Coherent laser studies of nonlinear and transient phenomena in Tb3+ activated solids
by Guokui Liu

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:
Spectral and dynamical properties of the concentrated rare earth compound LiTbF4 and the dilute isostructural compound 1%ztb3+:LiYF4 have been investigated with photon echo, spectral hole burning, and other spectroscopic methods. Coherent dephasing has been measured as a function of magnetic field, excitation frequency, excitation intensity, and temperature for the transition between 7F6 Γ2 and 5D4 Γ1 levels in both compounds. Various interaction processes responsible for the line broadening and splittings of the rare earth ions have been determined.

A possible transition from delocalized to localized states in the concentrated compound has been observed in the photon echo experiments.

When the excitation frequency was varied across the inhomogeneous line, a sharp change in dephasing rate by a factor of six was measured as expected for an Anderson transition or mobility edge. Quasiresonant interactions and exciton band dispersion processes have also been considered for interpreting the frequency-dependent dephasing.

Superhyperfine interactions (SHFS) between a Tb3+ ion and surrounding F nuclei have been studied through photon echo modulation for Tb3+:LiYF4. The theoretical coherent emission function has been derived by calculating the density matrix with a model Hamiltonian. That theory was in excellent agreement with the experiments, and both the field-dependent modulation frequencies and the SHFS parameters have been determined. Electron spin diffusion and instantaneous spectral diffusion have been observed in the dilute crystal. The echo decay time exhibited strong dependence on applied magnetic field and on the excitation intensity. These phenomena have both been interpreted as arising from the magnetic dipole-dipole interaction between Tb3+ ions.

Hyperfine spectral hole burning has been observed in 1% Tb3+:LiYF4. The hole lifetime was a function of magnetic field and reached a value of 10 minutes with an external field of 40 kG. Crystal field eigenfunctions, derived from an analysis of the observed levels, provided an excellent description of the electronic Zeeman splittings and allowed accurate calculation of the hyperfine structure. The resulting Zeeman eigenfunctions have been used to qualitatively explain the hole burning process and to calculate the field-dependent echo modulation and both field and power-dependent coherence dephasing in the dilute compound.
COHERENT LASER STUDIES OF
NONLINEAR AND TRANSIENT PHENOMENA IN
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by
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A thesis submitted in partial fulfillment
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of
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Bozeman, Montana
August 1988
APPROVAL

of a thesis submitted by

Guokui Liu

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.

August 24, 1988
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Chairperson, Graduate Committee

Approved for the Major Department

August 25, 1988
Date

Head, Major Department

Approved for the College of Graduate Studies

September 9, 1988
Date

Graduate Dean
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ABSTRACT

Spectral and dynamical properties of the concentrated rare earth compound LiTbF₄ and the dilute isostructural compound 1% Tb³⁺:LiYF₄ have been investigated with photon echo, spectral hole burning, and other spectroscopic methods. Coherent dephasing has been measured as a function of magnetic field, excitation frequency, excitation intensity, and temperature for the transition between \(^7F_{6\,\Gamma_2}\) and \(^5D_{4\,\Gamma_1}\) levels in both compounds. Various interaction processes responsible for the line broadening and splittings of the rare earth ions have been determined.

A possible transition from delocalized to localized states in the concentrated compound has been observed in the photon echo experiments. When the excitation frequency was varied across the inhomogeneous line, a sharp change in dephasing rate by a factor of six was measured as expected for an Anderson transition or mobility edge. Quasiresonant interactions and exciton band dispersion processes have also been considered for interpreting the frequency-dependent dephasing.

Superhyperfine interactions (SHFS) between a Tb³⁺ ion and surrounding F nuclei have been studied through photon echo modulation for Tb³⁺:LiYF₄. The theoretical coherent emission function has been derived by calculating the density matrix with a model Hamiltonian. That theory was in excellent agreement with the experiments, and both the field-dependent modulation frequencies and the SHFS parameters have been determined. Electron spin diffusion and instantaneous spectral diffusion have been observed in the dilute crystal. The echo decay time exhibited strong dependence on applied magnetic field and on the excitation intensity. These phenomena have both been interpreted as arising from the magnetic dipole-dipole interaction between Tb³⁺ ions.

Hyperfine spectral hole burning has been observed in 1% Tb³⁺:LiYF₄. The hole lifetime was a function of magnetic field and reached a value of 10 minutes with an external field of 40 kG. Crystal field eigenfunctions, derived from an analysis of the observed levels, provided an excellent description of the electronic Zeeman splittings and allowed accurate calculation of the hyperfine structure. The resulting Zeeman eigenfunctions have been used to qualitatively explain the hole burning process and to calculate the field-dependent echo modulation and both field and power-dependent coherence dephasing in the dilute compound.
CHAPTER 1

INTRODUCTION

In solid state physics, various interaction mechanisms responsible for energy transfer have received much attention, from both theoretical and experimental perspectives.\textsuperscript{1-17} The basic ideas are relevant to rare earth compounds,\textsuperscript{10-15} transition metal compounds,\textsuperscript{4-7,16-17} organic molecular crystals,\textsuperscript{8,9} and biological systems.

The efficiency of energy transfer in solids may not only be determined by the transfer mechanism but may also be strongly affected by whether the state of the donors (excited ions or molecules) is delocalized or localized. That question involves a subtle interplay between energy transfer coupling and inhomogeneous broadening in real systems. The concept of an Anderson transition\textsuperscript{1} between the localized states and delocalized states and its extension in terms of mobility edges\textsuperscript{2} within an inhomogeneous line have attracted wide attention for understanding energy transfer processes in such disordered systems. Recently, nonlinear spectroscopic methods such as time-resolved fluorescence line narrowing,\textsuperscript{3-5} transient gratings,\textsuperscript{16-17} and photon echoes\textsuperscript{6} have been used for determining energy transfer mechanisms and searching for Anderson transitions or mobility edges in ruby and molecular crystals. However, no unambiguous demonstration of an Anderson transition or mobility edge has
been found yet. The Anderson transition has thus become a very controversial topic for both theoreticians and experimentalists.

In rare earth compounds, energy transfer processes and ion-ion interaction mechanisms have been studied for some time. Energy transfer processes in Gd(OH)$_3$ and GdCl$_3$ have been observed by Meltzer and Moos$^{14}$ through the absorption line shapes of magnon-exciton transitions. By measuring the line shapes of band-to-band exciton fluorescence, Cone and Meltzer$^{11}$ have determined the energy transfer mechanisms in Tb(OH)$_3$. Both studies indicated that short range exchange interactions played a major role in energy dispersion in some exciton bands of those compounds. For another Tb$^{3+}$ compound TbF$_3$, energy transfer processes have been studied via trapping dynamics, and again short range interactions were important.

Evidence of energy transfer and short-range coupling mechanisms thus suggests that concentrated Tb$^{3+}$ compounds may be potential systems for finding an Anderson transition. For that reason, emphasis has been placed on Tb$^{3+}$ compounds in this thesis.

In low concentration rare earth compounds, all the excited states are localized, since short-range coupling and energy transfer processes are inhibited. Therefore, such a system is ideal for studies of crystal field splittings, local field perturbations, and the effects of long-range coupling mechanisms such as dipole-dipole interactions on the dynamic properties of an isolated rare earth ion. Results from those studies are interesting on their own merit and also provide a detailed basis for analyzing the results from the concentrated systems. Indeed, they are the first optical coherent transient and holeburning results reported for any Tb$^{3+}$ compound.
With the goal of studying the range of phenomena described above, spectral and dynamical properties of the concentrated (stoichiometric) crystalline rare earth compound LiTbF$_4$ and the dilute isostructural compound 1%Tb$^{3+}$:LiYF$_4$ have been investigated with photon echo, spectral hole burning, and other spectroscopic methods. Coherent optical dephasing has been measured as a function of magnetic field, excitation frequency, excitation intensity, and temperature for the transition between the ground state $^7F_6$ $^2T_2$ and excited state $^5D_4$ $^1T_1$ in both compounds. Various interaction processes responsible for the homogeneous line broadening and static line splittings of the rare earth ions have been determined.

A possible transition from delocalized to localized states in the concentrated compound has been observed in the photon echo experiments. When the excitation frequency was varied from the low energy side to the center of the inhomogeneous line, a sharp change in dephasing rate by a factor of six was measured as expected for an Anderson transition or mobility edge. Quasiresonant interactions and exciton band dispersion processes have also been considered for interpreting the frequency-dependent dephasing. Exchange coupling between neighboring Tb$^{3+}$ ions was alternatively demonstrated by measuring the exchange splittings of the absorption from the upper Zeeman component of the ground state in this concentrated compound.

Superhyperfine interactions (SHFS) between a Tb$^{3+}$ ion and surrounding F$^-$ nuclei have been studied through photon echo modulation for the dilute compound. The theoretical coherent emission function has been derived by calculating the density matrix with a model Hamiltonian for the SHFS. That theory was in excellent agreement with the
experiments, and both the field-dependent modulation frequencies and the SHFS parameters have been determined via regression analysis.

Electron spin diffusion and instantaneous spectral diffusion have been observed in the photon echo experiments on the dilute crystal. The echo decay time exhibited strong dependence on applied magnetic field and on the excitation intensity of the second laser pulse. These phenomena have both been interpreted as arising from the magnetic dipole-dipole interaction between Tb$^{3+}$ ions. Dephasing is caused by the random change in the dipolar coupling between an echo ion and surrounding ions which occurs when the surrounding ions are either optically excited or flipped to the upper Zeeman component of the ground state. Long-lived stimulated photon echoes have been observed in this dilute compound. A population grating within the ground state hyperfine levels could be easily produced by two subsequent pulses, so that stimulated echoes could be read out at any time during the persistence of the population grating.

Spectral hole burning via optical pumping of ground state hyperfine level populations has been observed in 1% Tb$^{3+}$:LiYF$_4$. The hole lifetime increased with applied magnetic field and reached a value of 10 minutes with an external field of 40 kG. Crystal field eigenfunctions, derived from an analysis of the observed levels, provided an excellent description of the electronic Zeeman splittings of the $^5D_4 \Gamma_1$ and $\Gamma_{3,4}$ and $^7F_6 \Gamma_2$ levels and allowed accurate calculation of the magnetic hyperfine structure. The resulting Zeeman eigenfunctions have been used to qualitatively explain the hole burning process and to calculate the field-dependent echo modulation and both field and power-dependent coherence dephasing in the dilute compound.
Spectroscopic Methods

With our emphasis on nonlinear and transient optical phenomena, the spectroscopic methods are an important part to be presented in this thesis. Before describing in detail the experimental and theoretical analyses, a brief introduction of the various spectroscopic techniques used in this work will be given along with some previous applications to rare earth compounds.

Conventional Spectroscopy

The classical spectroscopy of rare earth ions, in which the position and intensity of the lines are of fundamental interest, has been intensively studied in the last three decades.\textsuperscript{18-22} In trivalent rare-earth compounds, the rare earth ions have a unique configuration of $4f^n 5s^2 5p^6$. The unpaired 4f electrons are in the optically active states, which are far below the valence band. In a free rare earth ion, the energy level structure of the $4f^n$ electrons generally consists of degenerate $J$-multiplets due to the electron-electron repulsion and spin-orbit interaction. Since the 4f electrons are shielded from the crystalline environment by the outer 5s and 5p electrons which form two filled electronic shells with large radial extension, the crystal environment has only a moderate perturbation effect on the free rare-earth ion energy levels. This perturbation splits all or a part of the $(2J+1)$-degenerate states of the free ion. The solid state spectroscopic properties of rare earth compounds, such as sharp optical line widths, can be understood from a consideration of the weak
crystal field. In turn, the wave functions of the free ion constitute a
good zero order approximation for description of solid state properties.
This is why rare earth ions are such a useful probe in solids, and why
detailed studies of the interactions between the rare earth ions and their
environment can be carried out.

As an initial step in understanding the spectral structures and the
dynamical characteristics of the systems which will be reported in this
thesis, an analysis of the crystal-field splittings of the free-ion energy
levels of trivalent terbium ions in a single crystal of lithium yttrium
fluoride, Tb³⁺:LiYF₄, was carried out. That work, which will be presented
in Chapter 2, was based on a semi-empirical method developed by Judd, Wybourne, Judd et al, Crosswhite et al, and Carnall et al. With
this method, various interactions operating within the 4fⁿ-configuration
and the crystal-field parameters can be identified by reproducing the
observed spectral structure. The crystal field eigenfunctions resulting
from this analysis provided a fundamental base for further studies of both
spectral characteristics and dynamical behavior of the Tb³⁺ ions in the
crystal. First of all, the crystal field eigenfunctions were used to
calculate the electronic Zeeman interaction and the magnetic hyperfine
splittings for the energy levels of the ⁷F₆ and ⁵D₄ multiplets. Then
rediagonalization of the crystal-field, Zeeman, and hyperfine interaction
Hamiltonian yielded a new set of eigenfunctions for a complete
representation of individual Tb³⁺ ions in the presence of an external
magnetic field. This has enabled an extensive understanding of the ion—
ion, and the ion—environment interactions. Using the eigenfunctions or
the calculated expectation values of dynamical operators, various dynamical
properties probed by photon echoes, such as instantaneous diffusion, electron spin diffusion, and superhyperfine interactions, can be quantitatively described. This also provided a qualitative description of the mechanisms and the efficiency for spectral holeburning processes. All of these phenomena will be discussed in this thesis.

**Nonlinear Laser Spectroscopy**

In principle, the width of a spectral line yields information on the dephasing dynamics of the transition. Unfortunately, the spectral line shapes of electronic transitions in rare earth solids usually are determined not only by the ion-ion and ion-lattice interactions, but also by unavoidable crystal strains which may dominate the observed linewidth at low temperature. In spectroscopy, such physically different contributions to the spectral linewidth are classified into two categories: homogeneous line width and inhomogeneous line width. The homogeneous broadening of a spectral line arises from dynamical perturbations on the optical transition frequency due for example to lattice phonons or fluctuation of local magnetic fields. The inhomogeneous contribution can arise from static lattice strains or crystal defects. In rare earth crystals at low temperature, the inhomogeneous contribution is comparable to the homogeneous broadening for upper states in a J-multiplet but usually completely dominates the homogeneous linewidth of the lowest levels in a J-multiplet.

The existence of undesired effects such as inhomogeneous broadening obscures the dynamical information carried by the homogeneous dephasing processes and also masks spectral structures such as hyperfine and
superhyperfine splittings. Since the invention of lasers, nonlinear spectroscopy has developed into a significant subfield of physics.\textsuperscript{27-31} In solid state physics, its high resolution makes it possible to measure fine energy structures such as hyperfine and superhyperfine splittings in the frequency scale of kHz—MHz.\textsuperscript{29,30} The scale of resolution is usually limited to GHz in conventional spectroscopy by inhomogeneous broadening due to lattice strain and defects in solids. After the elimination of inhomogeneous broadening, the line width of an optical transition in a solid is determined by intrinsic interactions and fluctuations of the environment known as homogeneous broadening. Measurement of the homogeneous line width of an optical transition directly yields information about the dynamics of a physical system. Furthermore, very interesting nonlinear phenomena such as photon echoes\textsuperscript{32,33} and free induction decay\textsuperscript{34} have been exploited in the time domain. This branch of transient nonlinear spectroscopy has proven to be very powerful in studies of coherence dephasing, excitation transfer, and other fast processes.\textsuperscript{27-31} Various nonlinear spectroscopic methods developed with the application of tunable dye lasers have provided possibilities for increasing spectral resolution and extracting information which is obscured by the inhomogeneous broadening. For this purpose, time-domain photon echoes and frequency-domain spectral holeburning are the two major nonlinear spectroscopic methods used in this work.

Coherent Transient Spectroscopy

------ Photon Echoes

Since the pioneering work by Hahn\textsuperscript{35} on the discovery of spin
echoes and by Torrey\textsuperscript{36} on the transient nutation effect, coherent transient phenomena in electronic and nuclear spin dynamics have been intensively studied in radio-frequency and microwave spectroscopy. By measuring the decay characteristics of coherent emission, various spin-dephasing mechanisms could be examined.\textsuperscript{37-39}

It became possible, after the invention of the laser, that coherent transient spectroscopy could be introduced to the optical region.\textsuperscript{40,32,34} This branch of nonlinear laser spectroscopy has provided unique ways for exploring dynamical interactions in optically excited atoms, molecules, and solids.\textsuperscript{26-31,40} From a physical point of view, optical electric-dipole transitions behave in the same way as the magnetic-dipole transition of spin systems. In either case, a collection of two-level quantum systems can be prepared coherently in superposition states in which all dipoles (electronic or magnetic) are in phase with each other so that they radiate coherently. This was first proved by Dicke.\textsuperscript{41}

The equivalence of magnetic and electric dipole transitions was further shown by Feyman et al.\textsuperscript{42} who introduced a generalized treatment applicable to optical coherent transients. The dynamical response of any two-level system to a resonant excitation obeys a Bloch-type equation of motion\textsuperscript{43} the same as a magnetic spin-1/2 system does. This equation of motion is just the vector form of the Schrödinger equation.\textsuperscript{42} Therefore, the dynamics of an optical electric-dipole transition can be described in much the same way as those of a magnetic-dipole transition. This was not clear before the work of Dicke and Feyman et al. because in the case of electric dipole transitions the precession of the Bloch vectors takes place in an abstract space rather than in real space.
Photon echoes are the optical analog of the spin echoes in magnetic resonance. They were predicted and first observed in ruby by Hartmann et al.\textsuperscript{32,33} Since that time, photon echoes have been widely applied to studies of the coherent decay of optical transitions and are still the subject of active experimental and theoretical investigations.\textsuperscript{44-49}

In the photon echo process, two short pulses of coherent light from one or two independent lasers separated by a time delay $\tau$ are directed onto a sample. The first pulse creates a superradiant state which involves the coherent superposition of the ground and the excited state wavefunctions of the echo ions. In the superradiant state, there is a macroscopic oscillating dipole which is capable of emitting coherent radiation and which rapidly decays as the ions fan out of phase in the superradiant state due to the inhomogeneous distribution of their resonance frequencies. The decay time is given by the inverse of the inhomogeneous line width or the laser line width, whichever is narrower. The second pulse has the effect of reversing the sign of the accumulated phase for each given ion, so that the net phase shift is cancelled after an additional precessing time $\tau$. This rephasing process leads to an additional burst of coherent radiation. This coherent radiation burst is called a photon echo. Inhomogeneous broadening effects are removed by the photon echo pulse sequence, and the decay of the photon echo amplitude or intensity reflects only homogeneous relaxation due to dynamical interactions.\textsuperscript{28,29} A description of coherent emission theory and the formation of photon echoes is given in Chapter 3; the experimental methods are described in Chapter 4.

Since the photon echo technique can measure homogeneous line
widths in the presence of inhomogeneous broadening, it provides a powerful tool for studying the dynamical interactions of rare earth ions in solids. At liquid helium temperatures, thermally induced phonon contributions are often negligible. The dephasing in rare earth impurity compounds can be dominated by local perturbations affecting the rare earth ions. These perturbations include fluctuating magnetic fields due to magnetic dipole interactions with both ligand nuclear spins and neighboring electronic spins. Chapter 5 is devoted to discussion of these dephasing mechanisms along with the experimental results from the 1%Tb³⁺:LiYF₄ crystal.

The intrinsic ion-ion interactions can dominate homogeneous dephasing and create many new phenomena as the concentration of optically active ions is increased. In rare earth solids, various ion-ion interaction mechanisms and their spectroscopic effects have recently been reviewed by Cone and Meltzer. In addition to the long range coupling mechanism of dipole-dipole interactions, electric multipolar coupling and electronic superexchange coupling between neighboring rare earth ions can also significantly contribute to the coherence dephasing. These interionic interactions may also affect the nature of the excited states of the rare earth ions leading to optical excitation transfer and diffusion or exciton band effects in the strong coupling limit.

Since the photon echo decay is so sensitive to the nature of the excited state dynamics, it is possible to learn the nature of the energy transfer processes from photon echo experiments. The Anderson transition is a theoretical model for describing the transition from localized to delocalized electronic energy states. Great efforts have been made in
the last two decades to experimentally search for the Anderson transition in optical resonant transitions. There is still no clear evidence to prove if the Anderson transition exists.\textsuperscript{3-17}

The first photon echo measurement of coherent dephasing in a stoichiometric material was done by Shelby and Macfarlane on EuP\textsubscript{5}O\textsubscript{15}.\textsuperscript{50} The dephasing time was found to depend on the excitation frequency which was varied across the inhomogeneous line. This was interpreted as evidence for delocalization of the excitation due to energy transfer processes. This result was later fitted by Skinner et al\textsuperscript{49} with a theoretical model of quasiresonant interactions. That fit led to the conclusions that the frequency-dependent dephasing is due to a microscopic electric dipole-dipole coupling between neighboring resonant ions and that there is no energy-site correlation between the optically activated ions. Such a correlation is required in the Anderson model.

In the concentrated compound LiTbF\textsubscript{4}, a strong frequency-dependence of the echo decay has been observed. The decay rate exhibited an abrupt change on the low energy side of the inhomogeneous line.\textsuperscript{51} Chapter 6 is devoted to analysis of the experimental results along with consideration of the Anderson model and the Skinner model. Related measurements on the dilute compound 1\%Tb\textsuperscript{3+}:LiYF\textsubscript{4} are described in Chapter 5.

In addition to measuring the coherence dephasing or homogeneous line width of an optical transition via amplitude decay, a photon echo signal may carry another type of spectroscopic information via modulation within the decay envelope. Modulation phenomena are observed in echo decay when the ground and excited states of a two-level system are split into sublevels by hyperfine or superhyperfine interactions. Much of the
earlier experimental and theoretical work on photon echoes in solids was done in this area.\textsuperscript{52-60}

If the sublevel splittings in a quasi-two-level system are less than the Fourier width of the excitation pulses, all substates in the system can be excited or occupied. A quantum interference can occur between coherences excited on two transitions which share a common level.\textsuperscript{55} As a result, an echo decay spectrum exhibits beats at frequencies determined by the ground and the excited state energy splittings and their sums and differences. These modulation frequencies can be obtained by a Fourier transform of the echo decay spectra in the time domain.

Since echo modulation is a result of quantum interference, it is sensitive to both the eigenfunctions and the eigenfrequencies of the interaction Hamiltonian. Therefore, the deconvolution of echo modulation can provide a very useful tool for not only determining the energy splittings but also for testing the interaction Hamiltonian. By a regression analysis of the observed echo data, the interaction Hamiltonian can be experimentally determined. This sensitivity to phase is another advantage of photon echo spectroscopy over conventional spectroscopic techniques which only measure energy splittings and which may not be sufficient for correctly testing the model Hamiltonian.\textsuperscript{57}

A strong field-dependent photon echo modulation effect was observed in the dilute compound Tb\textsuperscript{3+}:LiYF\textsubscript{4}. The experimental results and a theoretical calculation with regression analysis will be presented in Chapter 7.

In the stimulated, or three pulse photon echo experiment, the second pulse puts ions with in-phase coherence into the exited state, and the
ions shift back into the ground state with an accumulation of \( \pi \) phase. This accumulated phase information is then stored in the form of a population difference which is called a population grating in the ground state. This coherence can be read out by the third pulse until the population difference disappears.\(^{44,47,48}\) Therefore, the stimulated photon echo can in principle be used in the investigation of slow spectral diffusion.\(^{30,55}\) Furthermore, if the excited state population can relax to some long lived population reservoir such as metastable electronic states or hyperfine levels, an echo can be stimulated by a readout pulse so long as the population difference in the ground state persists. This could open a new technique for optical information storage in the future. In Chapter 5, some initial results of the stimulated photon echoes from the Tb\(^{3+}\):LiYF\(_4\) will be discussed.

### Spectral Holeburning

Spectral holeburning is a very useful nonlinear spectroscopic technique to measure line splitting as well as line width in the presence of inhomogeneous broadening.\(^{30,31,61-65}\) The nonlinear spectroscopic information appears in the form of line structures obtained by selectively exciting a segment of the inhomogeneous line and then sweeping a probe laser across the inhomogeneous line. This was first demonstrated by Szabo in studies of ruby.\(^{61}\) The holeburning process becomes dramatic if a long-lived population reservoir can be used, such as a metastable excited electronic state or hyperfine levels. After the population is optically pumped from the ground state to a long-lived reservoir, narrow holes remain in the inhomogeneous line and can persist for a long time which is
determined by spin relaxation if the reservoir is the hyperfine levels. Spectral holeburning in rare earth insulators has proved to be very useful for measuring the hyperfine and superhyperfine structure of both ground and excited states. Its resolution is limited by spectral diffusion or by the laser linewidth. Therefore, holeburning spectroscopy can also be an effective method to study spectral diffusion and relaxation processes in rare earth doped materials.

Hyperfine spectral holeburning has been carried out on the dilute crystal Tb$^{3+}$:LiYF$_4$. The magnetic field-dependent holeburning efficiency and hole decay time seem to be explained by the Zeeman and hyperfine studies. Detailed analyses of the holeburning process in the dilute compound are given in Chapter 8.

The experimental setups and various transient signal detection techniques used in the photon echo and hole burning experiments are described in Chapter 4.
CHAPTER 2

ENERGY LEVEL STRUCTURE OF Tb$^{3+}$:LiYF$_4$

Free Ion

Rare earth (RE) ions in solids have remarkable spectral features due to their sharp $4f^n \rightarrow 4f^n$ transitions which have widths less than 1 cm$^{-1}$. This has enabled detailed studies of the nature of the interactions between RE ions and their environment. The sharpness of the spectral lines is due to the fact that the RE ions, which are usually trivalent, have the special electronic configuration: $4f^n5s^25p^6$. The 4f electrons are shielded from the crystalline environment by the filled outer 5s and 5p shells. The ligand fields and the lattice phonons have only weak perturbation effects on the atomic energy levels, so that the spectra are still atomic-like. Therefore, the study of free ion energy level structure is of fundamental importance for understanding the energy level structure and the dynamics of RE ions in solids. Extensive work has been done in this area.$^{18-21}$

Since all other spherical electron shells have the same effect on all the terms of a $4f^n$ configuration, the energy levels of a free RE ion are usually calculated by considering only the interactions between the 4f electrons themselves. The interaction energies of the Coulomb repulsion and the spin-orbit interaction are of the same order of magnitude, so
intermediate coupling also has to be accounted for in the calculation of the energy structures. In addition, there are some perturbation terms such as configuration interactions and many-body interactions that must be included to calculate accurate energy levels.

The basic structure of the free ion energy levels of all RE elements has been obtained in this way up to an energy of 40,000 cm\(^{-1}\). Figure 1 shows a very useful energy level diagram prepared by Dieke and Crosswhite,\(^{67}\) and Carnall et al.\(^{21}\)

The general procedure used to evaluate the energy levels of RE ions involves a semi-empirical approach in which free-ion interaction parameters are fit to some actually observed energy levels. The free ion Hamiltonian \(H_f\) includes\(^{24,68}\) the usual electrostatic (\(F^k\)), spin-orbit (\(\zeta_{4f}\)), and configuration interaction (\(\alpha, \beta, \gamma\)) terms plus spin-spin and spin-other-orbit interactions (\(M^k\)), two-body electrostatically correlated magnetic interactions (\(P^k\)), and three-body electrostatic terms (\(T^i\)):

\[
H_f = \sum_{k=0,2,4,6} F^k f_k + \sum_{i=1,n} \zeta_{4f} I^i s_i + \alpha L(L+1) + \beta G(G_2) + \gamma F(G_2) \\
+ \sum_{k=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k + \sum_{i=2,3,4,6,7,8} T^i t_i \tag{2.1}
\]

In principle, all the parameters can be freely varied in the fitting program, but usually only the parameters in the first line of Eq. (2.1), which are the Slater parameters \(F^k\), the spin-orbit parameters \(\zeta\), and the three configuration interaction parameters (\(\alpha, \beta, \gamma\)), are freely varied, and the parameters in the second line of Eq. (2.1) are usually not varied until a large number of levels are fitted.
Fig. 1. Energy level diagrams for RE$^{3+}$ ions in crystals (Ref. 21 and 67).
This procedure also provides good free ion wave functions as linear combinations of Russell-Saunders representation states. These wave functions can then be used to describe the energy splittings in crystals and other properties such as the Zeeman effect and hyperfine structures. In the following part of this chapter, the calculated wave functions of the Tb$^{3+}$ (4f$^8$) ion in the LiYF$_4$ crystal field are used as the zeroth order approximation for calculating the Zeeman effect and hyperfine structures.

Crystal Field Analysis

For 4f ions in a crystal, as discussed above, the ion-lattice coupling is much weaker than the spin-orbit interaction. The energy levels are calculated by diagonalizing the free ion and crystal field Hamiltonian in an LS basis. The (2J+1)-degenerate atomic energy levels of each J-multiplet will split corresponding to the crystal site symmetry. Due to the crystal field perturbation, J is not exactly a good quantum number. Slight J-mixing results from coupling by the crystal field.

A crystal field analysis of the observed energy levels has been used to determine the field-dependent eigenvalues and eigenfunctions of all $^7F_J$ states and $^5D_J$ states. Details are given below. The energy levels of concentrated LiTbF$_4$ are qualitatively the same and are discussed in Chapter 6.

Symmetry and Selection Rules

LiYF$_4$ crystallizes in a tetragonal scheelite structure which is shown in Fig. 2. The compound Tb$^{3+}$:LiYF$_4$ is constructed by substituting Tb$^{3+}$
ions for $Y^{3+}$ ions at sites having $S_4$ symmetry. The $(2J+1)$-degenerate free ion energy levels of each $J$-multiplet are split into singlets and doublets which are characterized by the irreducible representations $\Gamma_1$, $\Gamma_2$, $\Gamma_3$, and $\Gamma_4$. The $\Gamma_1$ and $\Gamma_2$ levels are singlets. The $\Gamma_3$ and $\Gamma_4$ representations are related by time-reversal symmetry, so their eigenvalues are degenerate. In the following they will be labeled $\Gamma_{3,4}$. The degenerate $\Gamma_{3,4}$ levels split into separate $\Gamma_3$ and $\Gamma_4$ levels in the concentrated compound at low temperature due to ferromagnetism which occurs below the critical temperature $T_c = 2.87$ K. The numbers of levels for each $J$ multiplet are listed in Table 1.

Table 1. Occurrence of each irreducible representation in the crystal-field splittings of $J$ multiplets in $S_4$ symmetry.

<table>
<thead>
<tr>
<th>$J$</th>
<th>$\Gamma_1$</th>
<th>$\Gamma_2$</th>
<th>$\Gamma_{3,4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>
Fig. 2. LiYF$_4$ structure. The six nearest neighbor sites of an Yttrium ion (O) are labelled by the index $i=1$ to 6. The lattice constants are $a=5.1668$ Å; $c=10.7330$ Å (Ref. 15).
In the presence of an applied electromagnetic radiation field, the two most significant terms in the interaction hamiltonian which lead to optical transitions between the \( \Gamma_1 \) levels are the electric and magnetic dipole interactions. Although the electric dipole transitions are parity forbidden within a pure single configuration, they do occur due to configuration mixing.\(^{18-20}\) In general for RE ions they are stronger than the magnetic dipole transitions. The selection rules for electric and magnetic dipole transitions in \( S_4 \) symmetry are given in Table 2.

### Table 2. Selection rules in \( S_4 \) symmetry.

<table>
<thead>
<tr>
<th>( \Gamma_1 )</th>
<th>( \Gamma_2 )</th>
<th>( \Gamma_{3,4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_1 )</td>
<td>( M_\sigma )</td>
<td>( E_\pi )</td>
</tr>
<tr>
<td>( \Gamma_2 )</td>
<td>( E_\pi )</td>
<td>( M_\sigma )</td>
</tr>
<tr>
<td>( \Gamma_{3,4} )</td>
<td>( E_\sigma M_\pi )</td>
<td>( E_\sigma M_\pi )</td>
</tr>
</tbody>
</table>

#### Two Important Levels

The dynamical experiments, photon echoes and hole burning, were carried out for the ground state \( \Gamma_2 \) to the excited state \( \Gamma_1 \) transition. Therefore, the study of the energy structures of these two levels is of fundamental importance for understanding the observed dynamical properties of \( \text{Tb}^{3+} \) ions. Figure 3 shows schematically the
energy level splittings of Tb$^{3+}$:LiYF$_4$ due to the crystal field plus an externally applied magnetic field parallel to the uniaxial c axis. That was the field geometry used throughout the experiments.

Laursen and Holmes$^{70}$ have studied the ground state hyperfine splittings for Tb$^{3+}$:LiYF$_4$ by electron spin resonance. The electronic ground state in zero magnetic field consists of two $\Gamma_2$ singlets separated by 0.9 cm$^{-1}$. For each $\Gamma_2$ state, the four hyperfine sublevels (nuclear spin $I = 3/2$) are grouped in two two-fold degenerate pairs. In the presence of an external magnetic field, however, the two electronic levels are admixed and rapidly split, becoming asymptotically $J_z = \pm 6$ states. Each then has four equally spaced hyperfine sublevels with 0.1 cm$^{-1}$ separation.

The hyperfine level splitting is larger than the laser line width (= 0.05 cm$^{-1}$), so optical pumping of individual hyperfine sublevels is possible. (Small effects due to nuclear quadrupole coupling$^{18,23,37}$ presumably modify this structure to a negligible degree for our present purposes.) The next electronic level is at over 100 cm$^{-1}$, so it has no effect on the ground state properties.

The lowest $5D_4$ level is the $\Gamma_1$ singlet at 20,553.5 cm$^{-1}$. As we shall see below, the Zeeman effect on this level is determined entirely by the field dependent coupling to another $5D_4 \Gamma_1$ level which is 14.4 cm$^{-1}$ higher in energy. The magnetic hyperfine splittings for the $5D_4 \Gamma_1$ levels are thus significantly smaller than those for the ground state. The complete $5D_4$ excited state level structure will be described in the following section.

**Observed Energy Levels**

To determine the crystal field splittings and identify the $7F_{0-6}$ and $5D_4$ energy levels, polarized absorption and excitation experiments were
Fig. 3. Energy level structure of Tb$^{3+}$:LiYF$_4$. 
made. The π and σ polarized fluorescence lines from the lowest Γ₁ level of $^{5}D_{4}$ to the Γ₂ and Γ₃,₄ levels of the $^{7}F_{0}$ to $^{7}F_{6}$ multiplets are all in the visible spectral region. Those levels have been identified and the Zeeman effect of the Γ₃,₄ levels has also been studied.

In an $S_{4}$ symmetry crystal field, the $^{5}D_{4}$ energy levels of the Tb$^{3+}$ ion are split into three Γ₁ singlets, two Γ₂ singlets, and two Γ₃,₄ doublets. In zero magnetic field, the absorption spectra gave three π polarized transitions to the Γ₁ states and two σ polarized transitions to the Γ₃,₄ states as expected for electric dipole transitions. The resulting energy levels are listed in Table 3.

Thermally populated transitions from the Γ₂ level at 0.9 cm⁻¹ at zero magnetic field were well resolved and confirmed its location as inferred earlier from electron spin resonance experiments.⁷⁰

The energy levels of $^{7}F_{6}$ to $^{7}F_{0}$ have been detected by fluorescence spectra at a temperature of 1.3 K. The observed fluorescence emissions from the lowest Γ₁ level of $^{5}D_{4}$ to the Γ₂ and Γ₃,₄ levels of the $^{7}F_{j}$ multiplets were not polarized. Each line had both π and σ components. This could be due to the emission of traps since a change in relative intensity of the two components was observed in time resolved fluorescence. The components which were not expected by the selection rules decreased as the delay time between the excitation pulse and signal gate was reduced. Further investigation of the trap emission may yield information about excitation transfer from donor ions to trap ions¹³ which is important for understanding aspects of the excited state dynamics as well as for determining the intrinsic energy levels.

In order to identify the $^{7}F_{j}$ energy levels, Zeeman experiments were
made. The fluorescence lines were identified assuming that the split lines are $\Gamma_{3,4}$'s and the non-split lines are $\Gamma_2$'s. The relevant energy levels are listed in Table 4. Figure 4 shows the fluorescence lines and the Zeeman splittings of the lower levels of the $^7F_5$ multiplet. All the $\Gamma_{3,4}$ lines are much stronger than the $\Gamma_2$ lines. The observed fluorescence lines to the highest levels in the $^7F_6$, $^7F_5$ and $^7F_4$ multiplets are strong and are thus assumed to be $\Gamma_{3,4}$ levels even though they are so broad (> 30 cm$^{-1}$) that the Zeeman splitting is obscured. These lines have side structures over an energy scale from decades to over one hundred wave numbers which probably are phonon sidebands.

Table 3. Eigenvalues and eigenfunctions of $^5D_4$ at 1.3 K. Each ket denotes the $M_J$ of a $^5D_4 M_J$ state.

<table>
<thead>
<tr>
<th>State</th>
<th>Absorption line (cm$^{-1}$)</th>
<th>Calc. Eigenvalue (cm$^{-1}$)</th>
<th>Calc. Eigenfunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>20644.8</td>
<td>$\pi$</td>
<td>20644.2</td>
</tr>
<tr>
<td>$\Gamma_{3,4}$</td>
<td>20626.5</td>
<td>$\sigma$</td>
<td>20626.1</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>20612.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\bar{\Gamma}_2$</td>
<td>20575.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>20567.9</td>
<td>$\pi$</td>
<td>20568.1</td>
</tr>
<tr>
<td>$\Gamma_{3,4}$</td>
<td>20558.8</td>
<td>$\sigma$</td>
<td>20558.7</td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>20553.5</td>
<td>$\pi$</td>
<td>20558.0</td>
</tr>
</tbody>
</table>
Fig. 4. The Zeeman splittings of the fluorescence lines of $^5D_4 \Gamma_1$ to $^7F_5 \Gamma_2$ and $^7F_5 \Gamma_3$ levels. The effective g-factors for these two strong yellow lines are 11.6 and 3.9. The line shifts to the low energy side are due to the shift of the excited state $^5D_4 \Gamma_1$ in the applied Zeeman field parallel to the c axis.
Another unexpected observation is that all the apparent $\Gamma_2$ levels are twins which are separated by 3.8 cm$^{-1}$. This again is presumably due to traps or to another kind of rare earth impurity ions. Further study is required to resolve the general questions of traps versus intrinsic fluorescence.

Calculations

The combined free-ion and crystal field Hamiltonian matrix was diagonalized, so both intermediate coupling and $J$-mixing effects were considered. The total Hamiltonian is then

$$H = H_f + H_{cf},$$

(2.2)

where $H_f$ is free ion Hamiltonian given in Eq.(2.1), and $H_{cf}$ is the crystal field Hamiltonian determined by the $S_4$ site symmetry. Based on previous work by Christensen$^{71}$ and others and for convenience in the calculation, the two imaginary crystal field parameters were set equal to zero. This gives $H_{cf}$ an effective $D_{2d}$ symmetry:

$$H_{cf} = B_0^2C_0^2 + B_0^4C_0^4 + B_4^4C_4^4 + B_0^6C_0^6 + B_4^6C_4^6.$$  

(2.3)

The crystal field parameters $B_0^2$, $B_0^4$, $B_4^4$, $B_0^6$, $B_4^6$ and all appropriate free ion parameters were automatically adjusted in the general calculation. The initial values of the free ion parameters which were used in the calculation are the free ion parameters for $\text{Tb}^{3+}:\text{LaF}_3$ listed in the Appendix II of Reference 21. As a first approach, the fitting procedure was carried out for $^7F_j$ and $^5D_4$ multiplets in the energy region 0 to
20,600 cm\(^{-1}\). The fit was first tried by varying the parameter \(E_{AV}\). Then the Slater parameters \(F^2, F^4, F^6\), and the spin-orbit parameter \(\zeta\) were simultaneously varied. After that step, the three parameters \(\alpha, \beta, \gamma\) for the configuration interaction were added, but those parameters were not sensitive to the energy levels of the experimentally observed multiplets. The six \(T\) parameters were not varied. The multiple spin coupling parameters \(M^k\) and two-body electrostatic parameters \(P^k\) were varied but the energy levels were not affected by those parameters. Then, the crystal field parameters were varied while the free ion parameters were held constant. Finally, both the crystal field parameters and the free ion parameters were varied simultaneously to achieve a best fit. The fitted eigenvalues of \(7F_J\) are listed in Table 4. A standard deviation of 16 cm\(^{-1}\) was obtained in this fit. The relevant free ion and crystal field parameters resulted from the fit of the \(7F_J\) and \(5D_4\) multiplets are listed in Table 5.

A second fit to only the \(5D_4\) energy levels was obtained by varying only the \(B^k_q\) parameters, and it gave much better calculated eigenvalues and eigenfunctions for those levels which are listed in Table 3. The resulting eigenfunctions are needed for calculating the Zeeman effect and hyperfine splittings which provide basic information on the spectral characteristics of those levels. The \(5D_4\) multiplet is very isolated; it is 5,000 cm\(^{-1}\) lower than the \(5D_3\) multiplet, and 14,000 cm\(^{-1}\) higher than the \(7F_0\) multiplet. The mixing of other \(J\)-multiplets is thus very small and can be ignored. Therefore, the eigenfunctions listed in Table 3 involve only the mixing of \(M_J\) components of the pure \(J = 4\) multiplet.
<table>
<thead>
<tr>
<th>$J$</th>
<th>$\Gamma$</th>
<th>$E_{\text{exp}}$ (cm$^{-1}$)</th>
<th>$E_{\text{cal}}$ (cm$^{-1}$)</th>
<th>$\Delta$ (cm$^{-1}$)</th>
<th>$g_{\text{exp}}$</th>
<th>$g_{\text{cal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
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Zeeman Effect

Since the z-component of the magnetic dipole matrix element \(<\mu_2> = 0\) for the \(\Gamma_1\) and \(\Gamma_2\) singlet states in zero field, there is no linear Zeeman effect for those levels. On the other hand, the \(\Gamma_{3,4}\) doublets are split into separate \(\Gamma_3\) and \(\Gamma_4\) levels by the linear Zeeman effect.

All seven \(^5D_4\) levels are relatively close to each other, and the field-induced coupling between those levels can be strong. Hence, the combined crystal field and Zeeman Hamiltonian was diagonalized as a function of field for each irreducible representation \(\Gamma_1\). (The \(S_4\) symmetry is not
Table 5. Free ion and crystal field parameters for Tb<sup>3+</sup>:LiYF<sub>4</sub>, (cm<sup>-1</sup>).

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changed by a parallel magnetic field.) As noted in the 5D<sub>4</sub> energy calculation, the 5D<sub>4</sub> multiplet is extremely isolated, so coupling to other manifolds is irrelevant. Within the 5D<sub>4</sub> multiplet, the matrix elements <l>\langle{\Gamma}_1|\hat{H}_z|{\Gamma}_1\rangle</l> were calculated using the zero field eigenfunctions |{\Gamma}\rangle = \sum_a(M_a)|M_a\rangle given in Table 3. Since J<sub>z</sub> transforms as \(\Gamma_1\), non-zero matrix elements occur only between the three \(\Gamma_1\) levels, the two \(\Gamma_{3,4}\) pairs, and the two \(\Gamma_2\)'s. The relevant eigenvalues are shown in Fig. 5. The calculation gave very good agreement with the experimental data at both low and high fields. The \(\Gamma_1\) levels vary quadratically at low field and asymptotically approach a linear Zeeman effect of \(M_j = \pm4\) levels at high field. The \(\Gamma_{3,4}\) splittings are quite linear at all fields, because the
Fig. 5. Observed and calculated Zeeman effect of the $^5D_4 \Gamma_1$ and $\Gamma_{3,4}$ levels. The zero-field position of the lowest $\Gamma_1$ level is $20,553.5$ cm$^{-1}$. The experimental data are from the absorption spectrum with the ground state Zeeman shift subtracted.
other $\Gamma_{3,4}$ doublet is 72 cm$^{-1}$ higher, and its admixture is small.

Since the $\Gamma_{3,4}$ levels of all $^7F_j$ multiplets are far away from each other (>70 cm$^{-1}$), the magnetic field coupling between those levels is negligible, and their Zeeman splittings are all linear. They have been measured up to 40 kG by the fluorescence spectra of the $^5D_4 \Gamma_1$ to $^7F_j \Gamma_{3,4}$ transitions. The measurements of the Zeeman splittings $\Delta(\Gamma_{3,4})$ allow determination of the effective g-factors $g'$ for these effective spin-1/2 levels by the relation

$$\Delta(\Gamma_{3,4}) = g'\mu_B H_z.$$  \hspace{1cm} (2.4)

Therefore, comparison between calculation and measurement can be made similar to that for the $^5D_4$ multiplets. For these effective spin-1/2 states

$$\Delta(\Gamma_{3,4}) = 2g_j\mu_B \langle M_j \rangle,$$ \hspace{1cm} (2.5)

where $g_j=3/2$ for both $^7F_j$ and $^5D_j$ multiplets, and $\langle M_j \rangle = \Sigma_i a_i^2 \langle M_j \rangle_i$. The effective g-factor then can be calculated by

$$g' = 3\Sigma_i a_i^2 \langle M_j \rangle_i.$$ \hspace{1cm} (2.6)

The contribution of the $^5D_4$ multiplet to the J-mixing in the $^7F_j$ multiplets is small ($a_i<0.01$). The sum $i$ is then only over the $\Gamma_{3,4}$ states of $^7F_j$ multiplets. The measured and calculated g-factors for the $\Gamma_{3,4}$ states of the $^7F_j$ multiplets are listed in Table 4. As discussed in the subsection—Observed Energy Levels, the top $\Gamma_{3,4}$ fluorescence lines of each $^7F_j$
multiplet are so broad that their Zeeman splittings are obscured.

**Hyperfine Structure**

The electron spin resonance study of Tb$^{3+}$:LiYF$_4$ by Laursen and Holmes$^{70}$ provided a complete description of the ground electronic doublet. A later study of the LiTbF$_4$ ground state by magnetic resonance$^{73}$ gave similar results for it. Both of those results are completely consistent with our crystal field analysis.

Pelletier-Allard and Pelletier$^{73}$ have reported an optical fluorescence line narrowing study of Tb$^{3+}$:LaCl$_3$ hyperfine splittings. They observed and analyzed the hyperfine splittings for the ground doublet in $^7F_6$ and for several levels in $^5D_4$. Their value of the ground state magnetic hyperfine interaction constant was in excellent agreement with that for LiYF$_4$. This is to be expected since the magnetic hyperfine interaction is a free ion effect not sensitive to the host lattice.$^{18,23,37}$

Focusing our attention on the ground state, the two slightly separated $\Gamma_2$ levels may be described by the following effective spin-1/2 Hamiltonian:

$$H_{\text{eff}} = g_{//}\mu_B H_z S_z + \Delta S_z + A S_z I_z,$$

(2.7)

where $g_{//} = 17.8$, $\Delta/\hbar = 27.98$ GHz is the gap between the two $\Gamma_2$ levels at zero field, and $A/\hbar = 6.26$ GHz ( $A = 0.209$ cm$^{-1}$ ) is the magnetic hyperfine interaction parameter. Alternatively, the interactions may be expressed in terms of $J_z$.$^{18,37,72}$ There is no perpendicular Zeeman term
for these states. The energy levels evaluated from this Hamiltonian are given by

\[ E(M_s M_l) = M_s [(g_s \mu_B H_z + A M_l)^2 + \Delta^2]^{1/2}. \]  

(2.8)

Figure 6 (a) shows the hyperfine splittings of the ground state. The four hyperfine sublevels of each electronic Zeeman component quickly split; for \( H_z \) higher than 4.5 kG, they are equally separated with the separation \( \Delta/2 = 0.1 \text{ cm}^{-1}. \)

For the \( ^5D_4 \Gamma_1 \) excited state, the hyperfine structure is different. As discussed in the section entitled Zeeman Effect, this level has no linear electronic Zeeman effect, and the next \( \Gamma_1 \) state coupled to it is \( 15 \text{ cm}^{-1} \) away. Compared to the ground state, the hyperfine splitting is a much slower function of field. Using the crystal-field eigenfunctions as unperturbed eigenfunctions, the hyperfine interactions can be treated as a perturbation using the following Hamiltonian:

\[ H_{hf} = \frac{[3I_z^2 J(J+1)] [3I_z^2 I(I+1)]}{4J(2J-1)I(2I-1)} \]

(2.9)

The first two terms represent magnetic dipole interactions between the nucleus and electrons, and the third term is the electric quadrupole interaction.

In the absence of an applied magnetic field, the diagonal elements \( <\Gamma_1 |J| \Gamma_1> \) are zero for \( i = x, y, z, \) and the first order magnetic
Fig. 6. Hyperfine splittings of (a) $^7F_6 \Gamma_2$ and (b) $^5D_4 \Gamma_1$. The electronic Zeeman shifts have been subtracted.
hyperfine interaction is zero. The only contribution to the hyperfine splitting in this case is due to the quadrupole interaction which partially removes the hyperfine degeneracy, giving two levels separated by $B$, since

$$E_{hf} = \begin{cases} 
  B/2 & \text{for } M_I = \pm 3/2 \\
  -B/2 & \text{for } M_I = \pm 1/2.
\end{cases} \quad (2.10)$$

For Tb$^{3+}$:LaCl$_3$, $B = 11 \times 10^{-3}$ cm$^{-1}$. The value for Tb$^{3+}$:LiYF$_4$ is unknown, but it would presumably be of the same general order of magnitude and would thus make only very small contributions to the level shifts.

In the presence of an external magnetic field, there is strong coupling between the first two $\Gamma_1$ states. Then, the field-dependent hyperfine splitting is mostly due to the first magnetic dipole term $A \mathbf{J}_z \mathbf{I}_z$ since the matrix elements of $A (\mathbf{J}_x \mathbf{I}_x + \mathbf{J}_y \mathbf{I}_y)$ between those states are zero. The hyperfine structure of the $\Gamma_1$ level in a magnetic field can thus be evaluated by diagonalizing an 8 X 8 matrix using the following Hamiltonian:

$$H_{hf} = g_J \mu_B H_z \mathbf{J}_z \mathbf{I}_z + A \mathbf{J}_z \mathbf{I}_z + B \frac{[3J_z^2 - J(J+1)][3I_z^2 - I(I+1)]}{4J(2J-1)I(2I-1)}.$$  \quad (2.11)

The perpendicular magnetic dipole term $A(\mathbf{J}_x \mathbf{I}_x + \mathbf{J}_y \mathbf{I}_y)$ has non-zero...
matrix elements between the $\Gamma_1$ and the $\Gamma_{3,4}$ states. Considering it as a second order perturbation, the hyperfine structures shift by

$$\delta = \frac{|<\Gamma_1|\mathbf{A} (J_{xx} + J_{yy})|\Gamma_{3,4}>|^2}{E_{\Gamma_{3,4}} - E_{\Gamma_1}} = 1.4 \frac{A^2 <I_+> <I_->}{E_{\Gamma_{3,4}} - E_{\Gamma_1}}.$$  \hspace{1cm} (2.12)

The average energy difference between $\Gamma_{3,4}$ and $\Gamma_1$ is 4 cm$^{-1}$, and $A = 16 \times 10^3$ cm$^{-1}$.$^{72}$ This gives $\delta \approx 3 \times 10^{-4}$ cm$^{-1}$ which is two orders of magnitude smaller than the first order contribution of the $AJ_{zz}$ term.

Ignoring the perpendicular magnetic hyperfine term and the electric quadrupole term, the hyperfine splittings of $^5D_4\ \Gamma_1$ versus magnetic field are shown in Fig. 6 (b). The splittings continuously increase with field up to 50 kG.
CHAPTER 3

THEORY OF COHERENT EMISSION

A collection of independent quantum radiators (ions or molecules) can radiate in two different ways. First, if there is no particular phase relation between the radiators, the radiated field will be weak ($\propto N$) and random. However, if a significant fraction of the radiators are in phase with each other, they will radiate collectively to form a coherent pulse at a rate $\propto N^2$. The property of coherence in such a radiation system is the nature of the correlations between individual radiators. Coherent emission can be observed by various techniques of non-linear spectroscopy such as free induction decay (FID)\textsuperscript{34,36,74} and photon echoes.\textsuperscript{32,33} A superradiant state, for which a large fraction of the oscillators are in phase, can be created after an excitation process in a two-level system.\textsuperscript{41} The dynamical properties of this superradiant state are described by a macroscopic oscillating electric dipole moment between the two levels of the quantum system. This macroscopic dipole moment is the ensemble average of the correlation between the oscillators. It exists until the system loses phase coherence or the population decays back to the ground state; then there is no more coherent emission.

As discussed in the Introduction, the study of the coherence decay can yield dynamical information about ion-ion interactions and ion-
environment coupling. The contribution of the dynamical interactions to the coherence decay, which is known as homogeneous dephasing, is usually obscured by inhomogeneous broadening arising from the static inhomogeneous crystal strains. Due to the existence of crystal strains and defects in rare earth solids, the decay time of the coherent emission is limited by inhomogeneous broadening. However, the dephasing due to this static inhomogeneous distribution can be removed by a particular pulse sequence so that the macroscopic dipole moment reappears after a rephasing process. In company with the reappearance of the macroscopic dipole moment, the system again radiates coherently. This coherent emission is called a photon echo. The decay of the coherent emission in the form of photon echoes is only due to the non-static or homogeneous dephasing by intrinsic interactions or fluctuation of the environment. The photon echo technique thus provides an effective way for measuring the homogeneous line width in the presence of inhomogeneous broadening and allows us to study the nature of the intrinsic interactions. In this chapter, the theories of optical dephasing and photon echo formation are briefly introduced.

**Density Matrix and Optical Bloch Equation**

When the information available about a quantum system is not sufficient to determine its state, the density matrix formalism is the most convenient method for calculating the expectation values of operators, which represent the physical quantities of the system. The density matrix is defined by \(^{75-77}\)
\[ \rho(t) = |\Psi(t)\rangle\langle\Psi(t)|, \quad (3.1) \]

where \( |\Psi(t)\rangle \) is the wave function of an isolated system. For an ensemble in which each individual ion can occupy any lattice site of the inhomogeneous distribution and where further statistical fluctuations affect each site, an ensemble average has to be taken. Then, the density matrix is defined as

\[ \rho(t) = \sum_i |\Psi^i(t)\rangle p_i \langle\Psi^i(t)|, \quad (3.1') \]

where the summation over \( i \) is over all sites and all dynamical states, and \( p_i \) is the normalized probability.

For calculation of the time evolution of dynamical operators, instead of solving the Schrödinger equation to find eigenstates, one solves the Liouville equation for the density matrix

\[ \frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [H, \rho(t)], \quad (3.2) \]

where \( \rho(t) \) is density operator and \( H \) is the Hamiltonian of the system. The formal solution of the Liouville equation (3.2) is

\[ \rho(t) = \exp[-iHt/\hbar]\rho(0)\exp[iHt/\hbar], \quad (3.3) \]

where \( \rho(0) \) is the initial density of the system.
Once the density matrix is known, then it is convenient to calculate the expectation values of dynamical operators \( \langle \hat{P} \rangle \) by taking the trace of the matrix product

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

For coherent emission, \( \hat{P} \) represents a macroscopic dipole operator, and its statistical or ensemble average \( \langle \hat{P} \rangle \) is known as the macroscopic polarization of the sample. The average is taken over all the states that the system may occupy. For a particular system, which is homogeneously and inhomogeneously broadened, the average must be taken over all the ions to sum both the inhomogeneous energy states and the homogeneous interaction couplings.\(^{49}\)

Consider a two-level system with \( |1\rangle \) and \( |2\rangle \) being the eigenstates of an unperturbed Hamiltonian \( H_0; H_0|1\rangle = 0|1\rangle \), and \( H_0|2\rangle = \hbar \omega_0|2\rangle \). The transition dipole matrix elements are assumed to be

\[
\mu = \langle 2|\mu_+|1\rangle = \langle 1|\mu_-|2\rangle.
\]  

In the presence of an electromagnetic field \( \hat{E}(t) = xE_x(t) + yE_y(t) \), the interaction Hamiltonian for the two-level system, in the dipole approximation

\[
H_I = - (\mu_+ E_+ + \mu_- E_-),
\]  

where \( E_\pm = (E_x \pm iE_y)/\sqrt{2} \). The dynamic response of the two-level system to
the applied field, including the relaxation term, can be derived from the Liouville equation

$$\frac{\partial \rho(t)}{\partial t} = -i \frac{1}{\hbar} [H_0 + H_I + H_{\text{relax}}, \rho(t)]. \quad (3.7)$$

A semiclassical picture of this equation of motion has been used to explain the time evolution of the system in the applied field.\textsuperscript{28,33} It is useful to define the pseudo-dipole as

$$\langle P^\gamma \rangle = \hat{x}\langle P_x \rangle + \hat{y}\langle P_y \rangle + \hat{z}\langle P_z \rangle,$$

with

$$\langle P_x \rangle = \mu(\rho_{12} + \rho_{21})/\sqrt{2}$$

$$\langle P_y \rangle = \mu(\rho_{12} - \rho_{21})(i\sqrt{2})$$

$$\langle P_z \rangle = \mu(\rho_{22} - \rho_{11}) \quad (3.8)$$

and an effective electric field as

$$\vec{E}_{\text{eff}} = \hat{x}E_x + \hat{y}E_y + \hat{z}E_z$$

with a dc component

$$\hat{z}E_z = -\hbar\omega_0/\mu. \quad (3.9)$$

The equation of motion Eq. (3.7) can be then written as\textsuperscript{28}
\[
\frac{\partial}{\partial t} \langle \mathbf{P} \rangle = -\frac{\mu}{\hbar} \mathbf{E}_{\text{eff}} \times \langle \mathbf{P} \rangle - \frac{1}{T_2} \langle \hat{x}\langle P_x \rangle + \hat{y}\langle P_y \rangle \rangle - \frac{1}{T_1} \hat{z}\langle P_z \rangle - \langle \mathbf{P}^0_z \rangle,
\]

(3.10)

where the relaxation terms have been phenomenologically added into the Liouville equation. The diagonal term characterized by \( T_1 \) represents the population decay of the system, and \( T_1 \) is known as the radiative life time or the longitudinal relaxation time. The off-diagonal term characterized by \( T_2 \) represents the dephasing of the system. The quantity \( T_2 \) is called the dephasing time or transverse relaxation time. The pseudo-dipole moment \( \langle \mathbf{P} \rangle \) in the effective field \( \mathbf{E}_{\text{eff}} \) has similar properties as the magnetic dipole moment \( \mathbf{M} \) in a magnetic field \( \mathbf{H} \) except that there is no corresponding individual electric dipole moment when an ion is completely in the excited or the ground state of the two-level system. Equation (3.10) is known as the optical Bloch equation.43 With the pseudo-dipole picture all methods from magnetic resonance can be applied to describe optical resonance.

**Photon Echo Formation**

For spin echoes, it is the magnetic dipole moment that precesses in the applied magnetic field and produces the spin echoes. This magnetic moment is associated with all the individual magnetic moments of nuclei or electrons in both the ground state and the excited states. In the case of
photon echoes, where the radiation is caused by an electric dipole transition, there is no corresponding electric dipole moment in either the ground or excited state. Thus there is no physical picture of a precessing dipole moment as in the magnetic case. In the discussion of photon echoes, however, the matrix element of the corresponding dipole moment operator between the ground state and the excited state is similar to the magnetic moment in spin echoes as described by the Bloch equation. By using the pseudo-dipole moments one can describe the formation of the photon echoes in much the same way as spin echoes.33

Individual ions and molecules in a solid have different resonant frequencies due to the variation in their environment. This is known as inhomogeneous broadening of a spectral line. In the pseudo-dipole picture, the dipoles precess with different frequencies. In the photon echo process, two sequential coherent optical pulses separated by time delay $\tau$ are applied to the sample. The first pulse produces a state in which all the dipoles are initially in phase. Therefore, all the dipoles in the ensemble are contributing coherently to a single macroscopic dipole moment. After the first pulse, the two-level system is expected to radiate much of the energy stored during the first excitation. The radiation is coherent until the pseudo-dipoles are out of phase with one another due to the inhomogeneous distribution of resonant frequencies. As a result, the coherent reradiation from the sample should decay away in a time $T_{2}^* = 1/\Delta\omega_1$, where $\Delta\omega_1$ is the inhomogeneous line width or the laser line width, whichever is smaller. The laser pulse duration is assumed to be negligible. This coherent reradiation is known as optical free induction decay (FID).34

It is possible that the dephasing dipoles can be rephased by a
second excitation pulse, so that they all are in phase again. After this rephasing process, the coherent emission reappears. Therefore, an echo is produced. This statistical rephasing effect was first discovered by Hahn\textsuperscript{35} in magnetic resonance where it is known as a spin echo. The photon echoes, which are analogs of spin echoes, were predicted and observed by Hartmann et al.\textsuperscript{32,33}

Let the two-level system have a central resonant frequency $\omega_0$, and consider the sequence of two linearly polarized optical pulses near-resonance, $E^\uparrow(t) = xE \cos\omega t$, with $\omega = \omega_0$. In a frame rotating at angular frequency $\omega$, the field $E^\uparrow(t)$ appears stationary. Neglecting the relaxation terms, we can write the equation of motion for the precessing dipole as

$$\frac{\partial}{\partial t} \langle P^\uparrow \rangle = -\frac{\mu}{\hbar} [\hat{x}E + \hat{z}(\frac{\hbar \omega_0}{\mu})] X \langle P^\uparrow \rangle. \quad (3.11)$$

In the rotating frame Eq. (3.11) becomes\textsuperscript{28}

$$\frac{\partial}{\partial t} \langle P^\uparrow \rangle = \frac{\mu}{\hbar} [\hat{x}E + \hat{z}(\frac{\hbar(\omega_0 - \omega)}{\mu})] X \langle P^\uparrow \rangle = \frac{\omega_0 - \omega}{\mu} X \langle P^\uparrow \rangle, \quad (3.12)$$

where $\Sigma^\uparrow = \omega_0 - \omega - \mu E/\hbar$, and the effective field is then $E^\uparrow_{\text{eff}} = -\Sigma^\uparrow/\mu$. The dynamic response of the pseudo-dipole, following Eq. (3.12), can therefore be described by its precession around $E^\uparrow_{\text{eff}}$ in the rotating frame. Before the initial excitation, all the ions in the two-level system
are in the ground state and the macroscopic dipole is pointing along the \( \hat{z} \) direction, as shown in Fig. 7 a. At \( 0 \leq t \leq t_1 \), the system is under the applied field of the first pulse. If the Rabi frequency \( \mu E/\hbar \) is much greater than \( |\omega - \omega_0| \), then all the dipoles should rotate around \( \hat{E} \) by an angle

\[
\theta_1 = \int_0^{t_1} (\mu/\hbar) E dt.
\]  

(3.13)

When \( \theta_1 = \pi/2 \) all dipoles end up together in the \( \hat{x}-\hat{y} \) plane at the end of the excitation pulse, as shown in Fig. 7 b. After the pulse is off, the dipoles will precess about the \( \hat{z} \) direction with different frequencies. Thus, the collective net dipole moment will decay away, as will the coherent emission. In the rotating frame the dipoles will be seen dispersing in both directions in the \( \hat{x}-\hat{y} \) plane, as shown in Fig. 7 c. At time \( t_2 \), a second excitation pulse is applied, which causes the individual dipoles again to precess about the strong field. The amplitude of this field is adjusted so that when the second pulse is off at \( t_3 \)

\[
\theta_2 = \int_{t_2}^{t_3} (\mu/\hbar) E dt = \pi.
\]  

(3.14)

The precession of all dipoles by \( \pi \) radians about the applied field \( \hat{E} \) is equivalent to a reflection about the \( x \) axis in the \( \hat{x}-\hat{y} \) plane. Since this intense pulse does not affect the oscillation frequency of the individual dipoles, they will continue to precess about \( \hat{z} \) after the second excitation pulse with the same angular velocity as that before the second pulse was applied. As a result, all the dipole groups will then rephase in
Fig. 7. Schematic description of photon echo. The upper picture shows the pulse excitation sequence. The lower picture shows the precession of the pseudo-dipoles on the rotating frame at various times.\textsuperscript{12}
precisely the time taken by them to dephase. There is no coherent emission after the second pulse until all the dipoles are back in phase. The coherent emission reaches a peak at $t_4$ when all the dipoles are completely in phase as shown in Fig. 7 e. As the dipoles fan out of phase again, the coherent emission signal decays away.

As described above, the existence of photon echoes depends on the reversibility of dipole dephasing due to inhomogeneous broadening. However, the dipoles should also experience an intrinsic dephasing process with the dephasing time $T_2$ related to the homogeneous broadening. This intrinsic dephasing is not static so that it is not reversible. Therefore the intensity of the photon echoes will decay as the time delay between the two excitation pulses increases. For a two-level system, the decay is a simple exponential

$$I(t) = I_0 \exp(-4\tau/T_2),$$

(3.15)

where $\tau$ is the time delay between the excitation pulses and the assumption that $T_2 \gg T^*_{\text{2}}$ has been made.

For arbitrary area pulses $(\theta_1, \theta_2)$, projection components of the field vector have to be used in the derivation of photon echo formation. This leads to a modification of echo intensity by a factor of $(\sin^2(\theta_2/2)\sin(\theta_1))^2$. The decay constant is not affected by the pulse areas. However, this is correct only for an isolated ion in a two-level system. As will be seen in Chapter 5, echo decay time can be pulse area dependent for other reasons in a real system.

In photon echo experiments, the propagation effects are also
important. A detailed discussion of this subject is given by Hartmann et al.\(^{33}\) Here a simple approach is presented.\(^{28}\) Assuming the photon echoes are detected at \( r^* = 0 \), and time \( t \), the actual interaction of the pulse with ions in the sample at \( r^* \) occurs at the retarded time \( t - \frac{k^*}{\omega} \). Thus, with the retarded times, the photon echo should then appear when

\[
(t_4 - \frac{k_e^*}{\omega}/(t_3 - \frac{k_2^*}{\omega}/(t_2 - \frac{k_1^*}{\omega})), (3.16)
\]

where \( k_1^* \), \( k_2^* \), and \( k_e^* \) are, respectively, the wave vectors of the first pulse, second pulse, and the photon echo. The above equation yields the conditions for the photon echo:

\[
t_4 - t_3 = t_2 - t_1
\]

and

\[
k_e^* = 2k_2^* - k_1^*.
\]

The second equation in Eq. (3.17) defines the direction of the echo propagation. Since the three \( k^* \) vectors are of equal magnitude, this requires that the excitation pulses be parallel to each other. If the excitation pulses are not parallel, the echo intensity is expected to be reduced. There will also be interference effects. These effects will be minimized in the direction of propagation satisfying the second equation in Eq. (3.17). For small angles \( \phi \) between \( k_2^* \) and \( k_1^* \), the echo is emitted at an angle \( = 2\phi \) with respect to \( k_1^* \) in the plane of \( k_2^* \) and \( k_1^* \). For a cubic lattice array of \( N = N_x^3 \) atoms of spacing \( a \), the first zeros in the echo radiation pattern occur when \( \phi \) is equal to \( 2\pi/(N_x ka) \).\(^{33}\)
Optical Dephasing Theory for Two-Level Systems

Dephasing is a process of phase relaxation by which some initial coherence properties of a macroscopic ensemble become irreversibly destroyed. Here in the case of an optically activated ensemble of ions in a solid, this refers to the decay of the initial ordering of the relative phase between two quantum states throughout the ensemble. This dephasing can be experimentally measured by the decay of the coherent emission in the time domain with time constant $T_2$, or by the line width of the intrinsic transition in the frequency domain $\gamma$. The Fourier transformation of $I(t)$ in Eq. (2-2.5) gives the Lorentzian line shape for homogeneous broadening

$$I(\omega) = \frac{\Gamma/\pi}{(\omega_0 - \omega)^2 + \Gamma^2},$$

(3.18)

where $\Gamma=1/(\pi T_2)$ defines the relation between the relaxation time and the homogeneous line width.

To obtain explicit theoretical expressions for the optical dephasing rate for a two-level system, one needs to consider the relaxation dynamics (electronic and vibrational), which may be quite complicated for a particular system. In the last two decades, great efforts have been made in this area. Jones and Zewail have formulated a rigorous theory of optical dephasing in the condensed phase by solving the Liouville equation using the Green function approach. Their attention has been given to molecular systems. The Hamiltonian includes the isolated optically active
molecule, a perturbing bath of the molecules, and the interaction between
the molecule and the bath. Wiersma et al.\textsuperscript{46,47} used the Redfield
relaxation theory\textsuperscript{79} to describe optical dephasing in mixed molecular
crystals where localized phonons play a dominant role in the dephasing
process. Recently Skinner et al.\textsuperscript{49} have formulated a theory of photon
echo decay for energetically and substitutionally disordered crystals using
the model of quasiresonant interactions. In this model only the electronic
interactions between the near-resonant impurity ions are accounted for.
This model achieved reasonable agreement with the experimental results on
the rare earth systems Eu\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} and EuP\textsubscript{5}O\textsubscript{14}.\textsuperscript{50,80}

If the ion-ion interactions are very strong so that the excitation is
shared by all the ions in the system, the dephasing is dominated by
energy transfer processes, and it is necessary to consider the theory of
exciton dispersion.\textsuperscript{10-14,81} Cone and Meltzer have applied this theory
successfully to interpret their observation of energy transfer phenomena in
Tb(OH)\textsubscript{3}.\textsuperscript{11}

The general relaxation Hamiltonian for ions in solids can be written
as

\[
H_{\text{relax}} = \sum_i \hbar \delta_i a_i^+ a_i + \sum_{ij} \hbar V_{ij} a_i^+ a_j^\dagger
\] (3.19)

where \(a_i^+\) and \(a_i\) are creation and annihilation operators for the electronic
excitation of \(i\)th ion. The summations are over all ion sites with the
restriction \(i \neq j\). The first term is due to inhomogeneous broadening,
where \(\delta_i\) stands for the deviations of the resonant frequencies of
individual ions from the central frequency \(\omega_0\) in the inhomogeneous line.
The second term represents various interactions which cause the irreversible phase relaxation process. The $V_{ij}$ are the off-diagonal matrix elements of these interaction mechanisms.

The dephasing mechanisms can arise in various ways by ion-ion and ion-lattice interactions. For rare earth materials, the ion-ion interactions can be:

- a. electric exchange,
- b. magnetic dipole-dipole interaction,
- c. electric multipole-multipole interaction,
- d. virtual phonon exchange.

The magnetic dipole-dipole interaction is the leading dephasing mechanism in the $\text{1}\%\text{Tb}^{3+}\cdot\text{LiYF}_4$ in which the short range coupling mechanisms are absent. In the concentrated compound $\text{LiTbF}_4$, the short range mechanisms such as electronic exchange must play an important role in the energy transfer and also in the optical dephasing processes. Results for both compounds will be discussed in the following chapters.

**Quasi-Two-Level Systems and Photon Echo Modulation**

The energy levels of the electronic states of ions or atoms in solids are generally split into sublevels due to weak couplings, such as the hyperfine interaction which was discussed in the last part of Chapter 2, or superhyperfine interaction between the optically activated ions and the nuclei of their host material which will be discussed in Chapter 7. A quasi-two-level system (QTLS) is a generalization of such a system where each of the single levels consists of several nearly degenerate sublevels.
If the ions in all the sublevels can be excited by the applied optical pulses in a photon echo sequence, the interference effect known as quantum beats or modulation is expected in the photon echo signal due to the coupling between the substates in both the ground state and the excited state.

Important theoretical work on the modulation of coherent transient signals from QTLS has been performed by Lambert et al., Skinner et al., and Grischkowsky et al. In the calculation of the density matrix after the echo excitation pulses, a unitary matrix can be used to diagonalize the Hamiltonian for the energy splittings in the ground state and the excited state. The matrix elements are time independent because the energy splittings are time independent, thus the modulation should not have an effect on the overall decay rate. The intensity of the photon echo after a two-pulse sequence with time delay $\tau$ is given by

$$I(2t) = I(0) |\text{Tr}C|^2 \exp\left(-\frac{4t}{T_2}\right), \quad (3.20)$$

where

$$\text{Tr}C = \sum_{klmn} P_{klmn} \cos[(\omega_{km} + \omega_{ln})\tau]$$

with

$$P_{klmn} = W_{kl} \cdot W_{ml}^* \cdot W_{mn} \cdot W_{kn}^*$$

and
\[ W = U_g U_e^+, \quad (3.21) \]

where \( U_g \) and \( U_e \) are the unitary matrices that diagonalize the interaction Hamiltonian for the ground and excited states which have energy splittings \( \hbar \omega_{km}^g \) and \( \hbar \omega_{in}^e \), respectively. The summations are over all the energy substates. The modulation frequencies are obtained by the Fourier transformation of the echo profile. Not only the energy splittings in both the ground state and the excited state but also the interaction parameters in the Hamiltonian can be determined through the regression analysis.

If the interaction Hamiltonian for the echo modulation is due to the coupling between the echo ions and their surrounding host ions via superhyperfine interactions, there will in general be a number of terms in the Hamiltonian for the couplings between an echo ion and each ligand. In this case each term can be diagonalized separately and Eq. (3.20) becomes

\[ I(2t) = I(0) \prod_j \text{Tr} C_j^2 \exp(-4\tau/T_2), \quad (3.22) \]

where

\[ \text{Tr} C_j = \sum_{kln} (P_j)_{kln} \cos[(\omega_{km}^g + \omega_{in}^e)_j \tau]. \]

The summation over \( j \) is over all the sites of the host material, but in most cases only nearest neighbors make significant contributions to the echo modulation.
CHAPTER 4

EXPERIMENTAL APPARATUS AND TECHNIQUES

All the experiments described in this thesis were performed in Professor Cone's laser spectroscopy laboratory. The experimental setup for these experiments consists of lasers, optics, cryostats, signal detectors, and a computer control system. The lasers, optics and cryostats are operated in much the same way as for previous experiments reported by former graduate students in this laboratory.\textsuperscript{82,83}

In this chapter, a detailed description of the experiments will be given with emphases on the special techniques of timing control, laser frequency stabilization, field sweeping, and transient signal detection, that have been developed for the photon echo experiment.

**Experimental Setup for Photon Echoes**

The important features of the setup for the photon echo experiment are laser-frequency overlapping, synchronized time delay, and transient signal detection. A diagram of the setup is shown in Fig. 8.

**Lasers**

Two thyratron-triggered nitrogen lasers are used to pump two
Fig. 8. Setup for photon echo experiment, where NL stands for nitrogen laser, DL dye laser, L lens, T wave plate, P polarizer, CP compensator, and A aperture.
tunable dye lasers. The laser pulses have a duration of 5 nsec and repetition rate of 6 Hz. The nitrogen lasers are operated at 337.1 nm and produce a peak power of 400-500 kW.

The time delay between the nitrogen lasers is electronically controlled. It can be adjusted manually or can be scanned by the computer with a resolution and stability of 1 nsec. The stability and synchronization of the timing system will be discussed in a later section of this chapter.

Two Hansch type dye lasers produce peak powers of 20 to 40 kW. Both lasers can be operated in an etalon-narrowed high resolution mode with a linewidth of ~ 0.05 cm\(^{-1}\). Without the etalon in the cavity, the lasers operate in multiple modes with a linewidth of ~ 0.3 cm\(^{-1}\). To tune the laser frequencies, one of the dye lasers is equipped with a pressure-scanning chamber, in which the nitrogen gas pressure can be scanned by the computer to achieve a frequency tuning range of 10 cm\(^{-1}\). The other dye laser can be tuned by rotating the grating in the laser cavity with a computer-controlled stepper motor. These features have been used in the absorption spectra and hole burning experiments. In the photon echo experiments the two dye lasers have to operate at the same frequency. This will be described in the following section.

Cryostat and Field Sweeping

For most of the experiments, the sample was placed in a superconducting magnet cryostat in which the temperature could be reduced to 1.2 K by efficiently pumping the vapor above the liquid helium in the sample space. A magnetic field is generated by a superconducting
magnet coil. The structure and the operation of this cryostat have been discussed in Reference 83. There are two new features that have been added to the cryostat system:

1. **Temperature Monitor.** A tiny temperature sensing element (Lake Shore—CGR-1) was mounted on the sample holder near the position of the sample. A dc current supplied by a Keithley 227 current source is sent through the element. Both the current and the voltage across the element are measured with a four-wire connection during the experiments. A calibration program (TEMP.EXE) can be used to calculate the temperature from the measured current and voltage.

2. **Field Sweeping.** An important feature of the photon echo experiments on both the dilute and concentrated compounds was to study the frequency dependence of the echo decay. This will be discussed in Chapter 5 and Chapter 6. For this purpose, the photon echo intensity is recorded as a function of the excitation frequency across the inhomogeneous absorption line. This requires the frequency of the two excitation pulses to vary synchronously. With current facilities, it is almost impossible to scan the two independent lasers synchronously and keep their frequency overlap condition unchanged. Instead of varying the laser frequency, a magnetic field sweeping method has been developed. For the resonant optical transition between two Zeeman components, the resonant frequency shift is linearly proportional to the change in the applied magnetic field.

\[ \Delta v = \gamma \Delta H. \] (4.1)
From a physical point of view, varying the laser frequency across the inhomogeneous line at a fixed magnetic field is equivalent to sweeping the magnetic field to tune the resonant frequencies of the ions across the same region at a fixed laser frequency. This technique has been used successfully in the photon echo experiments on LiTbF$_4$ and Tb$^{3+}$:LiYF$_4$ in which the Tb$^{3+}$ ion has a quasi-linear Zeeman effect for the optical transition between the $^7F_6\Gamma_2$ to $^5D_4\Gamma_1$ states.

The field sweep is accomplished by sending a dc voltage from the computer's D/A convertor to the current control circuit of the superconducting magnet power supply. As a part of the echo program, the procedure for the field sweep is included in the computer program SDE5P1.C which is given in the Appendix. The sweeping speed and resolution are adjustable in the program. The high speed limit is due to the slow response of the magnet power supply. The change in field strength can be converted into a change in frequency according to Eq. (4.1). For Tb$^{3+}$:LiYF$_4$ and LiTbF$_4$, the value of $\gamma$ has been experimentally determined. At the applied field region 15-25 kG, the measured value of $\gamma$ is about 0.25 cm$^{-1}$/kG for both compounds.

The incident laser beams enter the cryostat from a window at the bottom of the cryostat. The two beams cross in the sample at their waist. With an $f$=100 cm lens, the beam waist is about 200 $\mu$m. A long focal length lens is necessary in the photon echo experiments on the Tb$^{3+}$:LiYF$_4$ and LiTbF$_4$ samples to keep the power density low because the laser intensity plays a very important role in the echo decay process, as will be discussed in Chapter 5. The transmitted laser beams and the photon echoes are all collected and sent to individual detectors which are mounted
on a separate optical table.

A razor blade has been used to locate the beam waist position in the sample and to ensure that the two beams crossed at the waist position. The laser induced thermal effect in the sample is also an effective method to adjust the beam focusing and overlapping.\textsuperscript{82,83}

**Photon Echo Detector**

Several techniques, such as polarization discrimination, spatial filtering, and Pockels cell gating are necessary for collecting the echo signal and discriminating it from the laser scattering. These techniques have been discussed in reference 83.

All the optical elements for these discrimination techniques and a photomultiplier for echo detection are lined up on an adjustable optical table, as shown in Fig. 8. This is an optimum arrangement for the echo detection and is very convenient for adjustments. Without this arrangement the photon echo detection would be more difficult. The propagation vectors for the laser and the echo beams satisfy the echo phase matching condition in Eq. (3.17). After the collection lens $L_2$, the three beams are parallel and equally spaced. Since the photon echo signal is too weak to see, the initial adjustments of all the components must be accurately made by using the laser beam. Then the micrometer is used to move the table across the laser beams to the expected echo position. After this procedure, no further adjustment is needed for this part of the detector during the experiment.
Transient Signal Processing

After the Pockels cell gate, a photomultiplier tube (Hamamatsu R928) was used to convert the photon echoes into electric pulses. These pulses were sent to a transient digitizer (Tektronix—7912AD), which is a good instrument for transient signal processing, for averaging over 5 nsec which was the actual duration of echo pulse, and storage. In the digitizer, 512 channels along the time axis can be arbitrarily assigned as signal locations, and the signal can be summed pulse by pulse. A typical number of assigned channels was 50. The background signal level was eliminated by subtracting the level obtained by summation of the same number of channels from a region after the assigned signal channels. An IEEE 488 "data bus" is installed for communication between the digitizer and the PDP-11 computer. The flow charts for the data-acquisition and control program for the photon echo experiment are shown in Fig. 9. The computer program in the C language (DECHP1.C) is given in the Appendix.

In the early stages of echo decay, the photon echo signals are strong enough to saturate the photomultiplier tube. To avoid saturation and to achieve a large dynamic range for the echo decay, several neutral density filters are used in the front of the photomultiplier to reduce the echo intensity for early delay times. This enables the echo signal to be recorded with an initial delay of 15 nsec and over a decay dynamic range of over 3 decades.

Laser Frequency Stabilization

Timing and frequency overlapping of the two independently operated
Fig. 9. Flow chart of data-acquisition and control program for photon echo experiment.
lasers are critical factors in the photon echo experiment. To generate photon echoes, the frequencies of the two excitation laser pulses have to be identical or mostly overlapped. Moreover, to record a set of echo decay data for extracting the decay rate of the photon echoes, the overlap condition should be perfectly stable throughout the scanning time period which is usually a few minutes to a half hour. Any deviation from the overlap condition can dramatically affect the echo intensity and make the data useless.

During the photon echo experiment, the laser frequency overlap condition was monitored by splitting the two laser beams and passing one leg of each beam through the monitoring Fabry-Perot etalon. The interference pattern was projected on a screen. The overlap condition was adjusted before taking each data set.

The laser frequencies could drift due to the thermal expansion of the Fabry-Perot etalon in the laser cavity. This frequency drift is sensitive to temperature change in the room. When the air conditioner turns on or off, the air flow can dramatically drift the laser frequency. This effect has been minimized by isolating the laser cavity from the air flow and keeping the cavities at an equilibrium temperature. This was achieved by using a wood-box cover on one laser and the brass pressure chamber around the other. With this improvement, the overlap condition could be kept for more than a half hour without obvious shift.

When the frequency dependence of the echo decay was not a critical factor, the photon echo experiment could be done without a Fabry-Perot etalon in the laser cavity. In that case, there was no significant laser frequency drift. However, the echo intensity could still jitter due to the
power fluctuation of the multiple modes of the lasers which have a linewidth of \( \sim 0.3 \text{ cm}^{-1} \). These fluctuations can be overcome by increasing the signal averaging time. The transient digitizer allows a maximum of 64 shots per data point, and the program has the option of repeating the average of one data point any number of times for a given delay time. It may take a long time for one scan, but time is not critical in this case where drift is not a factor.

**Time Delay Control**

For exploration of fast dephasing processes, the pulse duration must be short compared to the dephasing time of the system. Our laser pulses have a fixed duration of 5 nsec. The duration of the photon echo is about the same as that of the excitation pulses.

In order to achieve a good signal-to-noise ratio, the operation of the experimental system has to obey the rigorous timing condition given in Eq. (3.17). The gate chosen for analysis of the digitizer output (number and location of channels for input storage) for the photon echo signal was adjusted by the program. The gate width was set to be 4-5 nsec in the experiments and encompassed 40-50 channels. The laser firing and the detector triggering must be exactly synchronized. This timing schedule is executed through computer control by sending a dc control voltage to a fast pulse generator, which then produces three pulses at times \( t_0, t_1 \) and \( t_2 \). The first two pulses fire the lasers and the third pulse triggers the digitizer and the Pockels cell gate. The separation of the output pulses is linearly proportional to the input voltage from the computer. The
proportionality constant is previously set for a particular board in the pulse generator. Typically, varying the control voltage from zero to ten volts gives a variation of 0—1000 nsec for the pulse separation. The initial timing is adjusted at the beginning of the program execution for each run. This is done by setting the voltage for zero time delay between the two lasers. Then voltage for the initial delay is added while the two laser signals and the echo signal are monitored on the digitizer’s TV screen. Due to the different circuits, long wire and cable connections, as well as the different firing delays of the thyatrons in the nitrogen lasers, the actual laser firing times are $t'_{0}$ and $t'_{1}$, respectively. Usually, $t'_{1}-t'_{0} \neq t_{1}-t_{0}$, and the time condition $t'_{2}-t'_{1}=t'_{1}-t'_{0}$ is not satisfied either until some extra delay lines and compensation circuits are used. Elaborate adjustments were necessary to initially obtain the desired delays. Figure 10 gives a schematic description of these time relationships.

A typical problem of any thyatron-triggered nitrogen laser is the uncertainty of the firing time which causes a serious problem for the photon echo experiment. This uncertainty includes: (a) a long-term drift of the firing on the order of ~ 50 nsec per hour; and (b) jitter in the firing time which may be as large as 20 nsec shot-to-shot.

A drift compensator has been built to eliminate the long-term drift. The function of the compensator circuit has been discussed by P.Darejeh. A feedback pulse extracted from the laser by a photodiode and the delayed trigger pulse are sent to a time comparator to determine if the firing is early or late. Initially, the delayed trigger pulse is adjusted with an oscilloscope so that the position of the feedback pulse overlaps the trailing edge of the delayed trigger pulse. With this initial condition
Fig. 10  Time delay relations and photon echo detection.
the compensator has the same working region in both drift-up and drift-down directions.

The jitter is mostly dependent on the working condition of the thyratron. The temperature is the most sensitive factor for the jitter. It was found that the water flow to the thyratron can dramatically affect the jitter and also the drift. Proper adjustments and stable water flow can keep the jitter significantly smaller than 1 nsec and keep the lasers working for hours without drift at all.
In a very dilute rare earth compound, the short range ion-ion interactions, such as electric multipole interactions and electronic exchange, are weak and often negligible. The excited state dynamics of rare earth ions are then most strongly affected by fluctuations of the local magnetic fields. In 1% Tb$^{3+}$:LiYF$_4$, the Tb$^{3+}$ ion has a very large magnetic dipole moment, so its optical resonant frequency is quite sensitive to the local magnetic field. Thus the magnetic dipole-dipole interaction plays an important role in the line broadening in this dilute material.

The optical analog of the "instantaneous spectral diffusion" phenomenon of electron spin resonance has been dramatically observed in the photon echo experiments on the $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ transition in 1% Tb$^{3+}$:LiYF$_4$. If $\Gamma_0$ is the true homogeneous line width and $\Gamma'$ is the contribution of instantaneous spectral diffusion, the "apparent" homogeneous line width $\Gamma=\Gamma_0+\Gamma'$ determined from measured photon echo decays depends linearly on the energy density or power of the second laser pulse and is independent of the power of the first laser pulse. Changes in $\Gamma$ of greater than a factor of ten are readily observed. The
photon echo decay is also magnetic field dependent. To explain these experimental results, the magnetic dipole-dipole interaction between Tb$^{3+}$ ions has been considered. In the power dependent studies, a change in coupling between an echo ion and surrounding ions occurs when the surrounding ions are excited by an optical excitation pulse. This causes an instantaneous shift in the optical transition frequency of the echo ion and prevents complete rephasing. In the field dependent studies, spin diffusion is inhibited by the large ground state Zeeman splitting.

Review of Echo Decay

The photon echo technique has provided an effective way to measure homogeneous line widths of optical transitions in the time domain in solids, where direct measurements in the frequency domain are obscured by inhomogeneous broadening. Both the static inhomogeneous broadening and the random fluctuations of the local fields will participate in the phase relaxation as discussed in Chapter 3. The random part of the relaxation cannot be rephased by the echo sequence, since the phase shifts due to the random fluctuations in the first half of the echo sequence will be different from those in the second half of the echo sequence. Therefore, they will not exactly cancel, and the optical dephasing induced by the random fluctuations in local fields will be measured on the time scale of the pulse delay.$^{85}$

The new effect which we refer to as instantaneous spectral diffusion arises as follows. When generating echoes, the laser excitations can also cause abrupt long lasting changes in the local fields. These abrupt
changes induce extra dephasing. This effect is a direct analog of the instantaneous diffusion in electron spin echoes studied by Mims and by Klauder and Anderson. In the spin echoes, the change in local fields is caused by spin reorientation. The reoriented spins are responsible for generating the spin echoes, and also contribute to the local fields thus leading to an artificial or experiment-induced line-broadening.

This optical analog of the instantaneous spectral diffusion effect on photon echoes has recently been analyzed by Warren and Zewail. They indicated that in inhomogeneously broadened systems, when one molecule is excited its moments change, thus changing the resonance frequencies of all its neighbors through the dipole-dipole interaction. The dephasing due to inhomogeneous broadening is refocused by photon echoes, but the dipole-dipole interactions are bilinear and hence are unaffected by the echo pulse, so they give a contribution to the echo decay. This contribution will be particularly important if the permanent dipole moment changes substantially upon excitation.

It will be shown in this chapter that for an inhomogeneously broadened system, the abrupt change in local fields due to the change in permanent magnetic dipole moment upon the first excitation pulse, has no effect on echo rephasing when the excited state life time $T_1$ is much longer than the pulse delay time $\tau$. On the other hand, those changes caused by the second excitation pulse prevent complete rephasing. Thus the echo decay rate is independent of the excitation power of the first pulse and depends only on the excitation power of the second pulse. Based on the energy structure analysis of this material, electron spin diffusion also occurs in the ground state, and it is strongly dependent on
the energy splitting of the Zeeman effect. This leads to field and temperature dependence of the optical dephasing.

**Effect of Local Fields on Optical Dephasing**

For the optical transitions of impurities (ions and molecules) in crystals, the inhomogeneous broadening includes the effect of any local electric and magnetic fields and the interactions between the impurity and host. In the Tb$^{3+}$:LiYF$_4$ crystal, at low temperature, the dominant fluctuations in the energy of Tb$^{3+}$ ions are due to the local magnetic fields. As discussed in Chapter 2, in this crystal, Tb$^{3+}$ has a large magnetic dipole moment in the ground state $^7F_6 \Gamma_2$; its permanent moment $\mu = 8.9\mu_B$, where $\mu_B$ is the Bohr magneton. It has no first order magnetic dipole moment in the excited state $^5D_4 \Gamma_2$. The transition of an ion between those two states ($\omega_0 = 20554$ cm$^{-1}$), leads to a substantial change in the dipole moment and thus contributes to the change in local fields at other ion sites.

Due to the Zeeman effect in the ground state and the excited state, the optical resonant frequency of the Tb$^{3+}$ ion is sensitive to the local fields. For a local magnetic field change $\Delta H$ at site $i$, the shift of its resonance frequency is

$$\nu_i = g_{\text{eff}}\mu_B \Delta H / h,$$

where
$g_{\text{eff}} = \left| g_1 - g_2 \right|^{1/2}$  \hspace{1cm} (5.2)

is the effective $g$-factor for the two-level system and where $g_1$ and $g_2$ are the $g$-factors for the ground and excited state, respectively. For the excited state $^5D_4 \Gamma_1$, as discussed in Chapter 2, the zero field eigenfunction in the $|M_j\rangle$ representation is

$$|\Gamma_1\rangle = 0.42|0\rangle - 0.642(|4\rangle + |4\rangle),$$  \hspace{1cm} (5.3)

so there is no first order Zeeman effect. Due to the coupling to other higher $\Gamma_1$ states in the same multiplet, the energy level varies quadratically at low field and asymptotically approaches a linear Zeeman effect at very high field. Therefore, in Eq (5.2) $g_2$ is field dependent so that the fluctuation-induced frequency shift is expected to depend on the applied magnetic field too, particularly at low fields.

Fluctuations of local magnetic fields in Tb$^{3+}$:LiYF$_4$ can arise in several ways: (a) ion-lattice interactions; (b) electron spin diffusion between the two Zeeman components of the ground state; (c) spin-spin interactions among nuclear spins in the host material; (d) abrupt changes upon optical excitation and emission. At low temperature we neglect the effect of mechanism (a). The energy splitting between the two Zeeman components of the ground state is $\Delta E = 17.8 \mu_B H$, and when $H > 10$ kG at $T = 1.3$ K, $\Delta E >> kT$, and the electron spin population in the upper component becomes extremely low. Mechanism (b) is thus negligible at high field, but it will substantially dominate the optical dephasing once the splitting $\Delta E$ is comparable with $kT$. Mechanism (c) is a slow spectral
diffusion source. It causes the stimulated echo decay which is discussed in the last section of this chapter and also affects the spectral holeburning process as will be seen in Chapter 8. On the microsecond time scale of the observed echo decay, the contribution from (c) is a small constant part to the optical dephasing. As discussed above, the large change in magnetic dipole moment of Tb$^{3+}$ ions due to optical excitations will cause significant changes in local fields, therefore, mechanism (d) will dominate the echo decay at low temperature and high field.

**Instantaneous Diffusion**

As mentioned in the previous section, optical excitations cause changes in the magnetic moment of the excited ions and thus lead to changes in the local fields of neighboring ions. In the dipole-dipole interaction approximation, the change in local field at site $i$ after the excitation of a neighboring ion at site $j$ is

$$\Delta H_i = g_{\text{eff}}\mu_B (1-3\cos^2 \theta_{ij})/r_{ij}^3,$$

(5.4)

where $r_{ij}$ is the distance between site $i$ and $j$, and $\theta_{ij}$ is the angle between the z-direction and the line joining $i$ and $j$. All the dipoles are parallel to the z-direction, so we do not consider the effect of x-y components. The resonance frequency shift of $i$ is then

$$\nu_{ij} = g_{\text{eff}}^2\mu_B^2 (1-3\cos^2 \theta_{ij})/r_{ij}^3.$$  

(5.5)
The shifts due to the first pulse are present throughout the echo sequence ($T_1 \gg \tau$). This is equivalent to the normal static inhomogeneous broadening and will be removed by the echo sequence. Therefore, the shifts due to the first pulse have no effect on the echo rephasing. However, the shifts due to the second pulse are present for only a part of the echo sequence, so they will not be removed by the rephasing process and will thus prevent complete rephasing of the echoes. In the pseudo-dipole moment picture, if the amount of phase precession of individual dipoles in the dephasing period randomly differs from that in the rephasing period, the ensemble average of the moments will of course be reduced.

To evaluate the dephasing rate due to the instantaneous diffusion, the ensemble average of the frequency shifts has to be carried out for the crystal lattice. The continuous medium approximation of the crystal lattice is applicable for low concentration and long range coupling mechanisms such as magnetic dipole-dipole interaction. With this approximation and using either the statistical theory of line broadening or the density matrix method of photon echo decay, the effect of the instantaneous diffusion is to reduce the echo intensity by

$$I(t) = I_0 \exp(-4\tau/T'_2) \quad (5.6)$$

with the decay rate

$$1/T'_2 = 4\pi^2 J_{ne}/9\sqrt{3}$$
where $J = g_{\text{eff}}^2 \mu_B^2 / \hbar$ and $n_e$ is the ion concentration of the sample in the case of an ideal $\pi/2-\pi$ pulse sequence. When the pulsing condition is not the ideal $\pi/2-\pi$ sequence, say $\theta_2 < \pi$, the effective number of echo ions will be less than the total impurity ions in the line. Therefore, $n_e$ is no longer the ion concentration which is constant for the sample, instead it will depend on the excitation intensity and the pulse duration $t_d$.

A narrow-band laser pulse excites only a small portion of the line, most of the ions in the line do not make a contribution to the echoes. Thus echoes can be formed having different frequencies corresponding to different positions in the inhomogeneously broadened line. If the frequency distributions of two independent laser pulses do not completely overlap, only the overlapping part makes a contribution to the echo creation, but the entire second pulse makes a contribution to the instantaneous diffusion. Therefore, the effective number of ions that cause the instantaneous diffusion depends on the excitation frequency, duration and intensity of the second pulse.

Basic energy conservation requires the total energy stored in the sample during the excitation to equal the total energy of the excited ions,

$$E_T = \int \rho(\omega) \hbar \omega d\omega$$  \hspace{1cm} (5.8)

where

$$N_T = \int \rho(\omega) d\omega,$$  \hspace{1cm} (5.9)
is the total number of excited ions and \( \rho(\omega) \) is the density of excited ions. In the case of \( \omega_0 \gg \delta \), \( E_T = h\omega_0 N_T \), where \( \omega_0 \) is the center of the inhomogeneous absorption line. This energy is absorbed from the laser pulse, thus we have

\[
h\omega_0 N_T = t_d A I_2 \{1-\exp[-\alpha(\omega)L]\}, \tag{5.10}
\]

where \( A \) is the area on the sample exposed to the laser, \( L \) is the thickness of the sample, \( I_2 \) is the intensity of the second pulse, and \( \alpha(\omega) \) is the absorption coefficient. For low intensity excitation, the effective concentration then can be written as

\[
n_e = N_T / AL
\]

\[
= (t_d / Lh\omega_0)I_2 \{1-\exp[-\alpha(\omega)L]\}. \tag{5.11}
\]

From Eq.(5.7) and Eq.(5.11) we obtain the contribution of instantaneous diffusion to the apparent line width as

\[
\Gamma' = 1/nT_2
\]

\[
= \frac{0.2(g_1 - g_2)^2 \mu_B^2 t_d I_2 \{1-\exp[-\alpha(\omega)L]\}}{Lh^2\omega_0}. \tag{5.12}
\]

It is clear from the above equation that the dephasing rate depends
on (a) the excitation intensity of the second pulse, (b) magnetic field (as we indicated above, \(g_1\) is constant and \(g_2\) is field dependent), and (c) the excitation frequency if echoes are generated by two narrow-band pulses. The frequency dependence of the echo decay rate due to the instantaneous diffusion arises from the excitation of more ions at line center than in the wings.

**Electron Spin Diffusion**

Another important effect of the magnetic dipole-dipole interaction is the exchange of spin states. This is particularly important for the ground state of this material based on the analysis of Chapter 2. Through the magnetic dipole-dipole interaction which has an Ising-type Hamiltonian, a pair of ions can execute mutual flips between the two components of the effective spin-1/2 state. The random distribution of this flip-flop process leads to fluctuations of the local fields which cause homogeneous line broadening.\(^{39,87,88}\) This effect is called spin diffusion. In this case Eq. (5.4) becomes

\[
\Delta H_1 = g_1 \mu_B \frac{(1-3\cos^2\theta_{ij})}{r_{ij}^3}, \quad (5.13)
\]

where \(g_1=17.8\) is the ground state g-factor. The optical transition frequency shift due to the spin flip-flop is then

\[
\nu_{ij} = 17.8 g_{eff} \mu_B^2 \frac{(1-3\cos^2\theta_{ij})}{r_{ij}^3}. \quad (5.14)
\]
When comparing this frequency shift to the one of Eq. (5.5) due to an optical transition of a $j$ ion, we note that the two terms could have the same spatial distribution but have very different time scales. The instantaneous diffusion process occurs only during the laser pulses, while the spin diffusion is present through all the echo sequence. The statistical ensemble average is the same for these two cases. The dephasing rate due to the contribution of the spin diffusion then can be obtained by \(^{39}\)

\[
\frac{1}{T_{2}'''} = 2.53 J' n_e',
\]

(5.15)

where $J' = 17.8 g_{\text{eff}} \mu_B^2 / h$, and $n_e'$ is the spin density of the flip-flop ions. With the Boltzmann distribution, $n_e'$ can be written as \(^{87}\)

\[
n_e' = n_0 \exp(-\Delta E/kT),
\]

(5.16)

where $n_0$ is ion concentration and $\Delta E = 17.8 \mu_B H_z$ is the Zeeman splitting of the ground state. Substituting Eq. (5.16) into Eq. (5.15), the line width due to the contribution of the spin diffusion has the form

\[
\Gamma''' = \frac{1}{\pi T_{2}'''}
\]

\[
= 14.3 n_0 \frac{\mu_B^2}{h} g_{\text{eff}} \exp\left(\frac{-17.8 \mu_B H_z}{kT}\right).
\]

(5.17)
The field dependence of the dephasing rate in Eq. (5.17) is due to both the Zeeman effect of the ground state and the field dependence of the effective g-factor which is due to the nonlinear Zeeman effect of the excited state.

We assume that $\Gamma''$ plus a small term from nuclear spin diffusion combine to give the true homogeneous line width $\Gamma_0$.

**Experimental Details**

The setup for the photon echo experiments has been introduced in Chapter 4. The excitation laser pulse duration was 5 nsec and the line width of the lasers was 0.3 cm$^{-1}$ which was less than the inhomogeneously broadened absorption line width 0.4 cm$^{-1}$. The sample was put in the superconducting magnet cryostat with its c axis parallel to the applied magnetic field. The experiments were carried out at 1.3 K and over the field region from 10 to 50 kG.

The echo decays were recorded over 2 to 3 decades of dynamic range as a function of delay time. A typical decay is shown in Fig. 11. The dephasing rate was very sensitive to the power of the second pulse and also depends on the applied magnetic field as expected.

To study the effect of excitation intensity on the dephasing rate of photon echoes, the peak intensities of the first and second laser pulses on the sample were independently varied from 2 to over 15 MW/cm$^2$ by controlling the nitrogen laser intensity without any disturbance to the echo optical system. At $H=42$ kG and $T=1.3$ K, Fig. 12 shows the measured homogeneous line width $\Gamma=\Gamma_0+\Gamma'$ as a function of the intensities of the
Typical photon echo decay curve of Tb$^{3+}$:LiYF$_4$ at 1.3 K. The applied magnetic field is 32 kG and the excitation intensity is 7 MW/cm$^2$. The structure in the curve is due to modulation which will be discussed in Chapter 8.
Fig. 12 Excitation intensity dependence of the dephasing rate of Tb$^{3+}$:LiYF$_4$ at 1.3 K. The solid curves are the best fit of the experimental data points. Dephasing only depends on the intensity of the second laser pulse $I_2$. The slope of the curve, when the intensity of the first laser pulse $I_1$ is a constant, is 26 kHz/(MW/cm$^2$) and the intersection point is 28 kHz as $I_2$ tends to zero.
laser pulses. The experimental data obey a simple form

$$\Gamma = \Gamma_0 + \Gamma'' = \Gamma_0 + aI_2,$$

(5.18)

where $I_2$ is the peak intensity of the second laser pulse on the crystal, $a = 26 \text{ kHz/(MW/cm}^2\text{)}$ is the slope for best fitting the data, and $\Gamma_0 = 28 \text{ kHz}$, is the true homogeneous line width including the contribution from the remaining local field fluctuations due primarily to the nuclear spin diffusion in the applied magnetic field.

At high field and low temperature, $\Gamma''$ dominates the echo decay rate. Comparing Eq.(5.12) with Eq.(5.18), the power dependence coefficient $a$ is defined as

$$a = 1.26(g_1-g_2)^2\mu_B^2t_d(1-e^{-\alpha l})/L\hbar^2v_0. \quad (5.19)$$

For 1\%$\text{Tb}^{3+}$:$\text{LiYF}_4$, the peak absorption coefficient for this transition is 2.5 cm$^{-1}$, $L = 0.2 \text{ cm}$, thus 40\% of the laser power is absorbed in the inhomogeneous line center. In our experiments, the laser line width was 0.3 cm$^{-1}$ and the inhomogeneous line width of the sample was 0.4 cm$^{-1}$. With the assumption of Gaussian line shapes, an average absorption across the inhomogeneous line was then 30\% instead of 40\% in the center of the line. The $\Gamma_1$ levels of the excited state $^5D_4$ vary quadratically at low field and asymptotically approach linear Zeeman splittings at high field with $g_2 = 12$. At 42 kG, the value is 9.1. Substituting the above data with $t_d = 5\times10^{-9} \text{ sec}$ and $v_0 = 6.2\times10^{14} \text{ Hz}$ into Eq.(5.19) gives $a = 25 \text{ kHz/(MW/cm}^2\text{)}$. That value is in reasonable agreement with the
experimental value of 26 kHz/(MW/cm²) which is the slope best fitted to the data points in Fig. 12. The deviation is primarily due to the approximation of a continuous medium which was used in the calculation and the uncertainty of various experimental conditions such as the effective diameter of the focused laser beam, laser power loss due to the windows and prisms in the cryostat, and both space and frequency overlapping of the two laser pulses.

The power dependence coefficient $a$ has been measured as a function of applied magnetic field by recording the echo decay times as a function of the excitation intensity of the second laser pulse at several fixed fields. Figure 13 shows the experimental result fitted to the theoretical form given by Eq. (5.19). The data points were obtained from the slope which best fitted the dephasing rate for each applied field. The solid curve represents the value of Eq. (5.19) in which $g_2$ as a function of field was given by the calculated Zeeman effect and an adjustable constant was used to fit the curve to the experimental data points. To fit the data, a constant 0.67 was obtained instead of the factor 1.26 in Eq. (5.19) which was a result of continuous-medium approximation. It has also been noted that the experimental results from two series of experiments are not consistent. The value of 26 kHz/(MW/cm²) at 42 kG from earlier experiments is certainly higher than later experimental results plotted in Fig. 13. Since all results in one series of experiments are consistent, this indicates that some of parameters such as the space and frequency overlapping conditions are not identical for the two experiments which lead to different effective excitation intensities. Nevertheless, the theoretical calculation has provided a good functional description of the
experimental observations.

As noted in the previous section, $\Gamma_0$ represents the electron spin diffusion plus a contribution from the nuclear spin diffusion. The nuclear term is presumably a constant while the electron spin diffusion is dependent on the applied magnetic field as described by Eq. (5.17). The value of $\Gamma_0$ has been extracted simultaneously with the power dependence coefficient $a$ from the best fit of the experimental data for each applied field. Figure 14 shows $\Gamma_0$ as a function of magnetic field. From Eq. (5.17), $\Gamma_0$ is expected to vary faster than a simple exponential function because of the field dependence of $g_{\text{eff}}$. This fast variation has not been observed. At 1.3 K, the data could not be fitted to Eq. (5.17) unless a much smaller activation energy was used instead of the real ground state Zeeman splitting. This indicates that the Boltzmann factor is an oversimplification for describing the electron spin flip-flops. Therefore, a more general theoretical model has to be developed. On the other hand, since the Zeeman splitting is larger than 12 cm$^{-1}$ for applied fields higher than 15 kG, the Tb$^{3+}$ spin diffusion mechanism is inhibited in high field.

The experimental result of the echo decay as a function of magnetic field with constant excitation intensity is shown in Fig. 15. The field dependence of the echo decay is due to the combined contributions from the electron spin diffusion and the instantaneous diffusion. At high field, the electron spin diffusion has a negligible effect on the echo decay. At low field, the Zeeman splitting of the ground state, $\Delta E=17.8\mu_B H_z$, is comparable with the temperature $kT$, thus the spin diffusion is the dominant contribution to the echo decay. Since the effective $g$-factor
Fig. 13. Theoretical value of power-dependence coefficient (solid curve) fitted to the experimental data from the photon echo experiment on Tb$^{3+}$:LiYF$_4$ at 1.3 K.
Fig. 14 Measured homogeneous line width $\Gamma_0$ as a function of the applied magnetic field. The data could only be functionally fitted to Eq. (5.17) with an activation energy which was two orders of magnitude smaller than the real Zeeman splitting of the ground state.
Fig. 15. Photon echo decay as a function of applied magnetic field parallel to the crystal c-axis. The second laser excitation intensity is 7 MW/cm² and temperature is 1.3 K.
The echo dephasing rate has been studied as a function of excitation frequency across the inhomogeneous line by using an etalon in the laser cavity. The laser line width was about 0.05 cm\(^{-1}\), which was 1/8 of the inhomogeneous line width. Unfortunately, the direct measurement of the decay time becomes very difficult due to an efficient spectral hole burning process, which will be described in Chapter 8. At a fixed excitation frequency, the echo signal was quickly extinguished by the optical pumping process. An alternative method has been used to avoid the hole burning process. At fixed delay times, the echo intensity was recorded as a function of frequency when the excitation was tuned across the inhomogeneous absorption line. In this way we found that the echo decay rate is higher in the line center at fixed excitation intensity. This effect becomes substantial at high excitation intensity.

**Summary of the Dephasing results**

The experiment-induced instantaneous diffusion causes "apparent" homogeneous line broadening, thus the "real" homogeneous line width determined by the intrinsic ion-ion interactions is obscured. In other words, the echo decay time is not the coherent relaxation time \(T_2\) of the two-level system due to the existence of the instantaneous diffusion. This effect becomes significant for any system in which the permanent moment changes substantially upon optical excitation, and \(1\%\text{Tb}^{3+}\text{.LiYF}_4\) is just such a system. We observed in this system that the instantaneous
diffusion dominates the echo decay rate in the presence of a high Zeeman field while other dephasing mechanisms such as electron spin diffusion are obscured. The magnetic dipole model and the basic characteristics of the photon echo sequence gave a clear explanation that the dephasing rate is linearly proportional to the intensity of the second excitation pulse and independent of the intensity of the first pulse.

Stimulated Photon Echoes

When the $\pi$ pulse in the two-pulse echo sequence is broken into two $\pi/2$ pulses by the insertion of a long delay $T$, the two-pulse sequence becomes a three-pulse sequence. The second pulse puts ions with in-phase coherence into the exited state, and the ions shift back into the ground state with an accumulation of $\pi$ phase. This accumulated phase information is then stored in the form of a population difference which is called a population grating in the ground state. This coherence can be read out by the third pulse until the population difference disappears.\textsuperscript{44,47,48} The signal of the stimulated echoes gives information about dephasing during the two $\tau$ delays and spectral diffusion or population decay during the $T$ delay. Therefore, the stimulated photon echo can in principle be used in the investigation of slow spectral diffusion.\textsuperscript{30,55} Furthermore, if the excited state population can relax to some long lived population reservoir such as metastable electronic states or hyperfine levels, an echo can be stimulated by a readout pulse so long as the population difference in the ground state persists.

Stimulated photon echoes have been dramatically observed in the
Fig. 16. Stimulated photon echoes from Tb$^{3+}$:LiYF$_4$ at 42 kG and 1.3 K. The population grating in the ground state is prepared by two pulsed lasers with the pulse separation of 30 nsec, then the stimulated echoes are read out by sending subsequent individual pulses the rate of 6 Hz.
dilute compound. The population grating can be rapidly built up in the ground state by the two-pulse sequence. Due to the population storage of the hyperfine levels in the ground state, the population grating can last a long time and echoes can be stimulated by a single pulse any time before the population distribution is obscured by spectral diffusion processes. Figure 16 shows the single-pulse stimulated echoes after the two-pulse sequences are stopped. Echoes can still be read out over 20 seconds after the build-up process is stopped. The calculated decay time of the population grating is 4.5 sec which is short compared with the hole lifetime 10 min measured by hyperfine spectral hole burning which will be discussed in Chapter 8. The reason for this is probably that the read-out pulse destroys the population grating as well as stimulating the echoes.

As a result of the observed long population storage time, the repetitions of the first two pulses accumulate a much larger population frequency grating than that from an individual pair of pulses. Thus, intense stimulated echoes can be generated by a read-out pulse. In addition to generating a two-pulse echo, each of the two normal laser pulses can act as read-out pulses to stimulate an echo from the grating which is built up. The stimulated echo read out by the second pulse is overlapped with the two-pulse echo if the separation time $t_d$ between the first two pulses is unchanged. This effect has also been demonstrated for this compound. However, the amplitude or intensity of the multiple echoes still reflects the coherent dephasing during the two evolution periods of time $\tau$ and thus can be used to measure $T_2$.30
CHAPTER 6

FREQUENCY-DEPENDENT DEPHASING IN LiTbF$_4$

In stoichiometric solids, there is a general belief that homogeneous optical dephasing is extremely fast due to interactions between neighboring ions which lead to energy transfer, excitonic behavior, and rapid spectral diffusion.\textsuperscript{30,10} Therefore, coherent dephasing measurements can provide a new fundamental means of characterizing the dynamics of these processes and can thus extract new information about the nature of ion-ion interactions and the effects of disorder.

The efficiency of energy transfer due to ion-ion interactions in solids is, at present, an active topic both experimentally and theoretically based in part on interest in the concepts of the Anderson transition and mobility edges associated with inhomogeneously broadened optical transitions.\textsuperscript{1-17} According to a theorem of Anderson,\textsuperscript{1} if the interactions between ions are sufficiently short ranged, the excitation will be localized below a critical concentration of ions and will be delocalized above this concentration. Localized and delocalized states may also be observed in a single sample, for example in a stoichiometric compound, as the excitation frequency varies across a mobility edge in the inhomogeneous line. In general, there are two mobility edges in an inhomogeneously broadened line, which separate the delocalized states in the center from the localized
states in the two wings of the line.

Recently, Jessop and Szabo\(^6\) performed a photon echo experiment in attempts to observe mobility edges for the R\(_1\) line in 0.1\% ruby following the earlier report of such an effect by Koo et al.\(^3\) They suggested that a change in homogeneous line width or coherence time T\(_2\) would occur as the system switched from localized states in the wings to delocalized states in the center of the inhomogeneous line. They found however, that T\(_2\) was independent of excitation frequency as it was varied across the inhomogeneous line for that dilute system. Their conclusion was that no Anderson transition occurs in low concentration ruby materials. Other work by Chu et al.\(^5\) led to similar conclusions. According to Huber and Ching,\(^7\) the Anderson transition should occur only at a concentration of around 10\% for ruby.

As briefly noted in Chapter 1, previous work on Tb\(^{3+}\) compounds has provided evidence of energy transfer processes due to short range interactions,\(^{10-14}\) which may satisfy the criteria for an Anderson transition. Exciton band theory has been used by Cone et al.\(^11\) to determine the interaction mechanisms for the observed energy transfer effects in Tb\(^{3+}\)(OH)\(_3\) and other compounds. To investigate the effects of the energy transfer in those Tb\(^{3+}\) compounds on the optical dephasing and to determine if an Anderson transition or mobility edges could be observed, we have carried out photon echo experiments on concentrated LiTbF\(_4\). Indeed, the observed sharp variation of the dephasing rate across the inhomogeneous line which is described below suggests a transition from delocalized states to localized states in the concentrated compound.

In addition to work addressing the Anderson transition, other
theoretical models have been developed for testing ion-ion interactions and the nature of optical line broadening. The quasiresonant interaction model proposed by Root and Skinner\textsuperscript{49} provided reasonable agreement with the frequency-dependent dephasing observed in Eu\textsuperscript{3+} compounds.\textsuperscript{50,80} This model has also been considered in our work to interpret the observed frequency-dependent dephasing in the concentrated compound.

Following the summary of our experimental results for LiTbF\textsubscript{4} in the next section, detailed discussions of the Anderson transition, the quasiresonant interaction model, and possible exciton dispersion effects are given. Finally, the results of additional experiments searching for evidence of exciton bands and demonstrating observation of short-ranged electronic super-exchange coupling in the same compound are presented.

**Summary of Results**

For the concentrated (stoichiometric) crystal LiTbF\textsubscript{4}, the results from our photon echo experiments indeed yield clear evidence that Tb\textsuperscript{3+-Tb}\textsuperscript{3+} interactions dominate the coherent dephasing processes. The dephasing is far more rapid than for the dilute 1%Tb\textsuperscript{3+}:LiYF\textsubscript{4} crystal; moreover, the decay of the photon echoes exhibited a strong frequency dependence as the excitation was tuned across the inhomogeneously broadened absorption line. Such a variation would not be expected for dephasing via familiar mechanisms such as phonons or magnetic field fluctuations. The speed and frequency dependence thus confirmed that these compounds were interesting ones for further study.

Under the condition of low intensity pulse excitation and for
temperatures below 2 K, this novel frequency-dependent dephasing behavior was first demonstrated by measuring the echo intensity across the absorption line at fixed pulse separations. Figure 17 shows these photon echo excitation profiles (solid curves) at 15 kG and 1.25 K for pulse separations of (a) 20 nsec and (b) 140 nsec. The dashed curves show synchronized measurements of the absorption coefficient which were recorded simultaneously. Similar echo profiles have been presented in a three dimensional plot in Fig. 18 with pulse separation as a parameter.

From these plots, one can qualitatively describe the dephasing behavior as a function of excitation frequency. It is clear that the relative echo intensity is not proportional to the number density which is characterized by the absorption coefficient (or its square). This means that the decay time constant varies across the absorption line. In each plot, all the echo intensity curves are normalized at an arbitrary point on the low frequency edge of the line. Below that point on the low frequency side, an increase of the relative intensity with the pulse time delay indicates that the echo decay is slower than that at the edge. Above the edge in the center of the line, the rapid decrease of the echo intensity with pulse time delay shows that the echo decay is much faster in the center of the line. Above the high frequency edge of the line, the echo was not observed even at 20 nsec pulse time delay, which means that echo decay is even faster in that region. From the center to this high frequency region, the echo decay seems slightly slower than that in the center of the line.

The variation of the excitation frequency in the experiments described above was accomplished by the magnetic field-sweeping technique
Fig. 17. Variation of echo intensity (solid curves) as a function of excitation frequency for two different pulse separations (a) 20 nsec, and (b) 140 nsec. The dashed curves are the absorption coefficient which was simultaneously recorded across the inhomogeneous absorption for the lowest $^7$F$_6$ to $^5$D$_4$ transition. The echo intensity has been normalized by a factor of $\exp(4t/200)$, where $t$ (nsec) is the pulse separation and 200 nsec is the dephasing time at the low frequency edge of the line.
Fig. 18. Echo intensity (solid curves), at 15 kG and 1.3 K, as a function of excitation frequency with pulse separation as a parameter, qualitatively illustrates the variation of dephasing rate across the absorption line. The dashed curves are the absorption coefficient which was synchronously recorded across the inhomogeneous absorption for the lowest $^7F_6$ to $^5D_4$ transition. The echo intensity has been normalized by a factor of $\exp(4t/200)$, where $t$(nsec) is the pulse separation and 200 nsec is the dephasing time at the low frequency edge of the line.
described in Chapter 4. In using that method, we have taken advantage of the large Zeeman effect for the optical transition between the $^7F_6 \Gamma_2$ and $^5D_4 \Gamma_1$ levels of the crystal. Within the inhomogeneous line, a specific ion may be excited either by varying the laser frequency to the resonant frequency of the ion or by varying the applied field to tune the resonant frequency of the ion to match the laser frequency. Therefore, varying the laser frequency across the inhomogeneous line at a fixed magnetic field is equivalent to sweeping the magnetic field to tune the resonant frequencies of the ions across the same region at a fixed laser frequency. For external fields higher than 10 kG, the Zeeman splitting becomes quite linear over the small range of the applied magnetic field needed for the field sweep. Since only a small change in the large applied field is required to tune the resonant transition across the inhomogeneous line, no significant effect on the dephasing time $T_2$ is caused by changing the field.

The dephasing time $T_2$ was also directly measured as a function of excitation frequency by scanning the time delay between the two excitation pulses at many different fixed excitation frequencies across the inhomogeneous line. Figure 19 shows the variation of the separately observed dephasing times $T_2$ across the absorption line. The dephasing time $T_2$ varies sharply from 60 nsec above the line center to over 300 nsec on the low frequency side. The variation of the dephasing rate $1/(\pi T_2)$ is apparently proportional to the absorption coefficient except on the high energy side. Figure 20 gives such a comparison, where the dashed curve is the absorption coefficient, and the solid points are experimental data which have been splined to a solid curve by the
Fig. 19. Observed dephasing time $T_2$ as a function of excitation frequency across the absorption line of $^7F_6 \Gamma_2$ to $^3D_4 \Gamma_1$ transition. The experimental data points are best fitted into a solid line.
Fig. 20. Comparison of experimental dephasing rate with the absorption coefficient for $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ transition. The experimental data points have been splined by computer as shown by the solid curve, and the dashed curve is the measured absorption coefficient.
computer. The proportional relationship of the dephasing rate to the inhomogeneous line shape is expected from the microscopic model of quasiresonant interaction formulated by Root and Skinner. The decrease in $T_2$ as the excitation approaches the line center has to do with Tb$^{3+}$-Tb$^{3+}$ interactions. Near the absorption line center the effective concentration of the Tb$^{3+}$ ions with resonant frequencies near the laser frequency is high, so the resonant ion-ion interactions lead to faster energy transfer and consequently to faster coherent phase relaxation. In the wings of the line, the effective concentration of Tb$^{3+}$ ions is lower, so the excited Tb$^{3+}$ ions do not interact as effectively, and the dephasing time becomes longer. The detailed comparison of the microscopic quasiresonant interaction model with a numerical fit to our experimental data will be given in a later section of this chapter.

The dephasing behavior has also been studied as a function of temperature and magnetic field. The observed dephasing time was independent of temperature in the region of 1.2 to 2.1 K as shown in Fig. 21. On the other hand, these results are consistent with the field dependence described below. It was found that the dephasing time was affected by the applied magnetic field only at low fields (<10 kG). The dephasing exhibited the same frequency-dependent behavior over a large range of the magnetic field from 16 kG to 38 kG. This result is shown in Fig. 22 where the observed homogeneous line width ($1/\pi T_2$) at three different applied magnetic fields of 16 kG, 24 kG and 38 kG has been plotted as a function of excitation frequency across the absorption line. The dephasing rate is independent of the applied magnetic field in this region. This temperature and field dependence is consistent with
Fig. 21. Photon echo decay time $T_2$ of LiTbF$_4$ as a function of excitation frequency varying from the low frequency side across the line center at two different temperatures 1.2 K and 2.1 K. The applied magnetic field is 34 kG. The decay time is apparently temperature independent at this field.
dephasing by quasiresonant energy transfer but would be incompatible with dephasing by other mechanisms as we note below.

This field-independent behavior is qualitatively different from the strongly field-dependent dephasing in the 1% Tb$^{3+}$:LiYF$_4$. In the dilute compound, as shown in the previous chapter, the novel frequency-dependent dephasing behavior is absent. In the dilute compound the dephasing time is two to three orders of magnitude slower than that in the concentrated compound, and the dephasing is dominated by magnetic dipole-dipole interactions which cause electron spin diffusion in the ground state and instantaneous diffusion arising from the change in magnetic moment of the Tb$^{3+}$ ions during optical transitions, between the ground and excited states. Since these magnetic dipole effects are strongly field dependent, the field-independent dephasing in the concentrated compound indicates that those mechanisms are not responsible for the observed dephasing rate. This leads thus to a conclusion that, in the concentrated compound LiTbF$_4$, shorter range interactions such as electronic superexchange coupling and electronic multipolar coupling significantly contribute to the dephasing processes and cause the strongly frequency-dependent dephasing behavior.

At very low fields, both the electron spin diffusion and the instantaneous diffusion become significant and have a similar contribution to coherence decay compared to the energy transfer effect. Therefore, in the energy transfer studies, an applied magnetic field is necessary for reducing the dynamical perturbations of the local fields. According to Anderson$^{93}$, if the homogeneous line width due to phonon broadening or the perturbations of the local fields is comparable to the interaction
responsible for the excitation diffusion, then it is reasonable to expect that an Anderson transition will not occur.\(^6\)

The echo decay time on the high energy side was too short to be measured with the 5 nsec pulses. From the echo excitation profiles, we found that the dephasing was significantly faster than the dephasing on the low energy side. This asymmetric dephasing behavior cannot be interpreted by the Anderson model. There must be some other dephasing mechanisms involved, which may also be responsible for the asymmetric absorption line shape. Two possibilities have been considered which will be discussed in later sections of this chapter.

**Anderson Transition**

According to Anderson's theorem,\(^1\) if the interaction between lattice centers (ions or molecules) has a sufficiently short range, excitations will be localized below a critical concentration of the ions and will be delocalized above this concentration. In Anderson's model,\(^1\) the active lattice centers are randomly distributed, and the transition energy of a center varies randomly from site to site. This randomness in energy gives an inhomogeneous line width \(\delta\). An excitation at site \(i\) can be transferred to site \(j\) due to the interaction between \(i\) and \(j\) which is characterized by \(V_{ij}(r_{ij})\). The probability that the excitation resides on site \(i\) at time \(t\) is written \(a_i(t)\). Initially, \(a_i(t)=1\) and the value of \(a_i(t)\) at a later time is calculated. If \(<|a_i(\infty)|^2>_AV\neq 0\) the excitation is said to be localized. If \(<|a_i(\infty)|^2>_AV=0\) the excitation is said to be delocalized. Anderson's conclusion is that if \(V_{ij}(r_{ij})\) falls off faster than \(1/r^3\), then there is a
critical concentration of centers below which transport cannot take place and the excitation is localized. The criterion for localization is

$$\frac{\delta}{V} \geq -2,$$

(6.1)

where $V$ is the average interaction between adjacent centers. $V$ increases as the average separation between adjacent centers decreases. As the concentration of centers reaches a critical value above which the criterion no longer holds then the excitation becomes delocalized. Indeed, the excitation will undergo an abrupt change from a localized state to a delocalized state when the concentration increases through the critical concentration.

Mott$^2$ and others$^{94,95}$ have extended Anderson's idea to the case where the concentration is above the critical value. In an inhomogeneously broadened line, the site-energy distribution varies from low to high as the excitation frequency moves from the wings to the center of the inhomogeneous line. This frequency distribution may be considered as a "concentration distribution" as well. Excitations at the line center can be delocalized if short range interactions exist to quasi-resonantly transfer the excitation among the sites with that energy, and the excitation might be localized in the wings of the line because the effective concentration is below the critical value. There are bounds called mobility edges which separate the delocalized states in the center from the localized states in the wings. The demonstration of mobility edges would be indicative of an Anderson transition.
Combining the experimental results from the dilute and the concentrated compounds suggests that the observed fast dephasing is due to energy transfer. The sharpness of the variation suggests a possible Anderson transition from the delocalized states in the center to the localized states in the wings of the inhomogeneous line in LiTbF$_4$. That is, the sharp change in $T_2$ could indicate a mobility edge.

As demonstrated recently,\textsuperscript{11-13} delocalization of optical excitations in terbium compounds is primarily due to short range interactions between Tb$^{3+}$ ions. This leads to strongly delocalized states in the main region of the absorption line and consequently to a shorter value of $T_2$. The position in the inhomogeneous line where $T_2$ suddenly changes to a longer value perhaps corresponds to the frequency at which this delocalization is inhibited. This position would then be a mobility edge which separates the delocalized states at the center of the absorption line from localized states at the low energy wing.

However, the above interpretation may not be consistent with the experimental observations on the high energy side. Phonon-assisted energy transfer is considered later in this chapter, but it cannot quantitatively explain the dephasing on the high energy side. Another important feature which could certainly be involved in the echo decay behavior on the high energy side is that the absorption line shape is asymmetric. That feature is not yet understood either. The experimental line shape could possibly indicate that there are two overlapping lines rather than a single broadened line. Since there are two ions per unit cell, a Davydov splitting\textsuperscript{81} is expected for this compound, so the second line on the high energy side could be a weaker remnant of the second Davydov component.
which will be discussed in a later section in this chapter. If this is true, the energy dispersion in the exciton bands could dramatically affect the coherence dephasing, and the non-radiative transition from the upper band to the lower band of the Davydov splitting could perhaps explain the short $T_2$ on the high energy side. Before considering the details of the exciton band effects, an alternative interpretation of the observed frequency-dependent dephasing is presented in the following section.

**Quasiresonant Interactions**

Root and Skinner,⁴⁹ and others,⁴⁵ have formulated a theory of photon-echo decay due to quasiresonant interactions in substitutionally disordered crystals. This theory can be alternatively used to interpret the frequency-dependent dephasing without directly addressing the Anderson transition. According to Skinner,⁹⁶ the coherence decay information from photon echo measurements is probably not sensitive to Anderson localization since the Anderson model is usually taken to mean that excitations are localized or delocalized over macroscopic regions, and the dephasing only depends on local environments or nearby interactions and can occur without any substantial population transfer.

Nevertheless, coherence dephasing is quite sensitive to ion-ion interactions. Moreover, the quasiresonant model can test the neighboring site-energy correlation, and it predicts frequency-dependent echo decay. Analyzing the dephasing data along with this model can thus yield information about the strength of the intrinsic interactions and the nature of the inhomogeneous broadening.
In the quasiresonant-interaction model, one assumes that the dephasing is due to the interactions between the nearby ions which have the same or very close resonant frequencies. Two limiting cases of "macroscopic" and "microscopic" inhomogeneous broadening have been discussed by Root and Skinner. In the limit of macroscopic broadening the system consists of large domains of resonant ions; dephasing is produced by resonant interaction within domains. In the limit of microscopic broadening the site-energies are completely uncorrelated. In this case dephasing is due to quasiresonant interactions between nearby ions in both space and frequency. With the assumption of electric dipole-dipole coupling, the microscopic inhomogeneous broadening model has given a reasonable agreement with the experimental results from EuP$_5$O$_{14}$ and Eu$^{3+}$:Y$_2$O$_3$, while the calculated dephasing rate resulting from the macroscopic inhomogeneous broadening model is independent of excitation frequency.

The dephasing rate for the concentrated crystal LiTbF$_4$ has been calculated by following previous work of Root and Skinner and fitted to the experimental data with the assistance of Skinner. Without considering phonon broadening, an assumption which is appropriate at low temperature, the interaction Hamiltonian can be written in terms of a diagonal inhomogeneous distribution and off-diagonal intrinsic interactions,

$$H = \sum_i \hbar \omega_i |i\rangle\langle i| + \sum_{ij} V_{ij} |i\rangle\langle j|,$$  (6.2)

where $|i\rangle$ is the single-ion (ground or electronic excited) state of the $i$th site. The excitation frequency at site $i$ is $\omega_i = \omega_0 + \delta_i$, where $\omega_0$ is the
central excitation frequency of the inhomogeneous line, and $\delta_i$ is the inhomogeneous deviation which is characterized by a distribution function $P(\delta_i)$. The interaction matrix element $V_{ij}$ between sites $i$ and $j$ is responsible for the homogeneous dephasing and the energy transfer processes. The summations are over all sites occupied by the optically active ions with $i \neq j$.

The basic restriction of this model is that the intrinsic interactions $V_{ij}$ are much smaller than the inhomogeneous broadening $\delta$, so the eigenstates in the system are assumed to be localized. Applying the Hamiltonian in Eq. (6.2) to solve the Liouville equation of Eq. (3.7) for the density matrix as a function of time, with the method of moments,\(^{38}\) the resulting echo intensity decays exponentially,\(^{49}\)

$$I(t) = \exp[-2\pi P(\omega)\sum_j (V_{ij})^2 t], \quad (6.3)$$

with a dephasing rate constant

$$\frac{1}{T_2(\omega)} = 2\pi P(\omega)\sum_j (V_{ij})^2, \quad (6.4)$$

where the normalized distribution function $P(\omega)$ is defined by

$$P(\omega) = \frac{\alpha(\omega)}{\int_{-\delta}^{\delta} \alpha(\omega) d\omega}, \quad (6.5)$$

and where $\alpha(\omega)$ is the absorption coefficient. For a particular system,
Fig. 22. Theoretical curve (solid) for homogeneous line width in LiTbF$_4$ calculated from Eq. (6.4) by varying the parameters $A$ and $\Gamma_0$ to fit the experimental data for three different measurements at 16 kG, 23 kG, and 37 kG, as a function of excitation frequency across the inhomogeneous line.
the summation in Eq. (6.4) is a constant, thus the dephasing rate is proportional to the height of the inhomogeneous distribution at the excitation frequency. In the center of the line, there are more ions with resonant frequencies near the excitation frequency, that is, an ion at the center of the line has more nearly resonant neighbors than do ions in the wings. This result qualitatively agrees with the observed echo decay rate except for the data on the high energy side.

To fit the echo decay data with Eq. (6.4), additional contributions from the perturbation of local fields and phonon broadening must be included. Without addressing phonon-assisted excitation transfer which could be frequency dependent and which we consider later, the contribution from the perturbation of the local fields can be approximated as a constant $\Gamma_0$, thus the homogeneous line width can be expressed as

$$\Gamma(\omega) = A\rho(\omega) + \Gamma_0,$$

(6.6)

where $\rho(\omega)$ is the normalized absorption coefficient measured with a narrow-band laser scanning across the inhomogeneous line, and the quantities $A=2\Sigma_j(V_{ij})^2$ and $\Gamma_0$ are parameters to be fitted. Figure 22 shows the result in which the calculated line width is best fitted to the observed values at three different magnetic fields. The fitted parameters are $\Gamma_0=0.5$ MHz, and $A=260$ (MHz)$^2$. For numerical estimation of the neighboring ion coupling strength $V$, the dephasing mechanism has been assumed to be dipole-dipole coupling and a simple cubic lattice structure has been assumed. In that case,
\[ A = 2(13.3)V^2, \quad (6.7) \]

and \( V=1 \text{ MHz} \), which is indeed much smaller than the inhomogeneous line width \( \delta=9 \text{ GHz} \). Therefore, the initial assumption of the model \( V<<\delta \) is satisfied. The constant \( \Gamma_0 \) presumably represents the contribution from the fluctuation of local fields of the host nuclear spins and the electronic spin flips in the ground state.

However, the question of what mechanism causes the fast dephasing on the high energy side remains. We now consider the possible role of spontaneous phonon emission processes. An excitation on the high energy side could transfer to a lower energy site and the energy mismatch could be released in the form of a phonon or phonons. As a result, the dephasing rate on the high energy side of the line would be faster since there are many acceptor ions with lower energy, but the dephasing rate on the low energy side of the line would be slow since in that case there are not many acceptors with lower energy. Thus an asymmetric dephasing rate across the inhomogeneous line is expected. In addition to spontaneous phonon emission, thermal phonons could assist the energy transfer both ways. Assuming only one phonon processes, the lifetime of an excitation as a function of excitation frequency across the inhomogeneous line has been calculated using the following equation.\(^97\)

\[
\frac{1}{T_1(\omega)} = b\Sigma(V_{ij})^2 \int_v \int_{\omega'=0}^{\infty} \rho(\omega+\omega')|\omega'||^3 d\omega'P(\omega+\omega')n(\omega') \text{l} + \int_{\omega'=0}^{\infty} \int_{\omega=0}^{\infty} \rho(\omega+\omega')|\omega'||^3 n(\omega')n(\omega') \text{l} \]

\[ (6.8) \]
where the constant $b$ depends on the Debye frequency of the crystal, and

$$n(T, \omega) = \frac{1}{\exp(h\omega/kT) - 1}$$

is the phonon density distribution function which is zero at $T=0$. The first term in Eq.(6.8) represents pure spontaneous phonon emission which is clearly larger for the frequencies $\omega$ on the blue side and is temperature independent. The second term in Eq.(6.8) stands for the thermal-phonon-assisted energy transfer. For temperatures in the range 1-2 K, $kT$ is comparable with the inhomogeneous line width, thus the second term will increase on both sides. Adding the phonon-assisted dephasing, Eq.(6.6) becomes

$$\Gamma(\omega) = AP(\omega) + \frac{1}{2\pi T_1(\omega)} + \Gamma_0. \quad (6.10)$$

Equation (6.10) has been fitted with the observed echo decay data and the experimental absorption coefficient by varying the parameters $A$, $b$, $T$ and $\Gamma_0$. Adjusting the parameter $b$, the experimental data could be fitted only by introducing a temperature $T$ far below the actual value of 1.3 K; otherwise the calculated value on the low energy side would deviate from the experimental data. Therefore, this one-phonon model was not successful for interpreting the asymmetry in the echo dephasing rate of this system. That problem is considered further in the next section.
So far the excited states of Tb$^{3+}$ ions have been considered either in the single ion picture as is generally done with rare earth ionic crystals or as disordered coupled ions. We now consider the alternate case where the ion-ion coupling is large compared to the inhomogeneous broadening. In that case, the ion-ion interactions lead to cooperative excitations where the eigenstates of a crystal are exciton bands with the electronic excitation energy shared by all the ions in the crystal.$^{39,42,77}$ In this case, the excited state energy migrates through the crystal as an excitation is transferred from one site to another.$^{11-14}$

In the single ion picture, the wave function $|\mu_j\rangle$ of an excited state is defined such that all the ions are in the ground state except that ion $j$ is in excited state $\mu$. Thus, $|\mu_j\rangle$ is an eigenstate of the single-ion Hamiltonian $H_j$ which includes all the intrinsic static interactions such as Coulomb interaction, spin-orbit coupling, crystalline field, and interaction with external fields.

In the concentrated crystal LiTbF$_4$, there are two ions in each unit cell, as seen in Fig. 2. Consider the crystal consisting of $N$ unit cells, the single ion product states can be expressed as$^{10}$

$$|\mu_{nj}\rangle = |g_{11}g_{12}...|_{nj}...g_{N2}\rangle,$$ (6.11)

where $g_{nj}$ and $\mu_{nj}$ represent the jth ion on nth unit cell are in the ground state and the excited state, respectively. Since all the sites are equivalent, there are $2N$ such states having the same energy. As the wave
functions of the crystal have to be consistent with the translational symmetry of the crystal, one can define the new crystal wave functions as linear combination of the single ion product states

\[ |\mu_{kj}\rangle = N^{-1/2} \sum_n e^{-i\mathbf{k} \cdot \mathbf{R}_n^*} |\mu_{nj}\rangle, \tag{6.12} \]

where \( \mathbf{R}_n^* \) is the lattice translation from the origin to the \( n \)th unit cell, and \( \mathbf{k} \) is a vector in the reciprocal space. This is known as the Bloch wave function for the crystal. Since \( \mathbf{R}_n^* \) has \( N \) possible values and \( j=1,2 \), there are still \( 2N \) degenerate states. This degeneracy is removed if one takes into account the off-diagonal ion-ion interactions. As defined in Eq. (6.2), the off-diagonal interactions \( V_{mj,nl} \) are responsible for the excitation transfer. The matrix elements between the states can be calculated with the Bloch wave functions. Note that the matrix elements between states differing in \( \mathbf{k} \) are zero because they belong to different irreducible representations. As a result, the matrix reduces to \( N \) 2-dimensional matrices, each of which has elements

\[ H_{jl} = \sum_{m,n} e^{i\mathbf{k} \cdot (\mathbf{R}_m^* - \mathbf{R}_n^*)} \langle \mu_{mj} | V_{mj,nl} | \mu_{nl} \rangle. \tag{6.13} \]

In principle the summation is over all unit cells, but if the interactions are short ranged, it is often adequate to include only nearest neighbor interactions. For each value of \( \mathbf{k} \), therefore, there are two excitation energy values which can be calculated by the 2X2 matrix diagonalization.
where $H_{11}(k^\parallel)$, $H_{22}(k^\parallel)$ include interactions among ions on the same sublattices and $H_{12}(k^\parallel)$, $H_{21}(k^\parallel)$ involve interactions among ions on the two different sublattices. The equivalence of the two sublattices requires that $H_{11}(k^\parallel)=H_{22}(k^\parallel)$, and $H_{12}(k^\parallel)=H_{21}^*(k^\parallel)$. The resulting eigenvalues are

$$E_{\pm}(k^\parallel) = E_0 + H_{11}(k^\parallel) \pm |H_{12}(k^\parallel)|,$$

(6.15)

where $E_0$ represents the single-ion energy of the exciton band. For a large crystal, the adjacent values of $k^\parallel$ differ little from one another, so the $N$ values of the excitation energy form two quasi-continuous bands of excited states. The energy difference between the two bands at $k^\parallel=0$ is known as the Davydov splitting.

In LiTbF$_4$, a Tb$^{3+}$ ion has four nearest neighbors (nn) which belong to a different sublattice and four next nearest neighbors (nnn) which are on the same sublattice. Including these nn and nnn ion interactions, the matrix elements in Eq. (6.15) can be written as

$$H_{11}(k^\parallel) = H_{22}(k^\parallel) = 2V_2 [\cos(k_x a) + \cos(k_y a)]$$

(6.16)

$$|H_{12}(k^\parallel)| = 2V_1 [2\cos(k_x a/2)\cos(k_y a/2)\cos(k_z c/2)$$

$$+ \cos^2(k_x a/2) + \cos^2(k_y a/2)]^{1/2},$$

(6.17)
where \( V_1 \) and \( V_2 \) are the nn and nnn interaction matrix elements, respectively, and \( a=5.2 \, \text{Å}, \, c=10.89 \, \text{Å} \) are the crystal lattice constants.

Since the ion-ion interactions are strongly dependent on distance, the nnn interactions may be much weaker than those of the nn ions, and presumably the line shape of the optical transitions is determined primarily by the nn interactions, particularly for short range interactions. Unlike \( \text{Tb(OH)}_3 \) in which the nn interaction element \( V_1 \) gives the amplitude of diagonal terms \( H_{11}(k^3) \) and \( H_{22}(k^3) \),\(^{11}\) the nn element of \( \text{Tb}^{3+} \) ions in \( \text{LiTbF}_4 \) determines the Davydov splitting as well as the energy dispersion of the exciton bands. At \( \vec{k}^2 = 0 \), the Davydov splitting is

\[
\Delta E = 2|H_{12}(0)| = 8V_1. \tag{6.18}
\]

The possibility that the two-peak inhomogeneous absorption line, as seen in Fig. 19, could arise from transitions to the two bands of the excited states \( \vec{k}^2 = 0 \) is intriguing. In that case the spectrum would directly reveal the Davydov splitting. It should be noted, however, that electric dipole transitions are restricted to only one band due to the crystal symmetry. On the other hand, the inhomogeneity of the crystal may partially break this selection rule and allow a weak remnant of the transition to the other band.

Figure 23 schematically shows the Davydov splitting for the hypothetical case \( V_1=0.025 \, \text{cm}^{-1} \) and \( V_2=0.006 \, \text{cm}^{-1} \) and describes the energy dispersion \( E_{\pm}(k^3) \) calculated using Eq.(6.16) and Eq.(6.17) along the (111) and (101) directions in the first Brillouin zone of the k-space.

The excitons have dispersion along all directions in the k-space. In
a fluorescence experiment, all the energy states could be occupied after an initial $\vec{k}^z = 0$ excitation. Thus, in the fluorescence emission, a continuous band could be observed instead of a single line. A broad band fluorescence emission from the excited state to a $^7F_5$ level would then be a direct demonstration of the energy dispersion. Alternatively, the exciton band could be probed via the $\vec{k}^z \neq 0$ absorption spectrum from the upper Zeeman component of the ground state. Both of these methods have been used in attempts to see the exciton dispersion. The fluorescence experiments yielded no conclusive evidence. The absorption experiments are discussed in the following section.

**Exchange Splittings and the Search for Exciton Band Effects**

In order to seek alternate evidence for exciton band states, the line shape of the transition from the upper component of the ground state has been compared to the $\vec{k}^z = 0$ transition from the lower component. The so-called magnon band is about 5 cm$^{-1}$ higher than the lower component due to the Zeeman splitting in the internal molecular field for this ferromagnetic material. For that band-to-band transition all $\vec{k}^z$ values are allowed; thus, the absorption line would exhibit the band structure.

Due to the Zeeman splitting in the internal field, the upper component was 4-5 cm$^{-1}$ higher than the lower component, so the upper level was not well populated in this temperature region. The absorption experiment from the upper component of the ground state $^7F_5$ to the excited state $^5D_4 \Gamma_1$ was thus made on a much thicker crystal with a thickness of 0.3 mm. The experiments covered the temperature region 1.2
Illustration of Davydov splitting in the excited state $^5D_4$ of LiTbF$_4$ with given values of $V_1=0.025$ cm$^{-1}$ and $V_2=0.006$ cm$^{-1}$ in the Eq. (6.15). The energy dispersion in the exciton bands along (111) and (101) directions in k-space is calculated from Eq. (6.16) and Eq. (6.17) with the given values of $V_1$ and $V_2$. 
K to 2.3 K, without an external magnetic field. The absorption coefficient and the fluorescence intensity were synchronously recorded. The reflection from the back surface of the sample was detected as the transmitted beam to obtain a higher ratio for the absorption, as in this way the beam passed through the sample twice. Absorption from the excited magnon state was also monitored by recording the intensity of the yellow fluorescence of $^5D_4 \Gamma_1$ to $^7F_5 \Gamma_{3,4}$ at frequency 18442 cm$^{-1}$.

Figure 24 and Figure 25 show the observed absorption and emission, respectively, as a function of excitation frequency with temperature as a parameter. The two spectra yield similar information about the line shape which varies dramatically as a function of the temperature. The spectrum consists of a main line and several additional lines. Those lines are dramatically broadened at high temperatures and are inhibited at low temperatures. These effects have been attributed to coupling to the neighboring ions. The overall splitting is often known as the exchange splitting of the ground state. The extra lines arise from various excited spin clusters, which are thermally populated. These phenomena were first realized in rare earth compounds by Bleaney et al.\textsuperscript{98} and later by Prinz.\textsuperscript{99} They have been extensively discussed by Leask,\textsuperscript{100} Hufner,\textsuperscript{22,101} and Cone and Meltzer.\textsuperscript{10}

The shift of the main line is due to the ferromagnetic ordering and approximately obeys the following equation from molecular field theory,\textsuperscript{102}

\[
\frac{\Delta}{\Delta_0} = \tanh \left( \frac{\Delta/\Delta_0}{T/T_c} \right)
\]  

(6.19)
Fig. 24. Absorption line shape for the magnon-exciton transition of $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ in LiTbF$_4$ with temperature as a parameter at zero external field. All four spectra have the same vertical scale and the energy axis is measured relative to the transition energy from the lower component of the ground state.
Fig. 25. Excitation line shape for the magnon-exciton transition of $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ in LiTbF$_4$ with temperature as a parameter at zero external field. The fluorescence is the emission from the excited state to $^7F_4 \Gamma_{3,4}$ at frequency of 18442 cm$^{-1}$. All four spectra have the same vertical scale and the energy axis is measured relative to the transition energy from the lower component of the ground state.
with $T_c = 2.874$ K, and $\Delta_0 = 5$ cm$^{-1}$.

There are two measurable lines on the high frequency side which have separations $d_1 = 0.6 \pm 0.05$ cm$^{-1}$ and $d_2 = 0.3 \pm 0.05$ cm$^{-1}$, respectively. The relative intensities of these lines were strongly dependent on temperature as expected by the Boltzman factor.

In general, the effect of the magnetic moments of the ions in a crystal can be approximated by an average internal field. This gives a reasonable description of the energy splittings or shifts for magnetic ions in many stoichiometric compounds. However, the crystal is made up of distinct ions each with a magnetic moment. The individual interactions of the nearest and next nearest neighbors of course have the most significant effect on the energy shift. Any variation of the spin configuration of the near neighbors can lead to a resonant frequency shift of the optically excited ion. Since there are only a few probable ways to vary the neighborhood spin configurations, the line is split into multiple lines rather than a continuous distribution.

At low temperature, the ground state of Tb$^{3+}$ ions in the compound LiTbF$_4$ is a very good approximation to an Ising system with $g_\parallel = 17.8$ and $g_\perp = 0$. All the magnetic dipole moments are either parallel or antiparallel to each other along the crystal c-axis. The couplings of the Tb$^{3+}$ ions include the magnetic dipole-dipole interactions (MDD) in addition to near neighbor exchange interactions. The MDD interaction is of course a long-range interionic interaction, which at high temperatures will tend to average to zero at any ion site. The short-range exchange interaction involves only nearby ions. The interaction Hamiltonian between site i and j can be written as
\[ H = A_{ij} s_{iz} s_{jz} + B_{ij} s_{iz} s_{jz}, \]

where \( A_{ij} \) is the exchange coupling parameter, and \( B_{ij} \) is the MDD coupling parameter which can be exactly calculated for the known crystal structure of the compound.

\[ B_{ij} = \frac{(1-3\cos^2 \theta_{ij})\mu_B^2 g_i^2}{r_{ij}^3} \quad (6.21) \]

where \( r_{ij} \) is the distance between site \( i \) and \( j \), \( \theta_{ij} \) is the angle from the \( z \) axis to the line joining site \( i \) and \( j \), and \( \mu_B \) is the Bohr magneton.

At very low temperature, an ion at site \( i \) in the upper component of the ground state with \( s_z = 1/2 \) is surrounded by neighbors all of which are in the lower component with \( s_z = -1/2 \). This is the most probable case as the temperature is raised, and thus it is often called a single-ion transition. One thus observes a strong narrow line shifted by the combined effect of the neighbors. When one of its neighbors is also in a thermally populated spin-down state, the resonant frequency has a shift

\[ \Delta \omega_i = (B_{ij} s_{iz} + A_{ij} s_{iz}) \Delta s_{jz} = \frac{B_{ij} + A_{ij}}{2}. \quad (6.22) \]
The excitation at the shifted frequency is called a pair transition. The population of the ion-pairs decreases much faster than the single-ion population as the temperature decreases, thus the relative intensity of the side lines decays faster than the main line. It is interesting to note that the shift has a negative sign if the transition is from the lower component. In that case all neighbors are in the spin-up state except one which is the spin-down state, so the frequency shift becomes

$$\Delta \omega_1 = -\frac{B_{ij} + A_{ij}}{2}.$$  \hspace{1cm} (6.23)

The calculated MDD contribution to the splittings due to the first six types of neighbors sets are listed in Table 6.\textsuperscript{103} The nn pairs and the 4th nn pairs have a negative effect on the energy splitting and should give side lines on the high frequency side. The three small splittings of the 3rd, 5th and 6th neighbors would be obscured by the main line. The splitting due to the second nn pairs has not been observed, since this splitting shifts the energy of the ion to the high energy side, and it is then not as favored by the Boltzman factor as are the two observed side lines on the low energy side.

It is important to note that the MDD splitting due to the 4th nn pair is in reasonable agreement with the observed value, and that the splitting due to the first nn pairs is $0.14 \pm 0.04 \text{ cm}^{-1}$ larger than the observed value. The difference is then due to the exchange interaction, thus the exchange parameter $A$ has the value of $0.28 \text{ cm}^{-1}$.

At low temperature, the excited spin configurations tended to be
Table 6. Energy level splitting due to the neighboring ion-ion interactions in the ground state of LiTbF₄.

<table>
<thead>
<tr>
<th>Type of nn pair</th>
<th>number of pair</th>
<th>calculated splitting</th>
<th>MDD (cm⁻¹)</th>
<th>observed splitting (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>4</td>
<td>-0.74</td>
<td>-0.6±0.04</td>
<td></td>
</tr>
<tr>
<td>2nd</td>
<td>4</td>
<td>+0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd</td>
<td>8</td>
<td>+0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4th</td>
<td>8</td>
<td>-0.26</td>
<td>-0.3±0.04</td>
<td></td>
</tr>
<tr>
<td>5th</td>
<td>4</td>
<td>+0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6th</td>
<td>4</td>
<td>+0.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

inhibited. Only the main line for the single-ion transition remained. The width of the main line was about equal to the line width of the ground state $\mathbf{K}^z = 0$ absorption, so that the exciton band effect was not revealed. On the other hand, the exciton dispersion could be around 0.1 cm⁻¹ and still not be observable in these line shape measurements. Thus, while exciton band effects are not completely ruled out by these experiments, they seem too small to explain the asymmetric absorption line shape or the frequency-dependent dephasing observed on the high energy side of the line.

Another potential interpretation for the asymmetry of the line involves the magnetic interaction of neighboring Tb³⁺ ions in the ground state. The energy splittings due to the magnetic dipole-dipole interaction plus the nearest neighboring exchange interaction between the Tb³⁺ ions have been observed in transition from the upper ground state component. At low temperature the energy splittings saturated, and the line shape of single-ion excitation was asymmetric with a line shape which was mirror
reflection of the line shape for the lower component excitation. Even in
the presence of a large external magnetic field, the exchange interaction
and the spin excitation process could still broaden the absorption line.
Further line shape calculations may fit the asymmetric line shape and yield
a complete understanding of the fast dephasing on the high energy side.

In summarizing this chapter, we have observed strongly frequency-
dependent dephasing due to short range ion-ion interactions in the
concentrated compound. To interpret our experimental results, the
Anderson transition, the quasiresonant interaction model in addition to
phonon-assisted energy transfer, and exciton band dispersion have been
considered. No exclusive connection with any one of these theoretical
models has been proved; however, the quasiresonant model indicates a
dramatic sensitivity of photon echo measurement to energy transfer effects
as small as 1 MHz in these compounds.

Further coherence measurements on Tb(OH)$_3$ are suggested for
determining the effect of energy transfer processes on coherence dephasing
since in that compound where the energy transfer processes and the
interaction mechanisms are all previously determined. Echoes in Tb(OH)$_3$
have already been observed in the two wings of the $^{7}F_6$ to $^{5}D_4$ transition
in an optically thick (20 μm) sample. This sample was still so thick that
the whole laser beam was absorbed at the center of the line. The
observed echoes in the two wings exhibited similar decay properties. That
means that the unexplained asymmetry present in LiTbF$_4$ will not be a
factor in this compound. Unfortunately, attempts to make a thin sample
for completing the last step in this series of photon echo experiments have
not yet succeeded.
CHAPTER 7

SUPERHYPERFINE INTERACTIONS IN Tb$^{3+}$:LiYF$_4$
PROBED VIA PHOTON ECHO MODULATION

The previous two chapters have been devoted to discussions of the ion-ion interactions and the dynamical effects of the interactions between the echo ion and its environment. As discussed there, the photon echo decay rate directly measures the optical dephasing or homogeneous line width of the resonant optical transition. In this chapter another important feature of spectroscopy — static optical line splitting is presented through deconvolution of the modulation of the photon echo spectra.$^{52-55,60}$ As discussed in Chapter 3, echo modulation is observed in a quasi-two-level (QTL) system in which the ground and the excited states are split into sublevels by hyperfine or superhyperfine interactions.$^{52-60}$

Since the photon echo signal is simultaneously sensitive to both the eigenfunctions and the eigenfrequencies of the interaction Hamiltonian, the deconvolution of the echo modulation spectra may result in a more accurate and complete determination of the model Hamiltonian.$^{55-60}$ This is an advantage of echo spectroscopy over conventional hyperfine spectroscopy techniques which usually measure only frequencies. Frequency information may not be sufficient to test the correctness of the model Hamiltonian. For instance, in the spin echo electron-nuclear-
double-resonance (ENDOR) studies of ruby, a more general Hamiltonian used by Liao and Hartmann\textsuperscript{59} resulted in only a 3\% change of the Al resonance frequencies compared with a simpler Hamiltonian used by Laurance et al.,\textsuperscript{104} but it produced large changes in the echo modulation.

Superhyperfine interactions (SHFS) between the rare earth ions and the fluorine and lithium nuclei in rare-earth fluorides have been classically studied in NMR experiments by measuring line shifts of the nuclear magnetic resonance.\textsuperscript{105,106} These studies found that the superhyperfine interactions make the local field lower than the applied field. The Li shifts are dominated by dipole interactions, whereas the F shifts also have comparable contributions from the SHFS interactions between the rare earth ion and the F nuclei.

Using the Tb\textsuperscript{3+} eigenfunctions for the ground and the excited states, the interaction Hamiltonian, which contains crystal-field splittings, the electronic Zeeman interaction, and hyperfine interactions, the echo modulation spectra can be deconvoluted with a regression-analysis procedure by treating the superhyperfine interactions between the echo ion and the surrounding nuclei as a perturbation. This regression analysis yields both eigenfunctions and eigenfrequencies as functions of the interaction parameters of the model Hamiltonian. These parameters are evaluated in the regression analysis and the correctness of the model Hamiltonian can be tested by doing the same regression analysis at different external fields. In the end, this gives a complete understanding of the observed echo modulation as a function of field and gives a quantitative description of the SHFS in this material.
In the presence of an applied external magnetic field $H_z$ parallel to the $c$ axis, the electronic Zeeman energy is the largest term in the Hamiltonian for the energy shifts of the Tb$^{3+}$ ion. This has been discussed in Chapter 2. Since the energy of the Tb$^{3+}$ ion is sensitive to the local magnetic fields because of its large magnetic moment, the magnetic dipole fields from nuclei of surrounding host ions play a role in the static energy splittings, as well as in the dynamical behavior of the Tb$^{3+}$ ion such as the optical dephasing, as discussed in previous chapters.

Considering the superhyperfine interactions (SHFS) between the Tb$^{3+}$ ion and its surrounding host nuclei, the Hamiltonian can be generally written as

$$H = H_{Tb} + \Sigma H_{F,Tb}$$

(7.1)

where the first term is the interaction Hamiltonian for an isolated Tb$^{3+}$ ion in the crystal, and the second term, including the Zeeman interaction of the nuclei and the coupling between the Tb$^{3+}$ ion and the nuclei, is responsible for the photon echo modulation. The hyperfine interactions (HFS) of Tb$^{3+}$ included in the first term in Eq. (7.1) have a large effect on the energy splittings, as seen in Chapter 2. The HFS splittings are two orders of magnitude larger than those of the SHFS which are in the MHz region. Therefore, the small superhyperfine interactions can be treated as perturbations.

The deep and rather simple modulation spectra which were observed
in the experiments suggest that only the nearest neighbors have significant effects on the echo modulation. The interaction Hamiltonian considered for the echo modulation thus includes the superhyperfine interactions between the \( \text{Tb}^{3+} \) ion and its four nearest surrounding \( \text{F} \) nuclei. For each type of pair of \( \text{Tb}^{3+} - \text{F} \) ions, the Hamiltonian can be written as

\[
H_{F,Tb} = -\hbar \gamma H_x I_z + \langle I_z \rangle [(A + B_z) I_z + B_t (I_x e^{i\Phi} + I_y e^{i\Phi})/2].
\]

(7.2)

The first term represents the Zeeman interaction of the \( \text{F} \) nuclear spin ( \( I = 1/2, \gamma/\hbar = 4.005 \text{ MHz/kG} \) ) with the external field parallel to the \( c \) axis. The \( A \) term is associated with the exchange (Fermi contact) interaction, which measures the density of the \( \text{Tb}^{3+} \) electron clouds at the nuclear sites as transferred through the fluoride electron clouds. The \( B \) terms are due to the magnetic dipole-dipole interaction. The transverse components of the spin operator are defined as \( I_\pm = I_x \pm i I_y \), and \( \Phi \) is the angle between \( x \) axis and the transverse components of the dipole field. In the point-dipole approximation, the values for \( B_z \) and \( B_t \) in Eq. (7.2) are

\[
B_z = B(3z^2 - r^2)/r^5
\]

(7.3)

\[
B_t = 3Bz(x^2 + y^2)^{1/2}/r^5
\]

where \( B = gJ\mu_B \gamma_p \hbar = 55.66 \text{ MHzA}^3 \) for both the ground and excited states.

The \( \text{LiR}_x Y_{1-x} F_4 \) is a tetragonal scheelite crystal. One unit cell
contains four formula units with the ions connected through (1/2, 1/2, 1/2) translations and inversions. Therefore, only the positions of ions in one formula unit need to be considered. If the Li and Y(R) are situated in the (0, 0, 0) and (0, 0, 1/2) positions on the \( \bar{4} \) axis is parallel to the c axis, and the four fluorine sites \( F_1, F_2, F_3 \) and \( F_4 \) are in general positions of \((x, y, z), (y, x, z), (x, y, z)\) and \((y, x, z)\), respectively. They are connected by the \( \bar{4} \) axis. Since two groups of the four sites, \( F_1 \) and \( F_3 \), \( F_2 \) and \( F_4 \), have the same z component and are related by inversion symmetry in the x-y plane, their parameters \( B_z \) and \( B_t \) must be identical. The sign of \( B_z \) can be either positive for the neighbors having large z or negative for the neighbors having small z. Furthermore, for tetragonal crystal structures, the coordinate axes which are determined by the crystal field symmetry are also the axes for other quantities such as the index of refraction and for every electronic state. Therefore, the superhyperfine interaction parameters associated with each space coordinate must be the same for the ground and excited states. In general the parameter A has been assumed to be the same for all the states in the lowest crystal-field split multiplet of the rare earth ions. With regards to the exchange interaction, the sign of A is negative for rare earth ions and the sign of the whole first term is negative so that the local field is lower than the applied field parallel to the crystal c-axis. This has been observed in the NMR measurements on lithium rare-earth fluorides \( \text{LiREF}_4 \). The expectation values of \( <J_z> \) for the \( \text{Tb}^{3+} \) ions have been calculated and experimentally tested as discussed in Chapter 2 for both the ground state \( (J = 6) \) and the excited state \( (J = 4) \). For the ground state \( <J_z> \)}
5.93, which is slightly smaller than -6 due to a small admixture of $M_j=\pm 2$ states.\cite{69,70} For the excited state, there is no first order Zeeman interaction for the singlet $\Gamma_1$ level. The non-linear energy shift is due to weaker field-induced couplings between this $\Gamma_1$ level and other $\Gamma_1$ levels in the same $^5D_4$ multiplet. Therefore, $<J_z>_e$ is not a constant even at high field. As discussed in Chapter 2, the combined crystal field and Zeeman Hamiltonian was diagonalized as a function of magnetic field for the entire $^5D_4$ multiplet. The eigenfunctions of the Zeeman Hamiltonian obtained from this diagonalization are given as mixtures of $M_j$ components and are field dependent

$$|\Gamma_1\rangle = \sum_{M_j} a(M_j, H_z) |M_j\rangle.$$

Thus, the expectation values of the Zeeman Hamiltonian are also field dependent. By using these eigenfunctions, the value of $<J_z>_e$ can be calculated as a function of magnetic field. It is linearly proportional to the applied magnetic field at low field and asymptotically approaches the value -4. Since $|<J_z>_e|$ is always much smaller than $|<J_z>_g|$ at low field, the SHFS is much weaker when a Tb$^{3+}$ ion is in the excited state than in the ground state. This causes a variation of the SHFS as the Tb$^{3+}$ ion oscillates between the ground and the excited states and thus leads to a deep modulation in the echo signals. This will be discussed in detail in a general analogy to the modulation in ruby in which the effects of the SHFS variation on echo modulation have been intensively studied for the $R_1$ line between different levels.\cite{52,53,57,60}
With a set of parameters and known values of $\langle J_z \rangle$, the SHFS Hamiltonian can be diagonalized in the nuclear spin space. According to echo modulation theory,\textsuperscript{52,53} as discussed in Chapter 3, the diagonalization can be carried out separately for each of the Tb\textsuperscript{3+} — F coupling terms in the SHFS Hamiltonian. Therefore, to calculate the echo modulation, one needs only to diagonalize $H_{\text{Tb,F}}$ in Eq. (7.2) over the different Tb\textsuperscript{3+} — F pairs. This is done by calculating a 2X2 matrix product. A unitary matrix $U$ can be found to diagonalize the Hamiltonian, $UH_{\text{F,Tb}}U^+=E$. The energy splittings due to a pair of coupled Tb\textsuperscript{3+} — F ions are obtained as

$$E(I_z=\pm 1/2) = \pm (1/2)(\alpha^2 + \beta^2)^{1/2}, \quad (7.5)$$

where

$$\alpha = \gamma h H_z - \langle J_z \rangle (A+B_z)$$

$$\beta = \langle J_z \rangle B_r, \quad (7.6)$$

The unitary matrix can be expressed as

$$U = \frac{1}{((\alpha^2+\beta^2)^{1/2}+\alpha)^{1/2}} \begin{pmatrix} \beta e^{i\theta} & (\alpha^2+\beta^2)^{1/2}+\alpha \\ (\alpha^2+\beta^2)^{1/2}+\alpha & -\beta e^{-i\theta} \end{pmatrix} \quad (7.7)$$
where the two columns in the right side of above equation are eigenfunctions for the spin-1/2 system. Applying Eq. (7.7) to Eq. (3.22), and assuming that the overall echo decay is a simple exponential, the echo intensity is of the form

\[
I(2t) = I_0 \exp[-4t/T_2] \prod_j (|W_1|^4 + |W_2|^4 + |W_1|^2|W_2|^2[2\cos(\omega_g t) + 2\cos(\omega_e t) - \cos(\omega_g t + \omega_e t) - \cos(\omega_g t - \omega_e t)])^2
\]

(7.8)

where \( j = 1, 2 \) for the two types of nearest F nuclei, \( T_2 \) is the echo decay time constant, and \( W_1 \) and \( W_2 \) are defined below. The primary modulation frequencies are given by

\[
\omega_{g,e} = \frac{1}{\hbar}(\alpha^2 + \beta^2)^{1/2}_{g,e}
\]

(7.9)

This gives the SHFS splittings of the ground and excited states. The sum and difference of the SHFS splittings also appear in the echo modulation but their effects are weaker by a factor of four compared to the primary-frequency terms. This explains the Fourier spectra of the observed echo modulation in the \( \text{Tb}^{3+}:\text{LiYF}_4 \) compound and is consistent with previous observations on \( \text{Pr}^{3+}:\text{LaF}_3 \).\(^{55}\) Note that in Eq.(7.8), echo modulation will disappear if either \( \omega_g \) or \( \omega_e \) is zero. This means that, at least in the case of spin-1/2, echo modulation depends on the co-existence of ground and excited state splittings. This has not been previously discussed in the
earlier echo modulation theory.\textsuperscript{54,53,55,60}

In Eq.(7.8), the products of 8 transformation matrix elements of the 2X2 matrices $W$ and $W^+$, as defined in Eq. (3.21), have been represented by using two values of $|W_1|$ and $|W_2|$ which are defined as

\begin{align*}
|W_1|^2 &= [(\hbar \omega_g + \alpha_g)(\hbar \omega_e + \alpha_e) + (\hbar \omega_g - \alpha_g)(\hbar \omega_e - \alpha_e) + 2\beta_e \beta_g]/\hbar^2 \omega_e \omega_g \\
|W_2|^2 &= [(\hbar \omega_g + \alpha_g)(\hbar \omega_e - \alpha_e) + (\hbar \omega_g - \alpha_g)(\hbar \omega_e + \alpha_e) - 2\beta_e \beta_g]/\hbar^2 \omega_e \omega_g
\end{align*}

(7.10)

In Eq. (7.10) the quantities of $\omega_{g,e}$, $\alpha_{g,e}$ and $\beta_{g,e}$ are not independent. They are functions of the external field $H_z$ and the SHFS parameters $(A+B_z)$ and $B_f$. At a given field the echo modulation is completely determined by the values of the SHFS parameters.

**Experimental Results and Regression Analysis**

The photon echo experimental setup and techniques have been discussed in Chapter 4. The modulation spectra are recorded as a function of time delay between the two excitation pulses at various external fields. In order to minimize the fluctuation of the echo signal due to the fluctuation of the powers of the excitation pulses, 16 shots were averaged by a programmable transient digitizer for each data point, and time scanning was repeated several times at each field. Low excitation powers were used to reduce the effects of instantaneous diffusion which were
described in Chapter 6. An observed echo modulation spectrum for the field of 11 kG is shown in Fig. 26 on a linear scale, and its Fourier transformation is shown in Fig. 27. In the Fourier spectrum, the four dominant modulation frequencies correspond to the excited and ground state SHFS splittings of the two sets of nearest F neighbors. This supports the suggested Hamiltonian $H_{Tb,F}$ in Eq.(7.2) and confirms that Eq. (7.8) correctly describes the major modulations. Since the SHFS splittings are smaller than the pure magnetic Zeeman splittings of the F nuclei (4.005 MHz/kG), the parameter $(A+B_z)$ must be negative for all the $Tb^{3+}$—F pairs.

The modulation strength was found to be sensitive to the applied field. At low field (< 15 kG), the modulation was very strong, but it became weak at high fields as shown in Fig. 11 for $H_z = 35$ kG. The reason for this can be understood from the field dependent eigenfunctions of the SHFS Hamiltonian which determine the modulation coefficients $|W_1|$ and $|W_2|$, or it can be seen by defining an effective field in a way similar to that which has been used in the analysis of echo modulation in ruby.\(^\text{10}\)

$$\hat{H}_{\text{eff}} = \frac{1}{\hbar\gamma} \left[ z(H_z - \langle J_z \rangle (A + B_z)) + t \langle J_z \rangle B_t \right], \quad (7.11)$$

where $\hat{z}$ and $\hat{t}$ are unit vectors parallel and perpendicular to the applied field, respectively. The F spins precess around this effective field. Since both $\langle J_z \rangle$ and $(A+B_z)$ are negative as noted above, the $\hat{z}$ component of the effective field $(\hat{H}_{\text{eff}})_z$ is always smaller than the applied field. In addition the expectation values of the electron spin operator are very different between the ground and excited states, with $\langle J_z \rangle_g / \langle J_z \rangle_e \approx 5$ at low field.
Fig. 26. Theoretical and experimental photon echo modulation spectra for the $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ transition in Tb$^{3+}$:LiYF$_4$ at $H_z = 11$ kG. The echo intensity is plotted on identical linear scales. The theoretical echo modulation function was fitted to the experimental echo modulation spectrum which has 176 data points, and MD is 0.02%.
Fig. 27. Fourier transformation of experimental echo modulation spectrum plotted in Fig. 26. The four strongest peaks in the center are the SHFS splittings in the ground and the excited states. Their sums and differences appear in the high and low frequency regions. Various frequencies in this spectrum arise from the products of the primary terms as described in Eq. (7.8).
The two terms in \((H_{\text{eff}})_z\) for the ground state are comparable at low field so that \((H_{\text{eff}})_z \leq (H_{\text{eff}})_t\), whereas the value of \((H_{\text{eff}})_z = H_z \gg (H_{\text{eff}})_t\) for the excited state. The effective field varies in both direction and magnitude as the echo ion oscillates between the ground and the excited states, thus the modulation is maximized. At high field, \(H_{\text{eff}} = H_z\) for both the ground and the excited states, and the F spins always precess around the applied field. This minimizes the variation of the coupling between the echo ion and the neighboring nuclei and thus minimizes the echo modulation.

In comparing theory and experiment, Eq.(7.8) was fitted to the observed modulation spectra. First the value of \(T_2\) was determined by the least-squares method. Then a regression program based on Marquardt's algorithm\(^{11}\) was used to fit the observed echo spectra with five variable parameters — four independent SHFS parameters plus \(I_0\). The fitted spectrum for \(H_z = 11\) kG is shown in Fig. 26. The mean deviation per point MD is 0.02% which is quite small. The value of MD is defined in Reference 60 as

\[
MD = \left(\frac{1}{N}\sum_{N}^{\text{exp}} I_{\text{the}} - I_{\text{exp}}\right) X 100\%, \quad (7.12)
\]

where \(N\) is the number of data points in the experimental observation.

This regression procedure was carried out independently for three different modulation spectra at \(H_z = 9.5, 11,\) and 14.7 kG, respectively. The agreement between the experiments and the theory was excellent. The calculated SHFS parameters are listed in Table 7. The four SHFS parameters obtained from these three independent analyses have mutual
deviations smaller than 3%, which are smaller than experimental errors and are primarily due to variations of the observed spectra due to laser power fluctuation and other variations of the experimental conditions.

Table 7. SHFS parameters for two types of nearest neighbor fluorines for a Tb$^{3+}$ ion.

<table>
<thead>
<tr>
<th></th>
<th>TYPE 1</th>
<th>TYPE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(A + B_z)$ (MHz)</td>
<td>$3.8 \pm 0.1$</td>
<td>$3.4 \pm 0.1$</td>
</tr>
<tr>
<td>$</td>
<td>B_t</td>
<td>$ (MHz)</td>
</tr>
</tbody>
</table>

The identical values of $|B_t|$ for the two types of nuclear pairs are expected by Eq. (7.3) due to the site symmetry. The sign of the parameter $B_t$ cannot be determined in the deconvolution. This was indicated by Eq. (7.6) and Eq. (7.10). The regression analysis was initially carried out with 8 SHFS parameters with the assumption that the symmetry of F site may not be perfect so that the parameters could be different for the four nearest F nuclei. In that case, the differences between the related parameters of the four F nuclei were just the same as the deviations from fitting different experimental spectra. This indicates that, at the current resolution, in this sample the sites of Tb$^{3+}$ and the four nearest F nuclei have good agreement with the expected structure.

Figure 28 shows the theoretical and experimental SHFS splittings as a function of applied magnetic field parallel to the crystal c-axis. The
two upper lines represent the excited state energy splittings of the SHFS between the Tb$^{3+}$ ion and its two types of nearest F neighbors. The linear relation between the SHFS energy splitting of the excited state and the applied field in this region can be understood from the expectation value of $\langle J_z \rangle_e$ as a function of the field. As indicated in the first section of this chapter, $\langle J_z \rangle_e$ is linearly proportional to the applied field at low field. Therefore, by defining

$$\langle J_z \rangle_e = \eta H_z,$$  \hspace{1cm} (7.13)

where $\eta = 0.12 \text{ kG}^{-1}$ for the region of the field in Fig. 28, the SHFS splitting of the excited state in Eq. (7.9) can be rewritten as

$$\omega_e = \gamma_{\text{eff}} H_z,$$  \hspace{1cm} (7.14)

where

$$\gamma_{\text{eff}} = [(\gamma - \eta (A + B_z)/\hbar)^2 + (\eta B_z/\hbar)^2]^{1/2} \approx 3.6 \text{ MHz/kG}.$$  \hspace{1cm} (7.15)

Comparing that value to $\gamma = 4.005 \text{ MHz/kG}$ for free fluorine, the F line will have a 10% shift due to the SHFS. For the ground state, $\langle J_z \rangle_g$ is large and constant. This causes a stronger SHFS shift and leads to smaller modulation frequencies.

In conclusion, the experimental and theoretical studies of photon
Fig. 28. Theoretical and experimental SHFS splittings versus the applied magnetic field parallel to the crystal c-axis. The points are obtained from the Fourier transformations of the experimental photon echo spectra. The continuous curves represent the theoretical values which are calculated by using Eq. (7.9) and Eq. (7.6) with the SHFS parameters from Table 7.
echo modulation in the dilute compound $\text{Tb}^{3+}:\text{LiYF}_4$ show that the existence of modulation in the echo amplitude is dependent on the energy splittings of the $\text{Tb}^{3+}$ ions in both the ground and excited states due to the SHFS interactions. The depth of the echo modulation is sensitive to the variation of the magnetic moment of the $\text{Tb}^{3+}$ ion as it oscillates between the ground and the excited levels. This causes changes in the relative orientation of the local magnetic field and thus results in deep echo modulation. This is consistent with previously observed echo modulation in ruby due to the SHFS between $\text{Cr}^{3+}$ and its surrounding Al ions.$^{53,57,60}$ The rather simple modulation spectra indicate that, in this compound only the first nearest neighbors have significant contributions to the observed echo modulation. This is similar to the $M_g=1/2$ echo modulation in ruby. In contrast, recent studies of the $M_g=-3/2$ echo modulation in ruby indicated that as many as 375 Al ions have been included for a best fitting of experimental data.$^{60}$ Furthermore, the resulting SHFS parameters from the regression analysis are identical for the ground state and the excited state, thus indicating that the echo modulation is solely due to the variation of the magnetic moment of the $\text{Tb}^{3+}$ ions in the ground and excited states. The identical SHFS parameters for the ground and excited states are also expected for the higher crystal symmetry of this compound. Further PENDOR experiments may be worthwhile for checking the SHFS parameters for both the ground and excited states with greater accuracy.
CHAPTER 8

HYPERFINE SPECTRAL HOLEBURRING FOR Tb$^{3+}$:LiYF$_4$

Spectral holeburning in rare earth insulators has proved to be very useful for measuring the hyperfine and superhyperfine structure of both ground states and optically excited states even in the presence of inhomogeneous broadening. Its high resolution is particularly useful for studying the effects of external perturbations such as nuclear Zeeman and electronic Stark splittings which can provide the kind of detailed structural information available from nuclear magnetic resonance experiments. Holeburning spectroscopy is also an effective method to study spectral diffusion and relaxation processes in rare earth doped materials.

Spectral holeburning via optical pumping of ground state hyperfine level populations has been observed in 1% Tb$^{3+}$:LiYF$_4$ for the blue optical transition from $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$. The hole lifetime increased with applied magnetic field and reached a value of 10 minutes with an external field of 40 kG applied along the c axis. The electronic and hyperfine levels that were discussed in Chapter 2 then provided a qualitative explanation for the field-dependent holeburning process. These experiments demonstrate that the high resolution of holeburning spectroscopy can be readily extended to Tb$^{3+}$. 
In this chapter, hyperfine population holeburning is discussed for the lowest \( ^7F_6 \) to \( ^5D_4 \) transition in the visible spectrum of Tb\(^{3+}\):LiYF\(_4\), along with holeburning rate, quantum efficiency, and lifetime.

**Holeburning Process**

The observed \( ^7F_6 \Gamma_2 \) to \( ^5D_4 \Gamma_1 \) optical absorption line involves the superposition of all allowed hyperfine transitions summed over all ion sites. The inhomogeneous line broadening of 0.45 cm\(^{-1}\) in this dilute crystal is greater than the hyperfine splittings described and calculated in Chapter 2, so it obscures the individual optical transitions between hyperfine sublevels. Holeburning, however, provides a way to probe individual hyperfine transitions for a subgroup of Tb\(^{3+}\) ions even in the presence of this typical inhomogeneity.

In the case of fixed-frequency excitation by a narrow band laser, a given ion undergoing optical transitions in the crystal is resonant with the laser on only one of the four allowed transitions between hyperfine sublevels of the ground and excited states (\( \Delta I_z = 0 \) for optical transitions). An excited ion, however, can relax to a different ground state hyperfine level than that from which it was excited, due to interactions with phonons and other neighboring ions or a small misalignment of the magnetic field. This optical pumping process leads to the redistribution of population among the hyperfine components of the ground state. At low temperature, the nuclear spin-spin and spin-lattice relaxation can be slow under appropriate conditions. Then, population changes in the ground state hyperfine components can accumulate and can last long enough for a
holeburning spectrum to be recorded by scanning a weak probe laser across the inhomogeneously broadened optical absorption line.

Experimental Details

In the experiments the holeburning spectrum, holeburning quantum efficiency, and hole lifetime have been measured as a function of magnetic field with two tunable nitrogen-laser-pumped dye lasers. The holeburning process is so strong that it can be easily detected by an absorption or excitation spectrum. Appropriate experimental power densities are noted below. Except for signal detection, the experimental setup for the holeburning is similar to that for photon echo experiments, which was shown in Fig. 8. The 0-60 kG magnetic field was supplied by the superconducting solenoid, and the crystal was immersed directly in liquid helium at 1.3 K. A photodiode monitored the laser intensity as the probe laser was tuned, and absorption was measured by a second photodiode after the sample. The PDP-11 computer which controlled the experiment calculated the ratio of the photodiode signals on a shot to shot basis, averaged it over ten shots, and displayed the resulting transmission data on the screen during a laser scan. The absorption coefficient was calculated directly from that data in the standard way. Fluorescence was detected by a Spex 14018 0.85 m double monochromator or via appropriate color glass filters and a photomultiplier.

Holeburning Spectrum and Mechanism

To observe the hole spectrally, a weak tunable "probe" laser was
sent through the sample at a 1° angle relative to the fixed frequency "pump" laser. The probe beam was twenty times weaker than the pump beam, so it had a negligible effect on the populations. Both beams were overlapped in the sample, with the probe beam delayed by 10 nsec in early experiments. After it became obvious that the hole lifetime was generally measured in minutes rather than nanoseconds or microseconds, the timing was obviously not critical. Since each laser had a relatively broad line width ($\approx 0.05 \text{ cm}^{-1}$), the resolution of the hole spectrum was limited to about 0.1 cm$^{-1}$.

Figure 29 shows a representative hole spectrum for the $\pi$-polarized electric dipole transition from $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ recorded by absorption of the probe laser at 12 kG and 1.3 K. An unperturbed spectrum showing the equilibrium inhomogeneous line shape is given on the same scale for comparison. At both sides of the hole, the absorption is enhanced. This is due to the increased population in the other ground state hyperfine components which are higher or lower in energy than that from which the holeburning transition originated. Thus, in company with a hole, antiholes are also created. The presence of these antiholes provides strong evidence that the holeburning mechanism involves optical pumping of the hyperfine levels as outlined above. Holeburning could possibly proceed via the frozen-core process observed earlier for Pr$^{3+}$:CaF$_2$ by Burum, Shelby, and Macfarlane,$^{63}$ but that process could not give antihole structure on the energy scale seen here.

Unfortunately the laser resolution was not adequate to reveal structure in the side hole or antihole spectrum which would have allowed measurement of the individual hyperfine splittings. To determine those
Fig. 29. Holeburning spectrum for the transition $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ at the magnetic field $H = 46$ kG (solid curve) compared with the unperturbed absorption spectrum (dashed curve). Both curves are displayed as absorption coefficients on the same scales. The full width at half maximum of the absorption is 0.45 cm$^{-1}$. The observed hole width was instrumentally limited, but, nevertheless, clear antiholes may be seen, implying optical plumping of hyperfine sublevels.
splitting, so that independent values of the hyperfine interaction parameters can be extracted from these experiments, a high resolution tunable laser—probably a single mode cw dye laser—will be required. The cw laser available in this laboratory, however, cannot presently operate in the blue region needed for Tb$^{3+}$ transitions.

Nevertheless, the dynamics and field dependence of the holeburning process still can be studied. The theoretical analysis of hyperfine interaction explains the observed field dependences and thus adds further evidence that the optical pumping of hyperfine sublevels is the dominant mechanism for the holeburning.

It was noted that the upper electronic level of the ground state could also be a possible population reservoir for holeburning, especially at high field and low temperature. At 1.3 K and in fields up to 50 kG, however, no observable population storage has been found in that level.

**Holeburning Rate and Quantum Efficiency**

At line center for this transition, the 0.2 cm thick crystal absorbed 40% of the laser energy, giving a peak absorption coefficient of 2.5 cm$^{-1}$. Upon exposure to the fixed frequency pump laser, the absorption quickly dropped to 15%, due to the holeburning process. Figure 30 shows the corresponding decrease in the fluorescence intensity. Both quantities exhibited exponential decays with a time constant of 47 sec. The magnetic field was 45 kG.

The peak laser intensity at the crystal surface was about 100 MW/cm$^2$, the pulse width was 5 nsec, and the pulse repetition rate was 6 per sec. Under these conditions, a hole depth of 10% could be obtained.
Fig. 30. Holeburning rate at the line center of the $^7F_6 \Gamma_2$ to $^5D_4 \Gamma_1$ absorption as shown by the extinction of the $^5D_4$ to $^7F_5$ fluorescence. The peak laser intensity was 100 MW/cm$^2$, pulse width was 5 nsec, and pulse rate 6 Hz. The curve is exponential with a decay constant of 47 sec.
in 5 sec, with an incident energy per ion of $3.4 \times 10^{-14}$ erg.

From an alternate point of view, the average laser intensity at the crystal surface was $3 \text{ W/cm}^2$. This value could be achieved readily with a typical unfocused cw dye laser. Moreover, the narrow laser line width would give one thousand times higher average spectral brightness. Based on these considerations and the long hole lifetimes described in the next subsection, holeburning experiments on rare earth compounds containing Tb$^{3+}$ or other ions with large ground state magnetic moments can be carried out easily.

The quantum efficiency is an important parameter of the holeburning process. Since the hole growth rate is not constant, the quantum efficiency $\eta$ has been defined by Moerner et al$^{113}$ as the ratio of the initial rate of decrease of the number of absorbing ions per unit volume $N(t)$ to the initial rate of absorption of photons. Thus,$^{113}$

$$\eta = \frac{(dT(t)/dt)_{t=0}}{\sigma T_0 (I/hv)(1-T_0-R)} \quad (7.1)$$

where $I$ is the incident laser intensity, $T(t)$ is the time-varying sample transmission during the growth of the spectral hole, $T_0$ is the initial sample transmission which is 0.6 at the inhomogeneous line center, $R$ is the total reflection loss at the sample, $h$ is Planck's constant, $v$ is the photon frequency, and $\sigma$ is the peak absorption cross section for the ions.

Using the laser line width of 1.5 GHz, which is much broader than the homogeneous line width of 30 kHz measured in the photon echo experiments, as in Chapter 5, the cross section has been calculated $\sigma = 2 \times 10^{-19}$ cm$^2$ by following Ref. 113. This gives a quantum efficiency of $\eta$
Hole Lifetime

Figure 31 summarizes the effect of an external field on the hole lifetime. These measurements were made by burning a hole with the pump laser, stopping that laser, waiting an appropriate interval, and then reading the hole depth with a single scan of the probe laser.

Obviously, hole lifetime is decreasing toward small values at zero field. No hole could be observed at zero field in the current experiments due to lifetime considerations and to the laser line width. Details of the Zeeman effect and the hyperfine structure discussed in Chapter 2 qualitatively explain these observations.

Experiments on LiTbF$_4$

Similar experiments were carried out on an appropriately thin sample of the stoichiometric compound LiTbF$_4$. No evidence was found for holeburning in that concentrated magnetic system. Presumably the strong coupling of the Tb$^{3+}$ ions leads to very much faster relaxation of the ground state hyperfine populations. Faster phase relaxation observed in the photon echo experiments on the stoichiometric compound is certainly consistent with this result.

Correlation of the Holeburning Phenomena and the Hyperfine Structure

The small values of the zero field ground state hyperfine splittings
Fig. 31. Hole lifetime as a function of applied field, which is correlated qualitatively in the text with level splittings.
for small magnetic fields are less than the laser line width, and this certainly explains the difficulty of burning holes by optical pumping of the hyperfine populations for that case with the pulsed lasers used in these experiments.

Relaxation processes affect the hole lifetime and thus affect the ease of holeburning. The fluctuating field due to the Tb$^{3+}$ electronic spins is dramatically reduced in an applied magnetic field due to the exceptionally large ground state electronic g factor. As discussed in Chapter 5, the photon echo experiments on the same crystal have shown a dramatic reduction in electron spin diffusion with increasing magnetic field, which is just what one expects based on these ground state properties and the 1% Tb$^{3+}$ concentration. The Tb$^{3+}$ nuclear spin-spin relaxation will be slowed by the increasing magnetic field-induced separation of the ground state hyperfine sublevels. Those splittings become over two orders of magnitude larger than the nuclear Zeeman energies of the fluorine ligands. Strong "frozen core" effects also constrain the fluorine ligands near Tb$^{3+}$ ions. All of these factors combine to explain the dramatic increase in hole lifetime with increasing magnetic field.
CHAPTER 9

CONCLUSIONS

The concentrated crystalline rare earth compound LiTbF$_4$ and the isostructural dilute compound 1% Tb$^{3+}$:LiYF$_4$ have been systematically studied with nonlinear spectroscopic methods such as photon echoes and holeburning. The effects of various interaction processes on the static energy structure and the dynamical behavior of the rare earth ions have been analyzed for both the ground and excited states. The experimental results from the dilute compound have been well understood, while the interpretation of the novel frequency-dependent dephasing in the concentrated compound involved several theoretical models, some of which are still controversial for describing the nature of the interactions in a real physical system.

In the 1% dilute compound Tb$^{3+}$:LiYF$_4$, the Tb$^{3+}$ ions are relatively isolated. The ion-ion interactions are weak and the short-range coupling is absent. Since the Tb$^{3+}$ ion has a large magnetic moment 8.9$\mu_B$ in the doublet ground state, its energy is sensitive to the local magnetic field. The magnetic dipole-dipole interaction among the Tb$^{3+}$ ions and between the Tb$^{3+}$ and the host F$^-$ ions thus determines its spectral properties. At liquid helium temperature, the observed echo decay behavior and the hyperfine spectral holeburning process exhibited strong magnetic field
dependence. The observed homogeneous line broadening, energy splitting, and spectral diffusion can be described by magnetic dipolar interactions plus the exchange interaction between the Tb$^{3+}$ ion and its nearest neighboring host nuclei.

In the photon echo measurements of the dilute compound at a small external magnetic field, the echo decay time was dramatically shortened by the electron spin diffusion process in the ground state. The spin flip-flops of the Tb$^{3+}$ ions between the two ground Zeeman components cause fluctuations of the local field and thus randomly shift the resonant frequencies of the echo ions. Since the Zeeman splitting is strong, the two components are well separated at large magnetic field and the electronic spin diffusion is inhibited.

The instantaneous spectral diffusion phenomenon has been dramatically observed in the photon echo experiments on this dilute compound. The measured dephasing rate depends linearly on the intensity of the second laser pulse and is independent of the intensity of the first laser pulse. Changes of greater than a factor of ten are readily observed for the dephasing rate. This effect is also magnetic field dependent. To interpret the experimental results, the magnetic dipole-dipole interaction between Tb$^{3+}$ ions was considered. The crystal field analysis and the Zeeman experiments on this material indicate that an optical transition of a Tb$^{3+}$ ion from the ground state $^7F_6 \Gamma_2$ to the excited state $^5D_4 \Gamma_1$ causes an instantaneous change in its magnetic moment which leads to a shift in the resonant frequency of its neighboring ions through the magnetic coupling. These random frequency shifts caused by the first pulse are removed by the echo sequence, but the shifts caused by the
second pulse are present for only part of the echo sequence. Since they cannot be removed by the rephasing process, thus lead to extra echo decay. The dephasing rate in the dilute compound has been calculated as a function of excitation intensity and magnetic field. The theoretical calculation is in reasonable agreement with the experimental measurements.

Due to the existence of the instantaneous diffusion, the measured echo decay time $T_2'$ is no longer the coherence dephasing time $T_2$ of the related two-level system. This "apparent" homogeneous line broadening must be avoided when the photon echo measurement is used to probe the "real" homogeneous line width determined by the intrinsic ion-ion interactions without external disturbances. On the other hand, this experiment-induced dephasing process provides a way for testing the sensitivity of an optically activated ion to the perturbation of its environment. The instantaneous diffusion is significant only in those systems in which the resonant frequency of the optical ions is sensitive to changes in the magnetic moment and hence in ion-ion coupling during the excitation.

Time-domain transient spectroscopy is not only sensitive to homogenous line broadening but also a very powerful tool for measuring small static energy splittings which are usually obscured by the inhomogeneous broadening. In the dilute compound superhyperfine coupling between the Tb$^{3+}$ ion and F$^-$ neighbors has thus been obtained from the echo modulation phenomenon.

The observed modulation characteristics confirmed that the magnetic dipole-dipole interaction and exchange interaction between an Tb$^{3+}$ ion and its first nearest neighboring F nuclei are responsible for the observed deep
A model Hamiltonian of the SHFS for this system has included both the magnetic and exchange interactions. Since the echo modulation is sensitive to both the eigenvalues and eigenfunctions of the splitting Hamiltonian, echo intensity as a function of time delay has been derived and tested by the experimental modulation spectra with the method of regression analysis. Both the modulation frequencies and the interaction parameters have been determined in the regression analysis. The excellent agreement between the theoretical calculation and the experimental data confirmed the correctness of the model Hamiltonian. This is the first investigation of the SHFS through photon echo modulation for rare earth materials.

Spectral holeburning in Tb\(^{3+}\):LiYF\(_4\) has been demonstrated with tunable pulsed lasers, and the hole lifetime has been measured as a function of applied magnetic field. Optical pumping of the ground state hyperfine level populations is responsible for the observed hole burning process. In the presence of an applied magnetic field, the spectral diffusion process is slow in the ground state, so the hole lifetime increases with an applied magnetic field. The quantum efficiency for the hole burning process has been calculated in terms of the measured absorption decay rate.

The observations and calculations indicate that experiments with a single mode cw dye laser are capable of yielding additional detailed information about both the ground state and excited hyperfine structure in Tb\(^{3+}\) compounds. Observation of side holes and antiholes or of optically detected nuclear resonance should allow accurate measurement of both the
magnetic hyperfine interactions and the nuclear quadrupole interactions. That in turn can yield detailed structural information about the Tb$^{3+}$ sites whether the ions are at intrinsic sites or are found near defects.

The crystal field eigenfunctions, derived from the crystal field analysis of the observed energy levels, provided important information required to understand the various phenomena observed in this system. With the crystal field eigenfunctions, the electronic Zeeman effect, and the hyperfine interactions of the ground and excited states have been calculated. The resulting energy states and eigenfunctions provided an excellent description of the electronic Zeeman splittings of the energy levels in both $^7F$ and $^5D$ multiplets for fields up to 50 kG and allowed accurate calculation of the strongly field-dependent magnetic hyperfine structure in the ground and excited states. Based on these calculations, all the experimental results can be qualitatively explained. The eigenfunctions obtained as a function of magnetic field have been used to calculate the field-dependent echo modulation and both the field dependent and power-dependent dephasing rate in the dilute compound.

Intense and long-lived stimulated echoes were observed in three-pulse photon echo experiments and could provide a probe for the study of spectral diffusion and coherent phase storage. They also suggest that accumulated grating echoes should be a practical method for studying faster dephasing at higher temperatures.

The observation of strong frequency-dependent dephasing in the concentrated compound and its absence in the 1% dilute compound indicated that Tb$^{3+}$ ion-ion interactions dominated the dephasing processes and suggested the existence of energy transfer through short-
range interactions. The energy transfer processes could cause strongly delocalized states in the main region of the absorption line and consequently lead to a shorter value of $T_2$. In the wings of the line, the effective concentration is low and the ions do not interact thus the excitations should become localized. This effect is just what is expected by the Anderson models; however, correspondence of our observed result to the Anderson transition remains controversial.

The apparent proportion of the dephasing rate to the absorption coefficient in the main region and on the low frequency side of the line suggests that the frequency-dependent dephasing is due to quasiresonant interactions among the Tb$^{3+}$ ions. The dephasing rate in this part of the line has been fitted by the quasiresonant interaction model. The assumption of phonon-assisted energy transfer processes in the inhomogeneous line can qualitatively explain the faster dephasing on the high energy side but the calculation made with the one-phonon emission approximation does not agree with the experimental data.

The line shape measurements for the transition from the upper component of the ground state to the excited state indicated no large exciton band effect in the excited state as observed in other Tb$^{3+}$ compounds such as Tb$^{3+}$(OH)$_3$. Therefore, the exciton dispersion must be significantly weaker in this compound.

The interpretation of the asymmetry of the absorption line as inhomogeneous broadening seems to oversimplify the nature of the line shape. The much faster dephasing rate on the high energy side could certainly be related to that line shape. A Davykov splitting is expected for this compound, because there are two ions per unit cell and the off-
diagonal interaction matrix elements responsible for the Davydov splitting are due to the nearest neighboring coupling. According to the calculation, a small interaction between the nearest neighboring ions could lead to the observed splitting between the two peaks in the absorption line. The validity of this explanation is questionable since the selection rules for the $\vec{F}^z=0$ ground state which allow only one band of the Davydov splitting to be excited.

Another potential interpretation for the asymmetry of the line involves the magnetic interaction of neighboring Tb$^{3+}$ ions in the ground state. The energy splittings due to the magnetic dipole-dipole interaction plus the nearest neighboring exchange interaction between the Tb$^{3+}$ ions have been observed in transition from the upper ground state component. At low temperature the energy splittings saturated, and the line shape of single-ion excitation was asymmetric with a line shape which was mirror reflection of the line shape for the lower component excitation. Even in the presence of a large external magnetic field, the exchange interaction and the spin excitation process could still broaden the absorption line. Further line shape calculations may fit the asymmetric line shape and yield a complete understanding of the fast dephasing on the high energy side.

Similar photon echo experiments on Tb$^{3+}$(OH)$_3$ are worthwhile for extracting information about the effect of exciton dispersion on echo dephasing. In this compound band-like exciton properties have been observed and the interaction mechanisms have been well determined.$^{39}$ Photon echoes have already been observed in this compound in an optically-thick sample (20 µm). This sample is so thick, however, that more than 95% laser beam was absorbed in the line center thus the photon
echoes were observed only in wings of the line. The observed echo decay rate was the same in both wings, and this is qualitatively different from the asymmetric dephasing behavior in LiTbF₄.
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APPENDIX

COMPUTER CONTROL PROGRAMS
FOR PHOTON ECHO EXPERIMENT
/* PHOTON ECHO PROGRAM SCANNING TIME DELAY BETWEEN TWO LASERS, INTERFACING DIGITIZER, AND RECORDING THE ECHO INTENSITY AND POWERS OF THE LASERS */

#include <std.h>
#include <rt11.h>
#include "da.c"
#include "ad.c"
#include "Itc.c"

main()
{
    long INITT(), DRWABS(), MOVABS();
    int x, y, x1, y1;
    int x0 = 30;
    int y0 = 100;
    int xmax = 660;
    int ymax = 760;
    int IBUP();
    int write = 0;
    int read = 1;
    int remote = 4;
    int local = 5;
    int digitizer = 1;
    char *comdl;
    char *comd2;
    char *comd3;
    char *comd4;
    int lenst1;
    int lenst2;
    int lenst3;
    int lenst4;
    char strip[3];
    unsigned char array[1024];
    long sumai-ay[512];
    int three = 3;
    int size = 1024;
    int two = 2;
    int one = 1;
    int bit9 = 256;
    int i, j, k, l, s;
char filnam1[20],filnam2[20];
FIO fio,fioo;
int shots,ends,wid,sep;
int chann,initial,init;
int range,delta,repts;
int zero,zer,bin,ech,ezero;
long pa[512],p0,p;
long w[64],a0,a,b0,b,c0,c;
long data[512];
char bell[2];
int baud = 1400;

bell[0] = 07;
bell[1] = 0;

/* INITIALIZE IN/OUT */
putinitO;
getinitO;
for(i=0;i<512;i++)
{
    sumaray[i] = (long)0;
}

/* GIVE FILE NAMES */
putfmt("What is the name of the echo data file?\n");
getfmt("%p\n",filnam1);
if(!fcreate(&fio,filnam1,1))
{
    putfmt("Error: can't open %p\n",filnam1);
    return;
}

putfmt("What is the name of the power data file?\n");
getfmt("%p\n",filnam2);
if(!fcreate(&fioo,filnam2,1))
{
    putfmt("Error: can't open %p\n",filnam2);
    return;
}

fcall(INITT,1,&baud);

/* SET VOLTAGE FOR ZERO TIME DELAY */
putfmt("Type delay for simultaneous pulses\n");
getfmt("%i\n",&zero);
while(zero>=0)
{
    zer = zero;
    putvolt(0,(int)(2047.0-204.8*(zer/100.0)));
    putfmt("Type delay for simult pulses\n");
    getfmt("%i\n",&zero);
}

/* SET INITIAL TIME DELAY */
putfmt("Type initial delay in ns\n");
putfmt("Adjust echo location on digitizer\n");
getfmt("%i\n",&initial);
while(initial>=0)
{
    init = initial;
    putvolt(0,(int)(2047.0-204.8*(init+zer)/100.0));
    putfmt("Type initial delay in ns\n");
    getfmt("%i\n",&initial);
}

/* SET ECHO SIGNAL LOCATION AND DURATION IN DIGITIZER'S TIME AXIS */
putfmt("Which channel is the center of echo?\n");
getfmt("%i\n",&chann);
putfmt("Type echo half width on digitizer?\n");
getfmt("%i\n",&wid);

/* SET NOISE-BACKGROUND LOCATION */
putfmt("Type separation to sum background?\n");
getfmt("%i\n",&sep);

/* SET TIME DELAY RANGE */
putfmt("Type scan range in ns?\n");
getfmt("%i\n",&range);

/* SET SCAN INCREMENT PER DATA POINT */
putfmt("Type delay increment in ns?\n");
getfmt("%i\n",&delta);

/* SET DATA AVERAGE NUMBER */
putfmt("How many shots do you want?\n");
getfmt("%i\n",&shots);

/* RECORD INITIAL VALUE OF LASER POWER */
w[0] = 0;
for(j=1;j<=shots;j++)
{
    gettrg();
a0 = getvolt(1);
b0 = getvolt(4);
c0 = (long)(a0*b0/4000);
putfmt("a0 =%i\n",a0);
putfmt("b0 =%i\n",b0);
w[j] = w[j-1]+c0;
putfmt("w[j] =%i\n",w[j]);
}
p0 = w[shots];
putfmt("p0 =%i\n",p0);

/* SET DIGITIZER MODE */
comdl = "DIG SA,0";
i = itob(comdl+7,shots,10);
comdl[7+i] = '0';
comd2 = "READ SA,0";
comd3 = "MOD TV,0";
comd4 = "MOD DIG,0";
lenst1 = lenstr(comd1);
lenst2 = lenstr(comd2);
lenst3 = lenstr(comd3);
lenst4 = lenstr(comd4);
fcall(IBUP,2,&remote,&digitizer);
fcall(IBUP,4,&write,&digitizer,comd4,&lenst4);
/* START */
putfmt("hit return key to start\n");
getfmt("\n");
/* DRAW AXES FOR PLOT */
fcall(INIT,1,&baud);
fcall(MOVABS,2,&xO,&ymax);
fcall(DRWABS,2,&xO,&yO);
fcall(DRWABS,2,&xmax,&yO);
fcall(MOVABS,2,&xO,&yO);
x1 = x0;
y1 = yO;
/* START SCAN AND RECORD DATA */
for(i=init;i<=init+range;i+=delta)
{    
putvolt(0,(int)(2047.0-204.8*(i+zer)/100.0));
for(k=1;k<=50;k++)
    {     
gettrg();
a = getvolt(1);
b = getvolt(4);
c = (long)(a*b/10);
w[j] = w[j-1]+c;
    }
p = w[shots];
bin = (i-init)/delta;
pa[bin] = p/pO;
/* SET DIGITIZER FOR SENDING DATA */
fcall(IBUP,4,&write,&digitizer,comd2,&lenst2);
fcall(IBUP,4,&read,&digitizer,strip,&three);
fcall(IBUP,4,&read,&digitizer,array,&size);
fcall(IBUP,4,&read,&digitizer,strip,&two);
for(k=0;k<512;k++)
    {     
data[k] = (long)(array[2*k]*bit9 + array[2*k+1]*one);
    }
ech = data[chan-wid];
ezero = data[chan+sep-wid];
for(k=chan-wid+1;k<=chan+wid;k++)
    {     
ech += data[k];
ezero += data[k+sep];
    }
sumarray[bin] = (long)(ech-ezero);
sumarray[bin] = (long)((float)(sumarray[bin]/(shots*(wid+1))));
/* PLOT DATA ON SCREEN */
x = (int)((float)630*(i-init)/range + 30);
y = (int)((float)(0.75*sumarray[bin])+100);
fcall(DRWABS,2,&x,&y);
fcall(MOVABS,2,&x1,&y1);

x1 = (int)((float)630*(i-init)/range + 30);

y1 = (int)((float)(0.75*pa[8*i]+100));

fcall(DRWABS,2,&x1,&y1);

fcall(MOVABS,2,&x,&y);

}

ends = i - delta;

fcall(IBUP,4,&write,&digitizer,comd3,&lenst3);

fcall(IBUP,4,&write,&digitizer,comd3,&lenst3);

fcall(IBUP,2,&local,&digitizer);

fcall(MOVABS,2,&xmax,&y0);

fcall(DRWABS,2,&xmax,&y0);

fcall(MOVABS,2,&xmax,0);

fcall(MOVABS,2,&x0,&y0);

fcall(IBUP,4,&write,&digitizer,comd3,&lenst3);

fcall(IBUP,4,&write,&digitizer,comd3,&lenst3);

fcall(IBUP,2,&local,&digitizer);

fcall(MOVABS,2,&xmax,&y0);

fcall(DRWABS,2,&xmax,&y0);

fcall(MOVABS,2,&x0,&y0);

/* WRITE DATA INTO FILES */

putf(&fio, "%
");

for(i=0;i<(1+range/delta/8);i++)

{

putf(&fio, "%06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1

%,(long)(8*i),sumaray[8*i+0],sumaray[8*i+1],sumaray[8*i+2],sumaray[8*i+3],sumaray[8*i+4],sumaray[8*i+5],sumaray[8*i+6]

,sumaray[8*i+7]);

}

fclose(&fio);

putf(&fioo, "%
");

for(i=0;i<(1+range/delta/8);i++)

{

putf(&fioo, "%06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1 %06d1

%,(long)(8*i),pa[8*i+0],pa[8*i+1],pa[8*i+2],pa[8*i+3],pa[8*i+4],pa[8*i+5],pa[8*i+6],pa[8*i+7]);

}

fclose(&fioo);

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

putfmt("done. Delay range =%i nsec\n",ends);

}
/* PHOTON ECHO PROGRAM SWEEPING MAGNETIC FIELD ACROSS ABSORPTION LINE AND RECORDING ECHO INTENSITY AND ABSORPTIONS OF TWO LASERS */

#include <std.h>
#include <rt11.h>
#include "da.c"
#include "ad.e"
#include "ltc.c"

main()
{
    long INITT(),DRWABS(),MOVABS();
    int x,y,x1,y1,x2,y2;
    int x0 = 30;
    int y0 = 100;
    int xmax = 660;
    int ymax = 760;
    int IBUP0;
    int write = 0;
    int read= I;
    int remote = 4;
    int local = 5;
    int digitizer = 1;
    char *comd1,*comd2,*comd3,*comd4;
    int lenst1,lenst2,lenst3,lenst4;
    char strip[3];
    unsigned char array[1024];
    long sumaray[512];
    int three = 3;
    int size = 1024;
    int two = 2;
    int one = 1;
    int bit9 = 256;
    int i,j,k,l,s;
    char filnam1[20],filnam2[20],filnam3[20];
    FIO fio,fioo,fioo;
    long z[64],pb[512],p1,a1,b1,c1;
    int wid,sep,ends,sran;
    int chann,initial,init;
    int range,delta,delay;
    int zero,zer,shots;
long w[64],pa[512],p,a,b,c;
long ech,ezero;
long data[512];
long echo[50];
int bin,ne,nt,incr;
float sweep;
char bell[2];
int baud = 1400;

bell[0] = 07;
bell[1] = 0;

/* INITIALIZE IN/OUT */
putinit();
getinit();
for(i=0;i<512;i++)
{  
    sumaray[i] = (long)0;
}

/* GIVE FILE NAMES */
putfmt("What is the name of the echo data file?\n");
getfmt("%p\n",filnam1);
if(!fcreate(&fio,filnam1,1))
{  
    putfmt("Error: can't open %p\n",filnam1);
    return;
}
putfmt("What is the name of 11 absorption data file?\n");
getfmt("%p\n",filnam2);
if(!fcreate(&fioo,filnam2,1))
{  
    putfmt("Error: can't open %p\n",filnam2);
    return;
}
putfmt("What is the name of 12 absorption data file?\n");
getfmt("%p\n",filnam3);
if(!fcreate(&fioo,filnam3,1))
{  
    putfmt("Error: can't open %p\n",filnam3);
    return;
}
fcall(INITT,1,&baud);

/* SET VOLTAGE FOR ZERO TIME DELAY */
putfmt("Type delay for simultaneous pulses\n");
getfmt("%i\n",&zero);
while(zero>=0)
{  
    zer = zero;
    putvolt(0,(int)(2047.0-204.8*(zer/100.0)));
    putfmt("Type delay for simult pulses\n");
}
getfmt("%i\n", &zero);
}

/* SET TIME DELAY */
putfmt("Type initial delay in ns\n");
getfmt("%i\n", &initial);
while(initial>=0)
{
    init = initial;
    putvolt(0,(int)(2047.0-204.8*((init+zer)/100.0)));
    putfmt("Type initial delay in ns\n");
    getfmt("%i\n", &initial);
}

/* SET ECHO SIGNAL LOCATION AND DURATION IN DIGITIZER'S TIME AXIS */
putfmt("Which channel is the center of echo?\n");
getfmt("%i\n", &chann);
putfmt("Type echo half width on digitizer\n");
getfmt("%i\n", &wid);
/* SET NOISE-BACKGROUND LOCATION */
putfmt("Type separation to sum background\n");
getfmt("%i\n", &sep);
/* SET DATA AVERAGING NUMBER */
putfmt("How many shots do you want?\n");
getfmt("%i\n", &shots);
/* SET FIELD SWEEP RANGE, INCREMENT, AND TIME DELAY BETWEEN INCREMENTS */
    w[0] = 0;
    z[0] = 0;
    putfmt("Type field sweep range 0.0 to 10.0(0 to 2KG)\n");
    getfmt("%f\n", &sweep);
    putfmt("Type field sweep increment (int)\n");
    getfmt("%i\n", &incr);
    putfmt("Type delay of field sweep (int)\n");
    getfmt("%i\n", &delay);
    for(k=0;k<=(int)(204.8*sweep);k+=incr)
    {
        putvolt(1,(int)(2047.0+k));
        for(i=0;i<=2*delay;i++){}
    }
/* SET DIGITIZER MODE */
    cmd1 = "DIG SA\n0";
i = itob(cmd1+7,shots,10);
cmd1[7+i] = \0;
cmd2 = "READ SA\n";
cmd3 = "MOD TV\n0";
cmd4 = "MOD DIG\n0";
lenst1 = lenstr(cmd1);
lenst2 = lenstr(cmd2);
lenst3 = lenstr(cmd3);
lenst4 = lenstr(cmd4);
fcall(IBUP,2,&remote,&digitizer);
fcall(IBUP,4,&write,&digitizer,cmd4,&lenst4);
/* START */
putfmt("hit return key to start
");
getfmt("\n");
/* DRAW AXES FOR PLOTS */
fcall(ININITT,1,&baud);
fcall(MOVABS,2,&x0,&y0);
fcall(DRWABS,2,&x0,&y0);
fcall(DRWABS,2,&x0,&y0);
fcall(MOVABS,2,&x0,&y0);
sran = (int)(409.6*sweep);
x1 = x0;
y1 = y0;
x2 = x0;
y2 = y0;
/* START SCAN */
for(i=0;i<=sran;i+=incr)
{
    putvolt(0,(int)(2047.0-204.8*(init+zer)/100.0));
    putvolt(1,(int)(2047.0+204.8*sweep-i));
    for(k=0;k<=delay;k++){}
/* SET DIGITIZER FOR RECEIVING SIGNAL */
fcall(IBUP,4,&write,&digitizer,comdl,&lenstl);
/* GET LASER ABSORPTIONS */
for(k=1;k<=shots;k++)
{
    gettrg();
a = getvolt(1);
a1 = getvolt(2);
b1 = getvolt(3);
b = getvolt(4);
c = (long)(a*500/b);
c1 = (long)(a1*500/b1);
z[k] = z[k-1]+c1;
w[k] = w[k-1]+c;
    bin = (int)(i/incr);
    pa[bin] = w[shots]/shots;
    pb[bin] = z[shots]/shots;
/* SET DIGITIZER FOR SENDING DATA */
fcall(IBUP,4,&write,&digitizer,comd2,&lenst2);
fcall(IBUP,4,&read,&digitizer,strip,&three);
fcall(IBUP,4,&read,&digitizer,array,&size);
fcall(IBUP,4,&read,&digitizer,strip,&two);
for(k=0;k<512;k++)
{
    data[k] = (long)(array[2*k]*bit9 + array[2*k+1]*one);
}
    ech = data[chann-wid];
ezero = data[chann+sep-wid];
for(k=chann-wid+1;k<=chann+wid;k++)
{
    ech += data[k];
}
ezero += data[k+sep];
}
echo[bin] = (long)(ech-ezero);
sumaray[bin] = (long)(echo[bin]/(shots*(wid+1)));

/* PLOT DATA */
x = (int)((float)630*i/sran + 30);
y = (int)((float)(0.75*sumaray[bin])+100);
fcall(DRWABS,2,&x,&y);
fcall(MOVABS,2,&x1,&y1);
x1 = (int)((float)630*i/sran + 30);
y1 = (int)((float)(0.75*pa[bin])+100);
fcall(DRWABS,2,&x1,&y1);
fcall(MOVABS,2,&x2,&y2);
x2 = (int)((float)630*i/sran + 30);
y2 = (int)((float)(0.75*pb[bin])+100);
fcall(DRWABS,2,&x2,&y2);
fcall(MOVABS,2,&x,&y);

/* RESET DIGITIZER AND PLOTER */
fcall(IBUP,4,&write,&digitizer,comd3,&lenst3);
fcall(IBUP,2,&local,&digitizer);
fcall(MOVABS,2,&x0,&y0);
fcall(DRWABS,2,&x0,&y0);
fcall(MOVABS,2,&x0,&y0);

/* WRITE DATA INTO FILE */
putf(&fio,"%n");
for(i=0;i<=(int)(sran/incr/8);i++)
{
    printf(&fio,"%06d %06d %06d %06d %06d %06d %06d %06d\n",(long)(8*i),sumaray[8*i+0],sumaray[8*i+1],sumaray[8*i+2],sumaray[8*i+3],sumaray[8*i+4],sumaray[8*i+5],sumaray[8*i+6],sumaray[8*i+7]);
}
fclose(&fio);
putf(&fioo,"%n");
for(i=0;i<=(int)(sran/incr/8);i++)
{
    printf(&fioo,"%06d %06d %06d %06d %06d %06d %06d %06d\n",(long)(8*i),pa[8*i+0],pa[8*i+1],pa[8*i+2],pa[8*i+3],pa[8*i+4],pa[8*i+5],pa[8*i+6],pa[8*i+7]);
}
fclose(&fioo);
printf(&fioo,"%n");
for(i=0;i<=(int)(sran/incr/8);i++)
{
    printf(&fioo,"%06d %06d %06d %06d %06d %06d %06d %06d\n",(long)(8*i),pb[8*i+0],pb[8*i+1],pb[8*i+2],pb[8*i+3],pb[8*i+4],pb[8*i+5],pb[8*i+6],pb[8*i+7]);
}
fclose(&fioo);
printf("%pn",bell);