remained constant as $Q_1$ was varied over a few hundred wave-numbers below the $^5\text{D}_4$ energy level.

No interference effect was observed, which implies that the resonant and nonresonant contributions have the same sign in this case (below both $^5\text{D}_4$ and higher excited configurations). When the $Q_1$ laser frequency was tuned higher than the $^5\text{D}_4(\Gamma_1)$ state to search for interference effects, vibronic absorption led to a large population of
the $^3D_4(\Gamma_1)$ intermediate state. Thus, two-step excitation
gave a strong and broad background, and the direct two-
photon transition could not be isolated.

The theoretical calculation was made by using Eq. (IV-1). Considering that the $^3D_4$ state gives the major
contribution to the enhancement, the summation over all
intermediate states in the expression can be separated into
a resonant part and a nonresonant part as given below

$$\left| \frac{\langle f | E \cdot D | i \rangle \langle i | E \cdot D | g \rangle}{\hbar \Omega_2 - \hbar \Omega_1} + B \right|^2$$

where $B$ presents the contribution from all nonresonant
intermediate states, and $\Omega_2$ is the resonant frequency for
the $^3D_4$ state.

The two $\Gamma_2$ levels of the $^7F_6$ ground state, separated
by 0.9 cm$^{-1}$, make the calculation slightly complicated.
The $^3D_4$ excitation spectrum obtained by monitoring the
yellow fluorescence is given in Fig. 19. This spectrum shows
that both the $\Gamma_2$ levels of ground state were populated
under the experimental conditions. The smaller peak
corresponds to the transition from the upper $\Gamma_2$ level to
the $^3D_4(\Gamma_1)$, while the larger peak is the result of the
transition from the lowest $\Gamma_2$.

To consider the two-photon transition under that
situation, an energy level diagram is given in Fig. 20. It
shows that when $\Omega_1 + \Omega_2$ matches the transition from the
Figure 19. Single photon excitation spectrum of Tb$^{3+}$ ion in Tb$^{3+}$:LiYF$_4$. The two peaks correspond to the transitions from two $\Gamma_2$ levels of ground state to $^3D_4$ ($\Gamma_1$) state.
Figure 20. Energy level diagram for the model calculation of direct two-photon absorption in Tb$^{3+}$:LiYF$_4$. 
lowest $\Gamma_2$ state to the $^5G_6$ state, it also contributes to the transition from the upper $\Gamma_2$ state to the $^5G_6$ state, since the FWHM for this transition is larger than 0.9 cm$^{-1}$. Also the fixed $\Omega_1$ laser frequency is even closer to the $^5D_4$ state for the latter case, therefore, the resonant enhancement effect should be relatively strong for it.

A calculation for this model is given below. The two terms correspond to the contributions from the two $\Gamma_2$ of the ground state.

\[
\frac{|\langle f | E \cdot D | i \rangle \langle i | E \cdot D | g \rangle|}{\hbar(\Omega_R - \hbar\Omega_1)} + A \cdot C + B^2 \quad (IV-3)
\]

where $A$ is a normalized parameter due to the population of the upper $\Gamma_2$ state, $C$ is another normalized parameter due to the line shape of the $^7F_6 - ^3D_4$ direct two-photon transition. The matrix elements are treated as adjustable parameters for simplicity. All these parameters shown in Table 6 were determined from the experimental data.

<table>
<thead>
<tr>
<th>Table 6. Parameters for model calculation of resonant enhancement of TPA in Tb$^{3+}$:LiYF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix elements</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

In Fig.18, the solid line shows the results of the calculation. The fit between the experiment and the theory is very satisfactory.
Resonant Four-Wave Mixing

Many details of the four-wave mixing process in LiTbF₄ and Tb(OH)₃ have previously been studied by Ender, Otteson and Cone in this laboratory. The experimental techniques, however, have been improved since the present thesis work started. As an example, the photodiode detecting technique (see Chapter III) has been widely used to reduce the noise level resulting from laser power fluctuations in the four-wave mixing experiments. Also, this technique provides a much larger dynamic range for measuring the signal strength. Other improvements include redesigning the laser trigger system and using the 'Timing Stabilization' unit to reduce the time jitter and drift of the lasers. The computer control system has also made the experiments more convenient and accurate.

The single-resonance four-wave mixing experiments were repeated for LiTbF₄ with greater precision. As expected, phase matching induced frequency selectivity in the four-wave mixing has been extended to new samples. The two-photon-resonant four-wave mixing, which holds promise as a new spectral tool, is presented in this section.

Single-Resonance in LiTbF₄, TbF₃ and ErPO₄

Typical results for the single-resonance four-wave mixing in the LiTbF₄ sample (0.3 mm thick), from the
present experiments, are given in Fig. 21. The four-wave mixing spectrum (solid curve) and the absorption spectrum (dashed curve) were taken simultaneously by scanning the $Q_i$ laser frequency and were recorded by the computer.

The third order nature of the mixing process was confirmed by examination of the power dependence and the temporal overlap effects for the three incident laser pulses. The generated $Q_4$ frequency was checked to meet the condition $Q_4 = Q_1 + Q_2 - Q_3$ when either $Q_1$, $Q_2$ or $Q_3$ varied.

In Fig. 21, a demonstration shows that when any one of the incident laser pulses was blocked the mixing signal vanished. Particularly when the $Q_1$ laser is blocked, both the four-wave mixing and the absorption signals drop to zero which shows that the two recorded spectra were well synchronized as expected.

The transient properties of this mixing process required that the three laser pulses had to meet in the crystal at exactly the same time and at the same tiny spot to obtain the mixing signal, which made it an extremely difficult experiment. The ability to meet this critical condition, however, was achieved by electronic and optical delays in the laboratory.

Besides the particular four-wave mixing process described in Chapter II, some other possible four-wave processes with the three laser pulses meeting in the crystal have been carefully considered and have been ruled
Figure 21. Single-resonance four-wave mixing spectrum (solid curve) and corresponding absorption spectrum (dashed curve) for the $^5D_4$ ($\Gamma_1$) state of LiTbF$_4$. 
out in the previous study. For instance, the Coherent Anti-Stokes Raman Scattering (CARS) was ruled out by choosing $\Omega_3$ to avoid Raman resonances, and the thermal grating effects were ruled out by large differences of the three laser frequencies for this nondegenerate four-wave mixing (when $\Omega_1=\Omega_2$, those beams were colinear.).

The nature of the observed single-photon resonances had been studied in detail in the previous investigations. The major results are summarized as follows:

1. The observed signals were always narrower than the inhomogeneous width of the corresponding $\Omega_1$ absorption line.
2. The line shape and the location, relative to the center of the absorption line, of the mixing signals were found to be exceptionally sensitive to the phase matching conditions.
3. The mechanism of the line narrowing could be well understood by taking into account the anomalous dispersion of the linear index of refraction near the $\Omega_1$ resonance which causes the phase matching to be over $10^3$ times more restrictive than it would be in the absence of this resonance.
4. Model calculations have been developed for the phase matching effect and have given a fit to the experimental results.

In order to demonstrate further the generality of this
single-photon-resonant four-wave mixing phenomenon, the experiments were performed in the single crystal of TbF₃. The experimental method was simplified by using \( \Omega_2 = \Omega_1 \). Two lasers of frequencies \( \Omega_1 \) and \( \Omega_3 \) were focused onto the TbF₃ crystal. The coherently generated beam at \( \Omega_4 = 2\Omega_1 - \Omega_3 \) was spatially and spectrally separated and used to monitor the mixing.

The absorption spectrum, in which the laser beam propagation was nominally parallel to the crystallographic c axis and the beam polarization was perpendicular to the b axis (\( \sigma \) polarization), was performed in TbF₃ and the strong \( ^7F_6-^3D_4 \) transition at 20,607.3 cm\(^{-1} \) was observed. In the mixing experiment, the \( \Omega_3 \) frequency was fixed at 17,422 cm\(^{-1} \) with \( \sigma \) polarization and the \( \Omega_1 \) frequency was scanned across the \( ^7F_6-^3D_4 \) transition.

Since the crystal was mounted with the b axis in the vertical direction, \( \sigma \) polarization relative to the b axis means that all the laser beams were polarized in the horizontal direction. Thus the generated coherent mixing signal beam with frequency \( \Omega_4 \), having \( \sigma \) polarization, falls into the less sensitive range of the Spex monochromator. This problem was solved simply by using a half-wave plate to rotate the polarization of the mixing beam before sending it to the monochromator. A strong four-wave mixing signal was observed at 23,793 cm\(^{-1} \) with the monochromator slits widely opened.
A number of different angles between the $\Omega_1$ and $\Omega_3$ beams were used to study the phase matching effects. The resonant behavior of the internal mixing signals is shown in Fig. 22 for: (a) $\theta=4.2^\circ$ and (b) $\theta=1.0^\circ$ between the two beams. The line center (dashed line) of the $\Omega_1$ absorption is also shown.

As before, these results prove that the phase matching effect due to the anomalous dispersion associated with the single resonance causes line narrowing of the mixing signal. For this crystal, as for LiTbF$_4$, the larger angle $\theta$ requires a "small" value of index of refraction $n_1$ (for appropriate $\Omega_3$) and locates the peak on the high energy side of the $\Omega_1$ resonance shown in (a). In contrast, the peak shown in (b) is for the small angle which requires a "large" value of $n_1$ and locates the peak on the low energy side.

An experiment demonstrating the same effects was also performed in the ErPO$_4$ crystal. To confirm the new observations, the nature of the mixing signals was checked by the same method as before. The data are plotted in Fig. 23 for both the four-wave mixing and the absorption spectrum. The strong absorption line at 20,492.7 cm$^{-1}$ is due to the $^4I_{13/2} - ^4F_{7/2}$ transition. The $\Omega_3$ frequency, fixed at 17,422 cm$^{-1}$, was the same as in the case for TbF$_3$.

It thus seems reasonable to suggest that similar effects will be observable in any other rare earth
Figure 22. Four-wave mixing signal in TbF$_3$ crystal:
(a) $\theta = 4.2^\circ$  (b) $\theta = 1.0^\circ$
Figure 23. Four-wave mixing spectrum (solid) and absorption spectrum (dashed) of Er$^{3+}$ in ErPO$_4$ crystal.
compound.

The simulation model of the phase matching mechanism developed by Otteson and Cone was discussed in Chapter II. Those calculations, which considered the four hyperfine components in the $^7F_6-^3D_4$ absorption profile, gave a good fit for the line narrowing due to the phase matching effects. But, since the previous experimental results did not clearly show the difference in the strengths of the mixing signals for different angles, some asymmetries were ignored in Otteson's simulation calculations.

The present experiments on LiTbF$_4$ have shown that the single-resonant four-wave mixing signals have obviously different strengths relative to the nonresonant background for each side of the absorption line. The results are shown in Fig. 24 for the LiTbF$_4$ crystal with a thickness of 0.3 mm. Strong resonant peaks are shown on the lower energy side, with small angles between the two laser beams. Weaker peaks are shown on the higher energy side with larger angles required. The location of the resonant peaks changes, as in the previous results, when the angle is varied.

To understand these results, it was realized that the nonresonant part of the third order susceptibility could not be negligible in the model calculation, and also that the absorption line shape from the ground state $^7F_6$ to the excited state $^3D_4$ for the four hyperfine levels$^{45,69}$ could
Figure 24. Four-wave mixing spectra corresponding different phase matching angle in LiTbF₄ with thickness of sample L=0.3mm. (The dashed curve shows the absorption line for \(^7F_6(T_2) - ^3D_4(T_{1})\) transition.)
not be simply considered to be symmetric. The latter consideration is the more important one. In fact, the asymmetric line shape had already been found in earlier experiments. These effects have been considered in the present four-wave mixing calculations to fit the experimental data. The simulation calculation, taking into account these new considerations, has been done by adding the nonresonant term and using appropriate transition rates for the four hyperfine components. The result given in Fig. 25 shows strong resonant peaks on the lower energy side and weak resonant peaks on the higher energy side which agrees with the experimental results (Fig. 24).

The experiments and the calculations have also been completed for the thinner LiTbF$_4$ sample (0.078 mm). The experimental results are given in Fig. 26, and the calculation results are given in Fig. 27. Compared to the case of the thicker sample (0.3 mm), the significant change is obvious.

It has been suggested by the simulation model that the primary parameter determining the degree of the peak narrowing is $\sigma_{\text{abs}} L$, where $\sigma_{\text{abs}}$ is the peak absorption coefficient of the $Q_1$ resonance, and $L$ is the thickness of the sample. When $\sigma_{\text{abs}} L \ll 1$, the line shape of the signals is determined primarily by the frequency dependence of the third order susceptibility. When $\sigma_{\text{abs}} L \approx 1$, the phase matching induced narrowing becomes significant.
Figure 25. Model simulation of four-wave mixing signal as a function of phase matching angle with thickness of sample $L=0.3$ mm.
Figure 26. Four-wave mixing spectra corresponding to different phase matching angles in LiTbF$_4$ with thickness of sample $L=0.078$ mm. (The dashed curve shows the absorption line for $^7F_6(\Gamma_2)$-$^5D_4(\Gamma_1)$ transition.)
Figure 27. Model simulation of four-wave mixing signal as a function of phase matching angle with thickness of sample L=0.078 mm.
These detailed experiments, which have been finished, are for a transition of the Tb$^{3+}$ ion which is very weak compared to those for other rare earths. The oscillator strength for the $^7F_6-^3D_4$ transition of Tb$^{3+}$ in LiTbF$_4$ is $f=9 \times 10^{-9}$. For other rare earths, where typical values are $f=10^{-6}$, the selective line narrowing effects will be more pronounced.

**Double-Resonance in LiTbF$_4$**

The ultimate goal for this thesis work was to study the four-wave mixing process as a new spectroscopy tool to investigate high excited states. For this purpose the two-photon-resonant four-wave mixing was carefully investigated. The first observation of this process in LiTbF$_4$ will be reported here.

The idea of this experiment has its basis in the results found in the previous experiments of this thesis work which include:

1. The high excited energy levels of $^3K_6$ in the LiTbF$_4$ have been found, and a strong transition has been accurately located at 40,987.6 cm$^{-1}$ by the two-step excitation spectrum.

2. The direct two-photon absorption process, which uses the same density matrix elements as the four-wave mixing process, has been observed for the Tb$^{3+}$ ion in the dilute crystal. The implication is that the same
process may also happen in the LiTbF₄ crystal, and the Q₁+Q₂ resonance may enhance the four-wave mixing process.

(3) The single-photon resonant four-wave mixing process has been studied in detail. The phase matching mechanism can be well understood by consideration of the dispersive behavior of the linear index of refraction near the single-photon resonance.

The experimental approach for two-photon-resonance four-wave mixing was similar to that for the case of the single-resonance experiments. To search for the Q₁+Q₂ resonance the Q₁ laser frequency was fixed at the ⁷F₆→⁵D₄ transition for the single-photon resonance, the Q₃ frequency was fixed at 17,422 cm⁻¹, and the Q₂ frequency was scanned to match the two-photon resonance.

To determine whether real resonance actually occurs for the mixing process when Q₁+Q₂ reaches the known energy level, the two-step excitation output of ultraviolet fluorescence was simultaneously monitored with the four-wave mixing experiment. The energy diagram shown in Fig. 28 illustrates this situation graphically. Figure 28 (a) shows that when the Q₂ laser frequency is scanned across the Q₁+Q₂ resonance the two-step excitation spectrum is recorded by monitoring the ultraviolet fluorescence, meanwhile the mixing process, shown in Fig. 28 (b), is monitored by the coherent generation at Q₄=Q₁+Q₂−Q₃.
Figure 28. Energy level diagram for LiTbF₄: (a) two-step excitation, (b) four-wave mixing.
Figure 29. Double-resonance four-wave mixing signal (a) and two-step excitation signal (b) for $^7F_6-^5D_4-^5K_8$ of Tb$^{3+}$ in LiTbF$_4$. 
The observed spectra are plotted in Fig. 29 versus \( \Omega_1 + \Omega_2 \). The two-step excitation in Fig. 29 (b) shows the resonance of \( 7F_6 - 3D_4 - 3K_6 \) when \( \Omega_1 + \Omega_2 \) satisfies the 40,987.6 cm\(^{-1}\) transition condition. As expected, the four-wave mixing spectrum in Fig. 29 (a) also gives the resonance at the same frequency \( \Omega_1 + \Omega_2 \). This demonstrates that the two-photon-resonance was achieved in the mixing process. Since \( \Omega_1 \) was fixed at the \( 7F_6 - 3D_4 \) transition, this result could be considered a double-resonant mixing process.

Various tests were made to confirm that the observed signal arose from the coherent four-wave mixing process. In particular, tests were made when the two-photon resonance occurred to rule out the remote possibility that the signal came from leaking of the ultraviolet fluorescence due to the resonance of the two-step excitation.

To describe these results the most important terms in the third order nonlinear susceptibility, related to this mixing process, have to be recalled from Chapter II as follows

\[
\chi^{(3)}(-\Omega_4, \Omega_1, \Omega_2, -\Omega_3) = \left( \frac{\mu_{ab} \mu_{bc} \mu_{cd} \mu_{da}}{(\Omega_a - \Omega_1 - i \Gamma_a)(\Omega_c - (\Omega_1 + \Omega_2) - i \Gamma_c)(\Omega_d - (\Omega_1 + \Omega_2 - \Omega_3) - i \Gamma_d)} \right) + \left( \frac{\mu_{ab} \mu_{bc} \mu_{cd} \mu_{da}}{(\Omega_a - \Omega_1 - i \Gamma_a)(\Omega_c - (\Omega_1 + \Omega_2) - i \Gamma_c)(\Omega_d - (\Omega_1 + \Omega_2 - \Omega_3) - i \Gamma_d)} \right)
\]

(IV-4)
where a, b, c and d label the states, the \( \Gamma \)'s represent linewidths, and the \( \mu \) factors represent electric dipole moments. For the two-photon resonant contributions in LiTbF\(_4\), a is the lowest \( ^7\!F_6 \) component, b is the lowest \( ^3\!D_4 \) component, and c is the observed \( ^3\!K_\ell \) component. The \( \Omega_3 \) frequency was chosen so that neither it nor combinations with \( \Omega_1 \) and \( \Omega_2 \) would be in resonance with a Tb\(^{3+} \) transition.

The constant intensity versus \( \Omega_1+\Omega_2 \) in Fig. 29 (a) arises from the \( \Omega_1=\Omega_b \) single-photon resonance in conjunction with the off-resonance condition in the other factors in the denominator. The peak occurring at \( \Omega_1+\Omega_2=40,987.6 \text{ cm}^{-1} \) corresponds to the additional resonance contribution which occurs when \( \Omega_1+\Omega_2=\Omega_c \).

Since the peak height is only comparable to the constant background level, other levels must also be contributing to the susceptibility. It is quite plausible that the observed susceptibility arises from a combination of many near-resonant contributions from other nearby states in \( ^5\!K_\ell \) and from other nearby \( 4f^8 \) levels. Some contribution from nearby \( 4f^75d \) levels may also be important.

There is nothing special about the states involved in the resonance observed in this experiment, so it is reasonable to assume that similar observations are feasible for all of the levels observed in the two-step excitation.
studies for \( \text{Tb}^{3+}:\text{LiTbF}_4 \). The same experiments should also be feasible for other rare earth ions.

At this point it should be mentioned that the disadvantage of this double-resonance four-wave mixing method is that the single-resonance background causes the signal to be very unstable. The major difficulties are: (1) The transient properties of the mixing process require that the laser timing has to be very stable to reduce the 'noise' resulting from the single-resonance background. (2) The phase matching condition around the \( \Omega_1 \) resonance is very critical, and scanning \( \Omega_2 \) may cause this condition to be changed. To obtain a relatively stable condition to scan the \( \Omega_2 \) frequency, the \( \Omega_1 \) frequency was not set to the best phase matching condition.

It is possible that the single-resonance with \( \Omega_1 + \Omega_2 \) may give better results, since the direct \( \Omega_1 + \Omega_2 \) two-photon absorption process has already been observed and this method can avoid the problem arising from the critical single-resonance phase matching conditions.
CHAPTER V

CONCLUSIONS

Direct two-photon absorption spectra have been obtained as excitation spectra by monitoring the anti-Stokes ultraviolet cascade fluorescence cascading from $^5D_3$ to $^7F_3$ for the Tb$^{3+}$ ion in the Tb$^{3+}$:LiYF$_4$ crystal. Resonant enhancement of over two orders of magnitude of this direct two-photon absorption from the ground state $^7F_6$ to the excited state $^5G_6$ of the 4f$^8$ configuration at 40,200 cm$^{-1}$ has been observed in the time resolved experiment.

Two different transition mechanisms were clearly shown in the experimental results. When the $\Omega_1$ laser frequency was off the single-photon resonance by 20 cm$^{-1}$ or more, the intermediate states making the largest contribution to the $\Omega_1+\Omega_2$ resonance were from excited configurations such as 4f$^7$5d and 4f$^7$5g of opposite parity which were far from the resonance. When the $\Omega_1$ laser frequency was near the single-photon 4f$^8$-4f$^8$ $^7F_6$-$^3D_4$ resonance, the results showed a stronger contribution from the real intermediate state ($^5D_4$).

The theoretical calculations, applied to the two $\Gamma_2$
levels of the $^7F_6$ ground state in the special experimental method gave a good fit to the experimental results.

A new time-resolved technique has successfully isolated the direct two-photon absorption signal from the unwanted two-step excitation signal. This technique takes advantage of the transient properties of the direct two-photon absorption. By varying the time delay of the two separately triggered lasers, the two-step excitation gave a "flat" step background, while the direct two-photon absorption resulted in a peak.

Presumably, the same resonance effect may be observable in other rare earths, since larger transition probabilities are expected due to larger one-photon oscillator strengths. The value of the oscillator strength for the $^7F_6$-$^3D_4$ transition in LiTbF$_4$ is $9 \times 10^{-9}$, but for other rare earths typical values are $10^{-6}$. In addition, general theories of two-photon processes$^6$ imply that the resonant enhancement will also be observable for Raman scattering in the rare earth compounds.

As a spectroscopy tool, direct two-photon absorption has been used to study the highly-excited energy levels. Since the direct two-photon absorption satisfies different selection rules than linear absorption, complementary information can be obtained. Good illustrations have been made for the transition of the Tb$^{3+}$ ion in Tb$^{3+}$:LiYF$_4$ from the ground state $^7F_6(\Gamma_2)$ to the excited configuration $^3G_6$. 
Nine out of the total of ten lines corresponding to these transitions have been clearly identified. Particularly, the $\Gamma_1$ states have been observed for the first time. These results provide important information for crystal field calculations. The implication is that the direct two-photon absorption could be used to complete the energy levels up to 45,000 cm$^{-1}$ for the Tb$^{3+}$:LiYF$_4$ crystal which have been observed in the previous studies and to confirm their identification. In addition, the observed direct two-photon absorption process of the Tb$^{3+}$ ion holds promise for studying the double-resonance four-wave mixing in LiTbF$_4$. This is because both processes involve the same density matrix elements.

The observations of line narrowing, resulting from the phase matching selectivity in single-resonance four-wave mixing, have been extended to new crystals: TbF$_3$ and ErPO$_4$. The studies of the thin and thick LiTbF$_4$ samples proved that the primary parameter determining the degree of the narrowing is $\alpha_{so}L$ as predicted by the model calculations. It will be interesting to study these effects in the other rare earth compounds with larger absorption coefficients and for thicker samples. Even with these favorable conditions, the line narrowing may reach a limit. It is possible that the homogeneous line width may be studied by these phase matching techniques.

Simulation calculations have been applied to analyze
the present experimental results, using several modifications. These modifications consist of adding the nonresonant term for the third order susceptibility and using the observed line shape for the four hyperfine splittings of the ground state of $^7F_6$. The calculation is in good agreement with asymmetric resonant strengths of mixing signals from the experimental results. The significance of these studies is that both the experiment and the model calculations demonstrate the sensitivity of these line narrowing effects to details of inhomogeneous broadening and confirm the accuracy of the model.

The two-photon-resonant four-wave mixing has been observed for Tb$^{3+}$ in the 4f$^8$ states of the LiTbF$_4$ crystal. This observation of the resonant behavior was confirmed by simultaneously monitoring the resonance of the two-step excitation process. This technique should be useful to detect and label the two-photon transitions in non-fluorescing materials or in systems where stronger overlapping features preclude the use of standard spectroscopic techniques.

Studies of the phase matching near the $\Omega_1 + \Omega_2$ resonance have not yet been completed, but any observation of such effects would be quite significant. A single-resonance behavior with total frequency $\Omega_1 + \Omega_2$ in the four-wave mixing would be very interesting to see in future experiments.
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APPENDIX

COMPUTER PROGRAM
Figure 30. Program for experiment of FWM (3 beams) with pressure scan laser

```c
#include <std.h>
#include <rt11.h>
#include "ad.cn"
#include "par.cn"
#include "mini.h"

main()
{
    FIO fio;
    char filnam;
    long INITT(),DRWABS(),MOVABS(),FINITT(),ANMODE;
    int x0 = 30;
    int x1 = 10;
    int y0 = 150;
    int y1 = 130;
    int x, y, xx, yy;
    int baud = 2400;
    int xmax = 660;
    int ymax = 730;
    float xs, yscale, yyscale;
    int xscale;
    int start, repeat;
    float vf, ef, init, fina;
    long v[500];
    int i, j, k, n;
    long av, avv, a, b, c, d, e;
    long data, dat;
    long z[1000], zz[500];

    char ready, beging, check, conti, newnam, end, epump, pump;
    char bell[2];
    bell[0] = 07;
    bell[1] = 0;
    getinit();
    parinit();
    parout('D', 0, 1);
    parout('D', 1, 1);

    /* SET THE INITIAL CONDITIONS */
    putfmt("CHECK INPUT:\n");
    putfmt("CHANNEL 0 : FWM; 1 : W1; 2 : W2; 3 : W3;
        4: ABS ;5 : PRESSURE. \n");
    putfmt("what is the name of the data file?\n");
    getfmt("#p\n", filnam);
```
if(!fcreate(&fio,filnam,1))
{
    putfmt("error: can't open %p\n,filnam");
    return;
}
putfmt("What is the initial pressure setting?\n");
getfmt("%f\n",&init);
putfmt("What is the final pressure setting?\n");
getfmt("%f\n",&fina);
putfmt("PLOT: How many data points do you want?\n");
getfmt("%i\n",&xs); 
xs = ((float)630/xscale);
goto beging;

/* GIVE A NEW NAME */

newnam:
putfmt("what is the NAME of the NEW data file?\n");
getfmt("%p\n",filnam);
if(!fcreate(&fio,filnam,1))
{
    putfmt("error: can't open %p\n,filnam");
    return;
}
xs = ((float)630°2/j);

/* START */
beging:
x = 0;
xx = 0;
parout(‘B’ ,8,1); /* CLOSE THE LASER SHUTTERS */
parout(‘B’ ,9,1);
parout(‘B’ ,10,1);
putfmt("Are you ready to get zero?\n");
getfmt("\n");
gettrg();
getzero(0),getzero(1),getzero(2),getzero(3),getzero(4);
for(i = 1;i <= 2°j;i++)
{
    z[i] = 0; /* CLEAR DATA ARRAY */
    zz[i] = 0;
}

j = 0;
parout(‘B’ ,8,0); /* OPEN THE LASER SHUTTERS */
parout(‘B’ ,9,0);
parout(‘B’ ,10,0);
for(i = 1;i <= 50; i++)
{
    pump: vf = getvolt(5)/VOLTS;
    if( vf >= (init-0.2))
Figure 30 -- Continued

parout('D',1,0);
goto pump;
}
parout('D',1,1);
}
putfmt("%p

",bell);
putfmt("Pump down the pressure. When the pressure is low\n
");
putfmt("then initial settling 0.3v, hit RETURN key to start\n

");
*/ INITIALIZE PLOT */
parout('D',0,0);
fcall(INITTT,1,&baud);
putfmt("DATA FILE : %p\n
",filnam);
*/ DRAW AXES */
fcall(MOVABS,2,&x0,&ymax);
fcall(DRWABS,2,&x0,&y0);
fcall(DRWABS,2,&xmax,&y0);
fcall(MOVABS,2,&x0,&y0);
/* CHECK PRESSURE */
check:
vf = ge tvolt(5)/VOLTS;
if(vf >= init)
goto ready;
ef = vf - init;
if(!((abs(ef) <= 0.1))
goto check;
/* TAKE DATA */
ready:
dat = 0;
data = 0;
for(i = 1; i <= 10; i++)
{
    getttrg();
    a = getvolt(0); /* FWM SIGNAL */
    b = getvolt(1); /* LASER 1 */
    c = getvolt(2); /* LASER 2 */
    d = getvolt(3); /* LASER 3 */
    e = getvolt(4); /* ABS SIGNAL */
    av = (e*500)/b; /* ABS */
    avv = (-1)*((((a*500/b)*1000)/c)*1000)/d; /* FWM */
    data += av; /* ABS */
    dat += avv; /* FWM */
}
yscale = ((float)500/data); /* SCALE FOR ABS */
yyscale = ((float)100/dat); /* SCALE FOR FWM */
x = 30;
Figure 30 -- Continued

\[ xx = 30; \]
\[ y = 150; \]
\[ yy = 150; \]
\[ \text{putfmt("\%p\n\n", bell);} \]

\text{conti:}
\[ j += 1; \]
\[ \text{dat} = 0; \]
\[ \text{data} = 0; \]
\[ \text{for}(i = I; i <= 10; i++) \{ \]
\[ \text{gettrgO;} \]
\[ a = \text{getvolt}(0); \quad /\text{FWM SIGNAL} /; \]
\[ b = \text{getvolt}(1); \quad /\text{LASER 1} /; \]
\[ c = \text{getvolt}(2); \quad /\text{LASER 2} /; \]
\[ d = \text{getvolt}(3); \quad /\text{LASER 3} /; \]
\[ e = \text{getvolt}(4); \quad /\text{ABS SIGNAL} /; \]
\[ \text{av} = (e^500)/b; \quad /\text{ABS} /; \]
\[ \text{avv} = (-1)^5((a^500/b)^o1000)/c)^o1000)/d; \quad /\text{FWM} /; \]
\[ \text{data} += \text{av}; \quad /\text{ABS} /; \]
\[ \text{dat} += \text{avv}; \quad /\text{FWM} /; \]
\[ \}
\[ z[j] = \text{data}; \quad /\text{ABS DATA} /; \]
\[ zz[j] = \text{dat}; \quad /\text{FWM DATA} /; \]

\[ /\text{. PLOT DATA} /; \]
\[ \text{fcall(MOVA}S,2,&xx,&yy);} \]
\[ xx = (\text{int})((\text{float})(j-1)^oxs + 30); \quad /\text{ABS} /; \]
\[ yy = (\text{int})((\text{float})\text{datyscale} + 150); \quad /\text{FWM} /; \]
\[ \text{fcall(DRW}S,2,&xx,&yy);} \]
\[ \text{fcall(MOVA}S,2,&x,&y);} \]
\[ x = (\text{int})((\text{float})(j-1)^oxs + 30); \quad /\text{ABS} /; \]
\[ y = (\text{int})((\text{float})\text{datyscale} + 150); \quad /\text{FWM} /; \]
\[ \text{fcall(DRW}S,2,&x,&y);} \]
\[ v[j] = \text{getvolt}(5); \]
\[ vf = (\text{float})(v[j])/\text{VOLTS}; \]
\[ \text{if}(\text{vf} >= 9.9000) \]
\[ \text{goto end;} \]
\[ \text{if}(!(\text{vf} == \text{fina})) \]
\[ \text{goto conti;} \]
\[ \text{putfmt("\%p\n\n", bell);} \]
\[ \text{putfmt("\n");} \]
\[ \text{putfmt("Shots = 10 Total data points = \%i\n", j);} \]
\[ \text{putfmt("V(init) = \%1.4f V(fina) = \%1.4f\n",} \]
\[ ((\text{float})v[1]/\text{VOLTS}),((\text{float})v[j]/\text{VOLTS});) \]

\[ /\text{. CLOSE GAS, OPEN PUMP} /; \]
\[ \text{parout('D',0,1);} \]
\[ \text{parout('D',1,0);} \]
Figure 30 -- Continued

/° READ DATA TO A FILE o/

k = j;
for(j = (k+2); j < (2^k+1); j++)
{  
z[j] = zz[j-k+1]; /* PUT TWO DATAS IN A FILE */
}
j = 2^k;
k = 0;
putf(&fio, "\n");
for(k = 0; k <= (j/8+1); k++)
{
  putf(&fio, "%
/° PUMP THE PRESSURE DOWN TO INITIAL CONDITION o/

epump:
vf = getvolt(5)/VOLTS;
if( vf >= (init-0.3))
goto epump;
parout(1D1, 1, 1);
getfmt("\n");
/° REPEAT RUN WITH SAME CONDITION ?? o/
putfmt("Are you going to run again with the same setting?\n");
putfmt("Answer: 1 for YES; else for NON\n");
getfmt("\n", &repeat);
if( repeat == 1)
  goto newnam;
else
  putfmt("END OF RUN\n");}
Figure 31. Program for experiment of FWM (3 beams) with stepper motor scan laser

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

main()
{
    FIO fio;
    char filnam;
    long INITT(),DRWABS(),MOVABS();
    int x0 = 30;
    int x1 = 10;
    int y0 = 150;
    int y1 = 130;
    int x,y,xx,yy;
    int baud = 2400;
    int xmax = 660;
    int ymax = 730;
    float xs,yscale,yyscale;
    int steps,step,repeat,shots;
    int i,j,k,n,m,rtn;
    long a,b,c,d,e;
    long fwm;
    long fwmtdt;
    long ab;
    long abdt;
    long z[1200];
    long zz[600];
    char fhk,newnam,start;
    char bell[2];

    bell[0]=07;
    bell[1]=0;
    getinit();
    parinit();
    putinit();

    /* SET INITIAL CONDITION */
    printf("CHECK INPUT:\n");
    printf("channel 0 : FWM; 1 : W1; 2 : W2; 3 : W3; 4 : ABS.\n");
    printf("what is the name of the data file?\n");
```
getfmt("%p\n",filnam);
if(!fcreate(&fio,filnam,1))
{
    putfmt("error: can't open %p\n,filnam");
    return;
}
putfmt("How many steps do you want for this runnig?\n");
getfmt("%i\n",steps);
xs = ((float)630/steps); /* X SCALE */
putfmt("What's the size of steps by stepper motor?(200/turn)\n");
getfmt("%i\n",step);
putfmt("Input the No. of shots to ave.\n");
getfmt("%i\n",shots);
getccw(100);
getcw(100);
goto start;

/* GIVE A NEW NAME */
newnam:
putfmt("what is the NAME of the NEW data file?\n");
getfmt("%p\n",filnam);
if(!fcreate(&fio,filnam,1))
{
    putfmt("error: can't open %p\n,filnam");
    return;
}
j = 0;

/* START */
start:
m = 0;
putvolt(1,2047);
parout('B',8,1);
parout('B',9,1); /* CLOSE SHUTTERS */
parout('B',10,1);
putfmt("Are you ready to get zero?\n");
getfmt("\n");
gettrg();
getzero(0),getzero(1),getzero(2),getzero(3),getzero(4);
for (j = 0; j <= steps+10; j++)
{
    z[j] = 0;
    zz[j] = 0;
}
parout('B',8,0);
parout('B',9,0); /* OPEN SHUTTERS */
parout('B',10,0);
getfmt("\n");
fcall(INITT,1,&baud); /* INITIALIZE PLOT */
putfmt("DATA FILE : %p\n",filnam);
fcall(MOVABS,2,&x0,&ymax);
call(DRWABS,2,&x0,&y0);  // DRAW AXES /
fcall(DRWABS,2,&xmax,&y0);
fcall(MOVABS,2,&x0,&y0);

// GET YSCAL FOR PLOT /
fwmdt = 0;
abdt = 0;
yscale = 0;
yyscale = 0;
ab = 0;
fwm = 0;
for(i = 1; i <= shots/5; i++)
{
    gettrg();
    a = getvolt(0);  // FWM SIGNAL FROM SPEX /
b = getvolt(1);    // LASER 1 /
c = getvolt(2);    // LASER 2 /
d = getvolt(3);    // LASER 3 /
e = getvolt(4);    // ABS SIGNAL AFTER SAMPLE /
fwm = (-1)(((a500/b)1000/c)1000)d;    // FWM /
ab = (e500)/c;     // ABS /
fwmdt += fwm;      // FWM /
abdt += ab;        // ABS /
}

yscale = ((float)500/(abdt/5));
yscale = ((float)100/(fwmdt/5));

// TAKE DATA /

x = 30;
y = 150;
xx = 30;
yy = 150;
putfmt("%p\n\n",bell);
putvolt(1,1023);
putfmt("%p\n\n",bell);
for(j = 1; j <= steps; j++)
{
    ab = 0;
    fwm = 0;
    abdt = 0;
    fwmdt = 0;
    getcw(step);
    m += step;  // TOTAL STEPS TO REVERSE /
    for(i = 1; i <= shots; i++)
    {
        gettrg();
        a = getvolt(0);  // FWM SIGNAL FROM SPEX /
b = getvolt(1);    // LASER 1 /
c = getvolt(2);    // LASER 2 /
Figure 31 -- Continued

d = getvolt(3); /* LASER 3 */
e = getvolt(4); /* ABS SIGNAL AFTER SAMPLE */
fwm = (-1)0(((a0500/b01000)/c01000)d; /* FWM */
ab = (e0500); /* ABS */
fwmdt += fwm; /* FWM */
abdt += ab; /* ABS */

z[j] = abdt; /* ABS */
zz[j] = fwmdt; /* FWM */

/* PLOT DATA */
fcall(MOVABS,2,&xx,&yy);
xx = (int)((float)j0xs + 30); /* ABS */
yy = (int)((float)abdt0yscale + 150);
fcall(DRWABS,2,&xx,&yy);
fcall(MOVABS,2,&x,&y);
x = (int)((float)j0xs + 30); /* FWM */
y = (int)((float)fwmdt0yscale + 150);
fcall(DRWABS,2,&x,&y);

/* READ DATA TO A FILE */
k = j;
for(j = (k+1); j < (2°k+1); j++)
{
    z[j] = zz[j-k+1];
}
j = 2°k;
putf(&fio,"%n");
for(k = 0; k <= (j/8); k++)
{
    putf(&fio, "+%06041 %+06061 %+06061 %+06061 %+06061 \n", (long)(8°k),
        z[8°k+0],z[8°k+1],z[8°k+2],z[8°k+3],z[8°k+4],z[8°k+5],
        z[8°k+6],z[8°k+7]);
}
fclose(&fio);
putfmt("%n",bell);
putfmt("% How many steps do you need to turn it back? (200/turn) \n");
getfmt("%i",&rtn);
putfmt("%i\n",rtn);
if(rtn == 0)
{
    goto fhk;
}
```c
else {
    rtn += 100;
    getccw(rtn); /* REVERSE THE MOTOR */
    getcw(100); /* GET TO THE STARTING POINT */
}

/* RUN THE EXPERIMENT WITH SAME SETTING */
fhk:
    putfmt("Are you going to run again with the same setting?\n");
    putfmt("Answer 1 for YES; else for NO\n");
    getfmt("%i\n", &repeat);
    if( repeat == 1 )
    {
        goto newnam;
    }
else
    {
        putfmt("END OF RUN\n");
    }
```
Figure 32. Program to scan the timing between two lasers

```c
#include <std.h>
#include <rt1I.h>
#include "da.c"
#include "ad.c"
#include "par.c"
#include "mini. h"

main()
{
  FIO fio;
  char filnam;
  long wx,wy,a,b;
  int s,shot;
  long z[500];
  int nsec,ns,range,nsn;
  int i,j,k,v,iv,n;
  char bell[2];
  char c[2];
  char star;
  float delta;

  bell[0] = 07;
  bell[1] = 0;
  putinit();
  getinit();
  parinit();
  for(;;)
  {
    /* SET INITIAL CONDITION */
    putfmt("Check DAC: A--laser trigger; B--NS575 ext. C--NS575
    putfmt("Check ADC: 1--W1; 2--W2; Trig--Trigger\n    putfmt("FOR 10V -> 1msec\n    putfmt("Input delay in ns for simultaneous pulses\n    getfmt("%i\n",nsec);
    putfmt("read in: delay = %i\n",nsec);
    while(nsec>0)
    {
      ns = nsec;
      putvolt(0,(int)(2047.0 - 204.8*(nsec/100.0)));
      putfmt("Input delay in ns for simultaneous pulses\n      getfmt("%i\n",nsec);
      putfmt("read in: delay = %i\n",nsec);
    }
  }
}
v = putvolt(0, VOLTGET);
iv = (int)(2047.0 - 204.80ns/I00.0);
putfmt("No. been send to CHANNEL 'A' = \%i\n", iv);
putfmt("CHANNEL 'A' OUTPUT = \%i\n", v);
putfmt("CHANNEL 'A' OUTPUT = \%9.4f\n", (10.0 - (float)v/204.8));
putfmt("Input scan range in ns\n");
getfmt("\%i\n", &range);
putfmt("read in: range = \%i\n", range);
putfmt("Input delay increment in ns\n");
getfmt("\%f\n", &delta);
putfmt("read in: delta = \%f\n", delta);
putfmt("How many SECONDS between the increments?\n");
getfmt("\%i\n", &s);
shot = s86;
putfmt("shot=\%i\n", shot);
rise = (int)(range/delta);
nsn = (int)(ns/delta);

/\ START 0/
start:
putvolt(1, 2047);
putvolt(2, 2047);
putvolt(0, (int)(2047.0 - 204.80(ns/100.0)));
putfmt("What is the name of file to record the POWER(W1\*W2)?\n");
getfmt("\%p\n", filnam);
if(!fcreate(&fio, filnam, 1))
{
    putfmt("error: can't open \%p\n", filnam);
    return;
}

/\ GET ZERO 0/
parout('B', 8, 1);
parout('B', 9, 1);
putfmt("Are you ready to get zero?\n");
getfmt("\n");
gettrg();
getzero(1);
getzero(2);
parout('B', 8, 0);
parout('B', 9, 0);

/\ START SCAN 0/
putfmt("Hit return key to start scan\n");
getfmt("\n");
putfmt("\%p\n\n", bell);
putvolt(2, 1023);
for(k=0; k<=200; k++)
{
    j=0;

...
Figure 32 -- Continued

```c
putvolt(2,2024);
putvolt(1,1023); /* TTL SIGNAL TO START NS575 */
n=0;
for(i=nsn;i<=nsn+range;i++)
{
    wx = 0;
    wy = 0;
    n=n+1;
    putfmt("DATA No. = %d\n",n);
    putvolt(0,(int)(2047.0 - 204.8*(float)(i*delta)/100.0));
    for(j=1;j<=shot;j++)
    {
      gettrg();
      a = getvolt(1)/10;
      b = getvolt(2)/10;
      wx = wx + a;
      wy = wy + b;
    }
    putvolt(2,1023);
    for(k=0;k<=200;k++)
    {
      j=0;
    }
    putvolt(2,2024);
    z[n] = (long)(float)((wx/shot)*(wy/shot));
    putfmt("LASER'S POWER = %f\n",z[n]);
}
putvolt(1,2047); /* INIT. TTL SIGNAL */
nsec = (int)(delta*(i-1-nsn));
putfmt("Scan is finished. SCAN RANGE = %i nsec.\n",nsec);
putfmt("Initial DELAY = %i nsec.\n",ns);
for(j=1;j<=n;j++)
{
    putfmt("z[%i]=%f\n",j,z[j]);
}

/* READ DATA TO DISK */
j = n;
putf(&fio,"\n");
for(k = 0;k <= (j/8+1); k++)
{
    putf(&fio,"%+06041 %+06061 %+06061 %+06061 %+06061
%+06061 %+06061 %+06061 %+06061 \n",long(8*8),z[8*k+0],
    z[8*k+1],z[8*k+2],z[8*k+3],z[8*k+4],z[8*k+5],z[8*k+6],
    z[8*k+7]);
}
fclose(&fio);
```
Figure 32 — Continued

/* MAKE OTHER RUN ? */

if (c[0] == '1') {
    putfmt("DO YOU WANT TO RUN AGAIN WITH SAME SETTING? Y/N\n");
    getfmt("%p\n", c);
    if (c[0] == 'Y' || c[0] == 'y') goto start;
    putfmt("\n");
}
}
Figure 33. Program to synchronize stepper motor and NS575 digital signal analyzer

```c
#include <std.h>
#include <rt11.h>
#include "ad.c"
#include "da.c"
#include "stp.c"
#include "lto.c"
#include "mini.h"

main()
{
    int nodd,i,step,steps,m;
    long ticks;
    long width;
    char bell[2];
    char c[2];
    char star,fhk,reset,set,end;
    float delta;
    int rtn;

    bell[0] = 07;
    bell[1] = 0;
    parinit();
    getinit();
    putinit();

    /\ START \/
    goto set;
    reset:
    putfmt("DO YOU REALLY WANT TO RUN AGAIN? Y/N
n");
    getfmt("%p\n",c);
    if(c[0] == 'Y' || c[0] == 'y') goto set;
    if(c[0] == 'N' || c[0] == 'n') goto end;

    /\ SET INITIAL CONDITION \/
    set:
    putfmt("This program can trigger NS575 by ext., or trigger\n");
    putfmt("NS575 to start scan using internal time base.\n");
    putfmt("\n");
    putfmt("Please check the output DAC:\n");
    putfmt(" B: ext. trig. of NS575; C: MCS trig. of NS575\n");
    putfmt("\n");
    putfmt("Please input the initial setting:\n");
    putfmt("\n");
```
Figure 33 -- Continued

putfmt("How many data points do you want?\n\n");
goforma("%i\n",&nodd);
putfmt("read in: No. of data = %i\n",nodd);

/\ INPUT SIZE OF STEP /\ 
putfmt("How many steps for each data point (200step/turn)?\n\n");
goforma("%i\n",&step);
step = stepoji nodd;

/\ INPUT DELAY TIME BETWEEN DATA /\ 
putfmt("How many delay ticks between increments?\n\n");
goforma("%i\n",&ticks);
putfmt("read in: delay ticks = %i\n",ticks);
ticks = ticks - 28;

/\ START SCAN /\ 
start:
putvolt(2,2047);
putvolt(1,2047);
width=5;
putfmt("%p\n\n\n",bell);
putfmt("Hit return key to start scan\n");
goforma("\n");
putfmt("%p\n\n\n",bell);
putfmt("Scanning started!!\n");
m = 0;
putvolt(1,1023); /* TRIGGER NS575 BY EXT. */
delay((long)width);
putvolt(1,2047);
for(i=1;i<=nodd;i++)
{
    putvolt(2,1023); /* TTL SIGNAL TO TRIGGER NS575 */
delay((long)width);
    putvolt(2,2047); /* INIT. TTL SIGNAL */
delay((long)ticks);
    getcw(step); /* TURN THE MOTOR */
    m += step;
    putfmt("No. of data = %i\n",i);
    putfmt("TOTAL steps=%i, Motor Turned=%i\n",steps,m);
}

/\ TAKE THE LAST DATA POINT /\ 
putvolt(2,1023); /* TTL SIGNAL TO TRIGGER NS575 */
delay((long)width);
putvolt(2,2047); /* INIT. TTL SIGNAL */
putfmt("\n\n\n\n",bell);
putfmt("Scan is finished. Total data points =%i\n",nodd);
putfmt("\n\n\n");
putfmt("Total scan is: %i steps\n",m);
Figure 33 -- Continued

putfmt("%p\n\n", bell);

/\ RESET THE START POINT /
putfmt("How many steps do you want to go back?\n");
getfmt("%i\n", &rtn);
if(rtn == 0)
{
    goto fhk;
}
else
{
    rtn +=100;
    getcw(rtn); // REVERSE /
    getcw(100); // GET TO STARTING POINT /
}

/\ RUN THE EXPERIMENT WITH THE SAME CONDITION ?/  
fhk:
c[0] = '0';
putfmt("DO YOU WANT TO RUN AGAIN WITH SAME SETTING? Y/N\n");
getfmt("%p\n", c);
if(c[0] == 'Y' || c[0] == 'y') goto start;
if(c[0] == 'N' || c[0] == 'n') goto reset;
end: putfmt("Good luk for your experiment!?!?!?!?!?!?\n");}