Resonant enhancement of direct two-photon absorption in Tb^{3+}:$LiYF_4$

Jin Huang,* G. K. Liu,† and R. L. Cone
Physics Department, Montana State University, Bozeman, Montana 59717
(Received 17 May 1988; revised manuscript received 5 December 1988)

Resonant enhancement by a factor of over 20 of direct two-photon absorption from the ground state $^7F_6$ to the excited state $^5G_6$ of the $4f^8$ configuration of the Tb^{3+} ion at 40 200 cm^{-1} has been observed in time-resolved experiments with two separate pulsed lasers. The results provide clear evidence for resonant enhancement of two-photon absorption in rare-earth compounds and imply a similar enhancement for Raman scattering and nonlinear-optical mixing. Two separate contributions to the direct transition moment were observed. When a single laser frequency was used, the intermediate states which made the largest contribution were from excited configurations of opposite parity; those intermediate states were far from resonance. Detailed two-frequency experiments showed, however, that near a single photon $^7F_6$-$^5D_4$ resonance, a much stronger contribution arose from the $4f^8$ configuration $^5D_4$ intermediate state. Two-photon absorption was clearly isolated from two-step (incoherent) excitation by varying the timing of two separately triggered lasers.

INTRODUCTION

Two-photon absorption has been observed in a number of rare-earth compounds since the basic theory was given by Göppert-Mayer in 1931.[1] Indeed, the first observation of this effect in any material was reported for the rare-earth crystal Eu^{2+}: CaF_2 by Kaiser and Garrett in 1961.[2] Recent experiments[3-7] on Gd^{3+} and Eu^{2+} in LaF_3, CaF_2, and other hosts have attracted wide attention. The leading terms in the transition moment were unusually small for the half-filled shell and near Russell-Saunders coupling limit appropriate to the $4f^7$ configuration of Gd^{3+} and Eu^{2+}, so the observations for those ions have led to several theoretical advances.[8,5-7,9] Experiments and analyses have now been reported for a majority of the lanthanide elements: Ce^{3+},[10-13] Pr^{3+},[14-16] Nd^{3+},[17,18] Sm^{2+},[19] Eu^{3+},[20-24] Eu^{2+},[2,7,25,26] Gd^{3+},[3-6,27-29] Tb^{3+},[20,30] Ho^{3+},[31,32] Er^{3+},[31,33] Tm^{3+}.[34] In each of these cases (except Ref. 17), only the two-photon resonance was reported. In some cases stepwise multiphoton processes may have contributed to the observed signals, since separating the two processes is not always straightforward.

The purpose of this paper is to report significant intermediate-state enhancement of the direct two-photon transition probability for a rare-earth system. Such enhancement of direct two-photon absorption was expected from the early theory and was observed dramatically in sodium vapor by Bjorkholm and Liao in 1974.[35] Large resonant enhancements have also been observed in semiconductors such as CuCl by a number of investigators.[36]

Specifically, we report both the observation of direct two-photon absorption from the ground state $^7F_6$ level of Tb^{3+} in $LiYF_4$ to the excited-state components of $^5G_6$ at 40 200 cm^{-1} and the observation of resonant enhancement of this direct transition by over a factor of 20 when one laser frequency ω_1 was tuned near the real $^5D_4$ intermediate state in a two-beam two-color experiment. A time-resolved technique involving two synchronized lasers with variable timing has been used to study the strength of the direct two-photon absorption as a function of intermediate-state detuning. The Tb^{3+} ion is ideal for studies of this type since there are large energy gaps on both the high- and low-energy sides of the $^5D_4$ energy levels (lowest $^5D_4$ component at 20 553.5 cm^{-1}, highest $^5D_4$ component at 20 644.8 cm^{-1}).

Recently we reported[37-41] evidence for multiresonant contributions to the third-order nonlinear optical susceptibilities of $Tb(OH)_3$ and $LiTbF_4$. Such contributions could have a close relationship to two-photon absorption. The experiments reported here provide further proof of observable multiresonant nonlinear processes in rare-earth systems.

The similar process of resonant electronic Raman scattering was inferred by Kiel and others[42] from experiments on the rare-earth chlorides with several fixed laser frequencies. More recently, resonant electronic Raman scattering has been explored with tunable lasers for Tb^{3+} in terbium aluminum garnet,[43] for the Tb^{3+}:$LiYF_4$ compound we describe here[44] and for Er^{3+} and Pr^{3+} in several phosphate crystals.[45-47]

EXPERIMENTAL DETAILS

A partial energy-level diagram for the $4f^8$ configuration of the Tb^{3+} ion is presented in Fig. 1. This is based on our previous studies[48] of excited-state absorption spectra for Tb^{3+}:$LiYF_4$.

For the single-beam, single-color, single-resonance direct two-photon absorption experiment, the laser frequency ω_L was tuned so that $2\omega_L$ matched the various $^7F_6$-$^5G_6$ transition energies. To investigate the additional intermediate-state resonance, a double-beam two-color direct two-photon absorption experiment was carried out. One laser was fixed at a frequency ω_1 chosen to be $\Delta\omega$

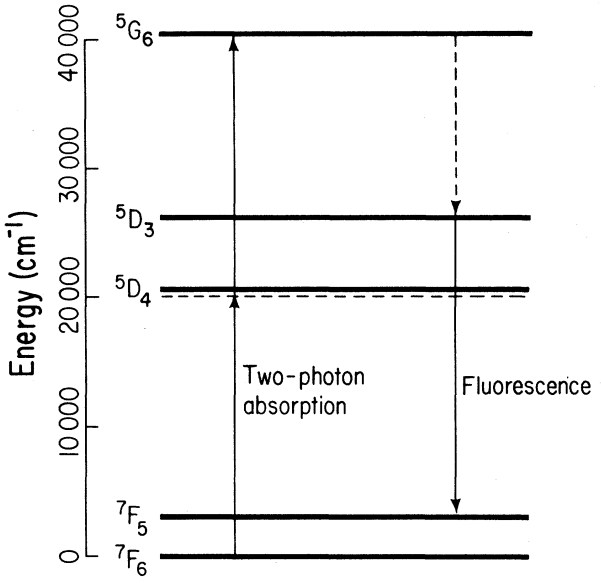

FIG. 1. Partial-energy-level diagram for Tb^{3+}:$LiYF_4$ obtained from earlier two-step excitation experiments. The upward transition corresponds to direct two-photon absorption between real $^7F_6$ and $^5G_6$ levels. The detuning between the photon energy illustrated by the dashed line and the lowest real $^5D_4$ level is varied from about 400 down to 2 cm^{-1}. Two-photon absorption is sensitively detected by cascade fluorescence from $^5D_3$ to $^7F_5$.

below the $^5D_4$ energy level, while the ω_2 laser was tuned so that $\omega_1+\omega_2$ scanned the two-photon transitions from $^7F_6$ to $^5G_6$. Care was taken to differentiate the direct two-photon absorption and the two-step absorption processes as we will discuss later. All experiments were performed at 1.3 K.

The 410-nm antistokes cascade fluorescence from $^5D_3$ to $^7F_5$ was used to sensitively monitor the direct two-photon absorption. That fluorescence was detected using a McPherson model-218 0.3-m monochromator whose slits were oriented parallel to the laser beam for maximum collection efficiency. A selected RCA C31034A-02 photomultiplier and gated photon counting gave high quantum efficiency and negligible dark counts. A Corning CS 5-58 glass bandpass filter was also placed between the sample and the monochromator to limit the laser background.

The laser powers were typically 12 kW, and pulse durations were 5 nsec. Each laser beam was focused to approximately 75 μm diam, and the maximum light intensity was about 300 MW/cm^2, a value well below the damage threshold for the material. In two-color experiments, the beams were crossed at a small angle $\approx 1°$. The two dye lasers were pumped by separate N_2 lasers, so the time relationship between the two pulses could be scanned electronically by computer. This feature played a critical role in the experiment as we note below. Relative timing jitter for the lasers was less than 1 nsec.

The following polarization configurations were used, with each light propagation vector **k** perpendicular to the c axis: (a) $\pi\pi$ with each laser linearly polarized **E** parallel to c, (b) $\sigma\sigma$ with each laser linearly polarized **E** perpendicular to c, and (c) $\pi\sigma$, $\sigma\pi$, $\pi\pi$, and $\sigma\sigma$ combinations of polarizations achieved with the polarizer at $\pi/4$ relative to the c axis.

DIRECT TWO-PHOTON ABSORPTION

First we consider the "single-color" experiments with a single tunable laser. Direct two-photon absorption spectra showing the ground state $^7F_6$ (Γ_2) to $^5G_6$ ($\Gamma_1,\Gamma_2,\Gamma_{3,4}$) transitions are given in Fig. 2. That figure also demonstrates the excellent signal-to-noise ratio obtained. The observed $^5G_6$ energy levels are listed in Table I.

The following arguments determine that these are real direct two-photon absorption signals. (1) The single-laser frequency is 400 cm^{-1} *below* the one-photon absorption to $^5D_4$. (2) The energy levels of $^5G_6$ determined from these spectra are in good agreement with our earlier two-color two-step excitation results[48] which involved a real population of the $^5D_4$ state and two *different* laser frequencies for each transition. (3) All nearby manifolds in the vicinity of both one- and two-photon transitions have been accounted for in the earlier two-color two-step experiments, and as noted above, no one-photon processes are possible in these single-beam single-color experiments. (4) We shall show later in this paper that, in two-color experiments at the same transition energy $\omega_1+\omega_2$, temporal overlap of the two laser pulses had to be achieved with nanosecond accuracy to obtain a signal. Timing requirements for an incoherent two-step process involve the lifetime of the real intermediate state. In this case that lifetime is approximately 1 msec. That is a difference of five orders of magnitude. (5) The selection rules for the direct process are obeyed in our spectra,

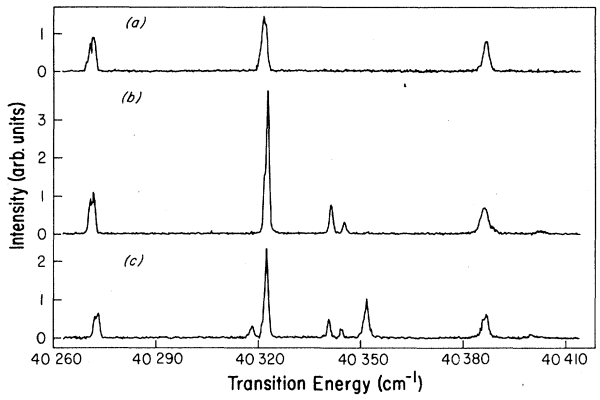

FIG. 2. Direct two-photon absorption spectra from $^7F_6$ to $^5G_6$ for three polarization conditions: (a) $\pi\pi$ with each laser linearly polarized **E** parallel to the c axis, (b) $\sigma\sigma$ with each laser linearly polarized **E** perpendicular to c, and (c) $\pi\sigma$, $\sigma\pi$, $\pi\pi$, and $\sigma\sigma$ combination achieved with the polarizer at $\pi/4$ relative to the c axis. The energy scale is twice the incident photon energy. The background for each of these laser spectra is essentially zero.

TABLE I. Observed $^5G_6$ energy levels for Tb^{3+}:$LiYF_4$ obtained by single-beam single-color direct two-photon absorption. Irreducible representations of the S_4 site group are used as labels. Nine of the ten levels are observed.

Sublevel	Energy (cm^{-1})
Γ_2	40 272.0
Γ_2	40 273.2
$\Gamma_{3,4}$	40 318.4
Γ_2	40 323.1
Γ_1	40 340.5
Γ_1	40 344.2
$\Gamma_{3,4}$	40 352.0
Γ_2	40 387.0
Γ_1	40 402.2

while different and more restrictive selection rules apply to the sequential or two-step process.

Those arguments leave no room for ambiguity that the signals we found are from direct two-photon transitions of the Tb^{3+} ion. In addition, the expected quadratic dependence of the fluorescence signal on laser power has been observed as shown in Fig. 3.

The ground state of the Tb^{3+} ion is a near-degenerate pair of Γ_2 levels split by 0.9 cm^{-1}. The next highest level is at over 100 cm^{-1}, so it is not populated in these $T=1.3$ K experiments. The S_4 symmetry crystal field in $LiYF_4$ splits the $^5G_6$ multiplet of the Tb^{3+} ion into three singlet Γ_1 states, four singlet Γ_2 states, and three doublet Γ_3, Γ_4 states. Since the Γ_3 and Γ_4 representations are related by time-reversal symmetry, their eigenvalues are degenerate, and they are labeled $\Gamma_{3,4}$. The single-photon

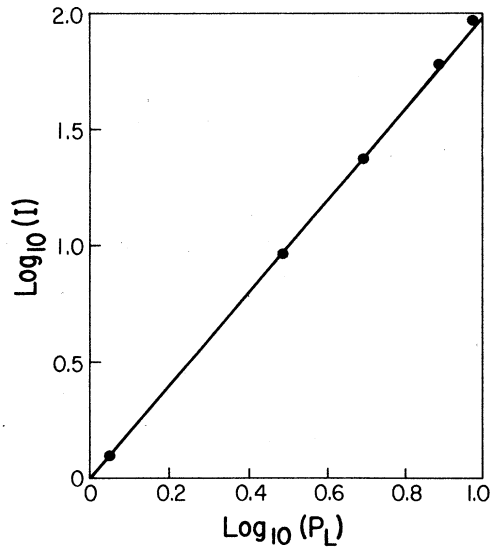

FIG. 3. Demonstration of the expected square law power dependence for the single-beam direct two-photon absorption signal.

TABLE II. Selection rules for single-photon electric dipole transitions in S_4 symmetry.

	Γ_1	Γ_2	$\Gamma_{3,4}$
Γ_1		π	σ
Γ_2	π		σ
$\Gamma_{3,4}$	σ	σ	π

selection rules for electric dipole transitions in S_4 symmetry are given in Table II.[49] Clearly, the Γ_2 levels of $^5G_6$ cannot be detected by one-photon ultraviolet absorption, since the ground state is $^7F_6(\Gamma_2)$. The two-step excitation process which uses $^5D_4(\Gamma_1)$ as an intermediate state is also forbidden for electric dipole transitions to Γ_1 states of $^5G_6$ (Γ_2-Γ_1 step allowed, but Γ_1-Γ_1 step forbidden). Therefore, neither one-photon absorption nor two-step excitation could be used alone to identify all the $^5G_6$ energy levels. For the direct two-photon absorption process, however, all transitions are allowed as shown in Table III.[50]

In Fig. 2(a) the four expected direct Γ_2-Γ_2 transitions from $^7F_6$ to $^5G_6$ have been identified clearly by direct two-photon absorption using pure $\pi\pi$ polarization. Both $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_1)$ and $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_2)$ transitions are shown in Fig. 2(b) where the laser was linearly polarized $\sigma\sigma$. Since the Γ_2-Γ_2 transitions had been identified in spectrum 2(a), the three new lines are clearly the three expected Γ_2-Γ_1 transitions. The $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_{3,4})$ transitions appeared in Fig. 2(c) where the combination of polarizations $\pi\sigma$, $\sigma\pi$, $\pi\pi$, and $\sigma\sigma$ allows all transitions. One of the three expected $\Gamma_{3,4}$ lines was not found there.

Nine out of the total ten transitions for $^7F_6(\Gamma_2)$-$^5G_6$ have been clearly identified. This provides a good illustration that two-photon absorption is complementary to both one-photon absorption and two-step excitation experiments, particularly in crystals with relatively high symmetry. Such crystals are obviously preferable when analyzing energy-level structure in unexplored high-energy regions via free-ion and crystal field calculations;[48] the high symmetry reduces the number of empirical parameters needed to describe the crystal field to a practical value.

RESONANT ENHANCEMENT OF DIRECT TWO-PHOTON ABSORPTION

We now focus our attention on the resonant enhancement of this direct two-photon absorption. We report here the clear observation of resonant enhancement of over a factor of 20 in a rare-earth doped crystal.

The intensity of a two-photon transition is proportional to

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

	Γ_1	Γ_2	$\Gamma_{3,4}$
Γ_2	$\sigma\sigma,\pi\sigma,\sigma\pi$	$\pi\pi,\sigma\sigma,\pi\sigma,\sigma\pi$	$\pi\sigma,\sigma\pi$

$$\left|\sum_i [\langle f|\mathbf{E}_2\cdot\mathbf{D}|i\rangle\langle i|\mathbf{E}_1\cdot\mathbf{D}|g\rangle/(\hbar\omega_1-\hbar\omega_i)+\langle f|\mathbf{E}_1\cdot\mathbf{D}|i\rangle\langle i|\mathbf{E}_2\cdot\mathbf{D}|g\rangle/(\hbar\omega_2-\hbar\omega_i)]\right|^2 ,$$

where $|g\rangle$ is the ground state, $|f\rangle$ is the final state, $|i\rangle$ is an intermediate state, **E** is the electric field, **D** is the electric dipole operator, and $\hbar\omega_i$ is the energy of the intermediate state $|i\rangle$, and ω_1 and ω_2 are the photon frequencies. Summation is carried out over all intermediate states. For our experiment, the $4f^7 5d$ and $4f^7 5g$ configurations of the Tb^{3+} ion give constant amplitude contributions to this summation, since they are very far from resonance. On the other hand, the $^5D_4$ energy level can act as the dominant intermediate state when the laser frequency ω_1 approaches that energy level. In the latter case, the nonzero dipole matrix elements arise from the usual forced electric dipole process[51] of Judd and Ofelt involving interconfiguration mixing of the electronic states. Those smaller matrix elements are offset by a smaller energy denominator near resonance. (Alternately, if one thinks of the electronic states as arising from a pure configuration, these resonant terms require a higher-order perturbation expression for the two-photon transition moment.)

To demonstrate the resonant enhancement of the direct two-photon absorption from $^7F_6$ to $^5G_6$ arising from the $^5D_4$ intermediate state, a series of spectra had to be recorded, each with a different intermediate state detuning $\Delta\omega$. Unlike the previously described case, two different frequencies had to be used to study this effect.

A further experimental problem also has to be overcome. Some weak broad-band laser dye fluorescence was present in the near-resonant ω_1 beam, even after filtering it with a prism monochromator. When the ω_1 laser was tuned near the $^5D_4$ resonance, the dye fluorescence weakly populated that level, and two-step excitation could not be completely avoided. (That small population could in principle also contribute a weak anti-Stokes fluorescence signal by two-ion up-conversion energy transfer.[52]) Since the anti-Stokes fluorescence from all these two-step excitation processes has a 1-msec lifetime, it provides no means for determining the original excitation mechanism.

In order to discriminate the real direct two-photon absorption signal under these conditions, we exploited the following time-resolved excitation technique. Each data point on the resonance curve was taken in several steps. First, a spectrum was recorded by scanning the frequency ω_2 so that $\omega_1+\omega_2$ scanned across the known direct two-photon transitions to $^5G_6$ with the timing of the two beams ω_1 and ω_2 kept exactly identical and the laser frequency ω_1 fixed below the $^5D_4$ resonance by $\Delta\omega$. Second, ω_2 was fixed at each observed peak excitation frequency, and the laser timing was scanned to isolate the direct two-photon absorption signal from the various background signals. A typical result, given in Fig. 4, shows the signal versus time separation between the two lasers. Each laser pulse duration was 5 nsec. The width of the timing peak shown in Fig. 4 is 10 nsec, which is the pulse overlap time, just as expected for the transient response for the direct two-photon absorption. The two-step excitation contribution appears as a long "flat" step background overlapping the peak and extending to the right where the ω_1 pulse is ahead of ω_2 in time. That step decays with the population lifetime of the $^5D_4(\Gamma_1)$ intermediate state, which is about 1 msec as noted above. The experimental data thus clearly show the expected transient property of the direct two-photon absorption and provide a means to classify the excitation mechanisms. By subtracting the background from the peak, the real strength of the resonant two-photon absorption was determined. The data from this series of runs were also corrected for power fluctuations of the lasers which were measured by two photodiodes and recorded by computer for each laser pulse.

The measured resonance behavior for one of the transitions is given by the solid points in Fig. 5. This result is for the $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_2)$ transition at 40 323.1 cm^{-1} with both laser beams π polarized. The horizontal axis $\Delta\omega$ shows the frequency detuning of the ω_1 laser below the $^5D_4(\Gamma_1)$ energy level at 20 553.5 cm^{-1}. The vertical axis shows the strength of the direct two-photon transition obtained from the series of spectra described above. The

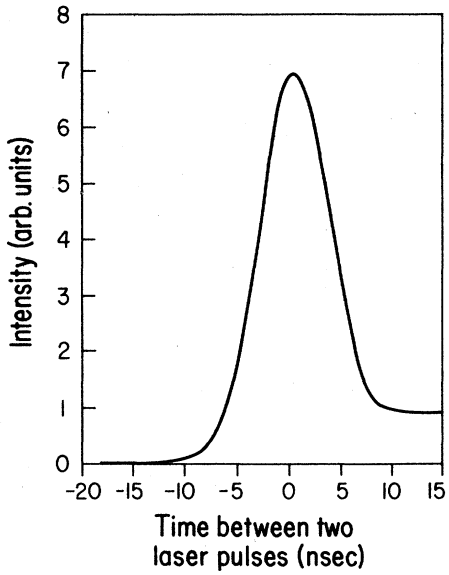

FIG. 4. Observed transient response of the two-photon absorption signal, which allows isolation of the direct two-photon absorption from the two-step excitation process near resonance. Variation of the arrival time of the incident ω_1 and ω_2 laser pulses, each of 5-nsec duration and each with a different frequency, gives a sharp peak due to the direct two-photon absorption and a "step" due to excitation of a real intermediate state ($^5D_4$) by the weak dye fluorescence continuum from the ω_1 laser. A delay of zero corresponds to perfect overlap of the two laser pulses. Positive delays correspond to ω_1 preceeding ω_2.

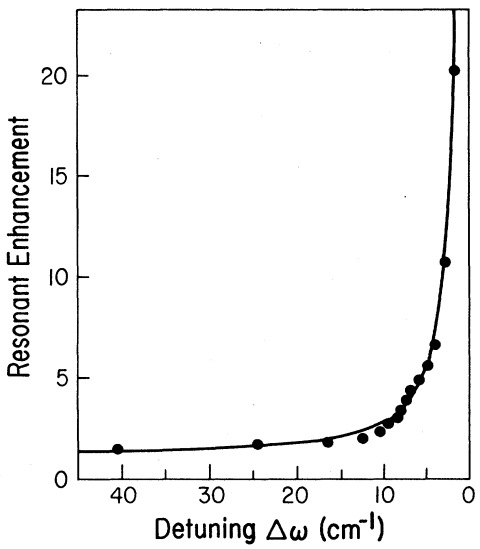

FIG. 5. Measured resonance behavior for the $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_2)$ transition at 40 323.1 cm^{-1} shown by the solid points, with a theoretical fit shown as the solid curve. The horizontal axis is the detuning $\Delta\omega$ of the ω_1 photon below the $^5D_4(\Gamma_1)$ intermediate state. The resonance enhancement is a factor of 20 at a detuning of 2 cm^{-1}.

vertical scale is normalized in terms of the strength of the transition far from the intermediate-state resonance. Resonant enhancement by a factor of 20 is evident when ω_1 was 2 cm^{-1} below the resonance with $^5D_4(\Gamma_1)$. For comparison, the inhomogeneously broadened absorption line width for $^5D_4(\Gamma_1)$ is 0.5 cm^{-1}. From Table II, both of the single-photon transitions from the $^7F_6(\Gamma_2)$ ground state to the $^5D_4(\Gamma_1)$ intermediate state and from the $^5D_4(\Gamma_1)$ intermediate state to the $^5G_6(\Gamma_2)$ final state are allowed. Similar results were also obtained for the $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_{3,4})$ transitions, when the ω_1 laser beam was π polarized and the ω_2 laser beam was σ polarized. No resonant enhancement was observed for the $^7F_6(\Gamma_2)$-$^5G_6(\Gamma_1)\sigma\sigma$ transition, as expected, since both the $^7F_6(\Gamma_2)$-$^5D_4(\Gamma_1)$ and the $^5D_4(\Gamma_1)$-$^5G_6(\Gamma_1)$ single-photon transitions are forbidden by the S_4 site symmetry for that polarization.

We thus conclude that the $^5D_4(\Gamma_1)$ level acts as the intermediate state for this resonant enhancement of the two-photon transitions from $^7F_6(\Gamma_2)$ to $^5G_6(\Gamma_2,\Gamma_{3,4})$.

A theoretical fit to the data, plotted as the solid line in Fig. 5, was based on a simple model. For a singlet ground state the intensity of the two-photon transition is proportional to the square of two significant amplitudes, only one of which is frequency dependent,

$$|\langle f|\mathbf{E}_2\cdot\mathbf{D}|i\rangle\langle i|\mathbf{E}_1\cdot\mathbf{D}|g\rangle/(\hbar\omega_1-\hbar\omega_i)+B|^2 .$$

The first term represents the resonant contribution involving the $^5D_4(\Gamma_1)$ intermediate state. The second term represents the total nonresonant part due to the contributions of $4f^7 5d$ and $4f^7 5g$ intermediate states. (For a discussion of the role of g electrons, see Ref. 47.) As noted earlier, dipole moments for these states are parity allowed, so they have large values which offset the large energy denominator. Changing the ω_1 frequency over the experimental range of 400 cm^{-1} below the $^5D_4$ energy level does not significantly change the energy denominators for those contributions, so their strength remains constant as ω_1 varies.

For our sample, a minor extension of this simple picture was appropriate. The $^7F_6(\Gamma_2)$ ground state is really a pair of levels separated by 0.9 cm^{-1}. The observed signal thus involved both a transition of type (a) and one of type (b) as shown in Fig. 6. The previous expression was generalized to describe these two transitions as follows:

$$|\langle f|\mathbf{E}_2\cdot\mathbf{D}|i\rangle\langle i|\mathbf{E}_1\cdot\mathbf{D}|g\rangle/(\hbar\omega_1-\hbar\omega_i)+B|^2+A|\langle f|\mathbf{E}_2\cdot\mathbf{D}|i\rangle\langle i|\mathbf{E}_1\cdot\mathbf{D}|g\rangle/[\hbar\omega_1-(\hbar\omega_i-0.9)]+B|^2 .$$

The matrix elements and constants B are essentially identical for each transition based on the calculated wave functions for the two $^7F_6(\Gamma_2)$ and $^5D_4(\Gamma_1)$ states. The only adjustable parameters affecting the resonance shape are thus A and B.

The parameter A may be estimated. For photons of frequencies ω_1 and ω_2, the resonance behavior for each type of transition will be different. Although ω_1 may be simultaneously near the separate one-photon resonances for transitions of types (a) and (b), the two-photon energy $\omega_1+\omega_2$ is significantly off resonance for those of type (b). The second $^7F_6(\Gamma_2)$ level responsible for the type-(b) transitions will also have only 25% population at the 1.3 K temperature of our experiments. Based on the measured line shape from the single-beam direct two-photon absorption experiments and the reduced population, we estimate that A has a value of 0.075. With the matrix element products set to an arbitrary value of 100 and the $\hbar\omega$'s given in cm^{-1}, the fitted value of B is 15.5.

As seen in Fig. 5, the fit is quite satisfactory. The nearest additional allowed ω_1 transition is to the other $^5D_4(\Gamma_1)$ level located 14.4 cm^{-1} higher in energy. Since we can again confidently predict similar dipole matrix elements for that resonance based on the known crystal field wave functions, it is clear that it would make a negligible contribution to the theoretical curve.

No interference effect was observed on the low-energy side of the resonance. This implies that the resonant and nonresonant contributions have the same sign in this case where we are below both $^5D_4$ and the excited configurations. When the ω_1 laser frequency was tuned higher than the $^5D_4(\Gamma_1)$ resonance to continue the search for interference effects, vibronic absorption led to a larger population of the $^5D_4(\Gamma_1)$ intermediate state. The two-

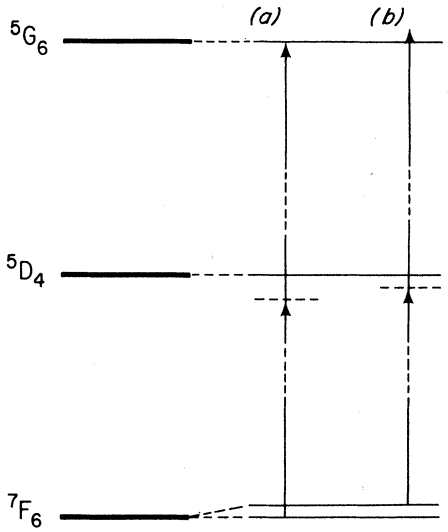

FIG. 6. Model for the observed signal showing the contribution of the two $^7F_6(\Gamma_2)$ levels separated by 0.9 cm^{-1}. (a) Transition has an exact two-photon resonance, while (b) transition is off resonance by 0.9 cm^{-1}.

step excitation process then gave such a strong and broad background that the direct two-photon transition could not be accurately isolated. This inherent asymmetry in phonon-assisted transitions above and below a pure electronic transition thus makes observation of interference difficult in this case in contrast to the situation in the gas phase.[35] (For further discussion of phonon-assisted processes see Ref. 53 and other references contained therein.) With further refinement in the spectral purity of the lasers, it may still be possible to observe the interesting interference effects.

More sophisticated fits to the line shape seem inappropriate at this time. With improvements to the experiment, however, it may become possible to exploit them to measure coherence times.

CONCLUSIONS

We have demonstrated both direct two-photon absorption from $^7F_6$ to $^5G_6$ in Tb^{3+}:$LiYF_4$ and the clear enhancement of this direct transition by the $^5D_4$ intermediate state. We have also confirmed that the selection rules for resonant enhancement match those for single-photon transitions as expected.

It is easy to envision application of this type of resonant enhancement to studies of other nonlinear optical processes such as four-wave mixing and to the closely related process of resonant Raman scattering (see Ref. 37–47 and 54). It would also be interesting to study resonant enhancement of direct two-photon absorption in other rare-earth compounds where much larger $4f^n$-$4f^n$ single-photon transition probabilities are known. Resonant enhancements are likely to be several orders of magnitude larger there.

The direct two-photon transitions also extended our previous studies[48] of excited-state absorption spectra of Tb^{3+} from the $^5D_4$ manifold to 46 000 cm^{-1} in 1 at. % Tb^{3+}:$LiYF_4$ by adding additional observed levels and providing additional information for identifying the observed energy levels. Two-photon absorption spectra will greatly expand our general knowledge of highly excited states of rare-earth ions, many of which have received little attention. The opportunities for better determination of the free-ion parameters and for improved understanding of single-photon and multiphoton transition intensities are quite significant.

The time-resolution technique we have exploited in this experiment may be useful for studying other transient multiphoton processes. Several variations and refinements may also allow it to be used for coherence measurements involving the intermediate states.

ACKNOWLEDGMENTS

We thank H. J. Guggenheim of AT&T Bell Laboratories for the Tb^{3+}:$LiYF_4$ crystal, Jan Hessler for suggesting the detection scheme, and J. M. Friedman, H. L. Carter, Steven Chu, B. Jacquier, J. C. Gacon, and N. Edelstein for helpful conversations.

*Present address: Physics Department, University of Oregon, Eugene, OR 97403-1274.
†Present address: Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

[1]M. Göppert-Mayer, Ann. Phys. (Leipzig) **9**, 273 (1931).
[2]W. Kaiser and C. G. B. Garrett, Phys. Rev. Lett. **7**, 229 (1961).
[3]M. Dagenais, M. Downer, R. Neumann, and N. Bloembergen, Phys. Rev. Lett. **46**, 561 (1981).
[4]M. C. Downer, A. Bivas, and N. Bloembergen, Opt. Commun. **41**, 335 (1982).
[5]M. C. Downer and A. Bivas, Phys. Rev. B **28**, 3677 (1983).
[6]N. Bloembergen, J. Lumin. **31&32**, 23 (1984).
[7]M. C. Downer, C. D. Cordero-Montalvo, and H. Crosswhite, Phys. Rev. B **28**, 4931 (1983).
[8]B. R. Judd and D. R. Pooler, J. Phys. C **15**, 591 (1982).
[9]M. F. Reid and F. S. Richardson, Phys. Rev. B **29**, 2830 (1984).
[10]S. K. Gayen and D. S. Hamilton, Phys. Rev. B **28**, 3706 (1983).
[11]S. K. Gayen, G. J. Pogatshnik, and D. S. Hamilton, J. Lumin. **31&32**, 260 (1984).
[12]S. K. Gayen, D. S. Hamilton, and R. H. Bartram, Phys. Rev. B **34**, 7517 (1986).
[13]R. C. Leavitt, Phys. Rev. B **35**, 9271 (1987).
[14]W. M. Yen, C. G. Levey, Shihua Huang, and Shui T. Lai, J. Lumin. **24&25**, 659 (1981).
[15]C. D. Cordero-Montalvo and N. Bloembergen, Phys. Rev. B **30**, 438 (1984).
[16]R. S. Rana, C. D. Cordero-Montalvo, and N. Bloembergen, J. Chem. Phys. **81**, 2951 (1984).
[17]M. A. Kramer and R. W. Boyd, Phys. Rev. B **23**, 986 (1981). These results are presented as three-photon absorption; an alternate interpretation mentioned by the authors involves step-

wise excitation.
[18]L. L. Chase and S. A. Payne, Phys. Rev. B **34**, 8883 (1986).
[19]J. C. Gacon, J. M. Marcerou, and B. Jacquier (unpublished).
[20]G. A. Skripko, A. G. Makhanek, and R. I. Gintoft, Zh. Prikl. Spektrosk. **24**, 968 (1976) [J. Appl. Spectrosc. (USSR) **24**, 685 (1986)].
[21]L. E. Kholodenkov and A. G. Makhanek, Phys. Status Solidi **112**, K149 (1982).
[22]A. K. Makhanek, R. I. Gintoft, L. A. Dzhuguryan, V. S. Korol'kov, and L. E. Kholodenkov, Zh. Prikl. Spektrosk. **40**, 964 (1984) [J. Appl. Spectrosc. (USSR) **40**, 684 (1984)].
[23]L. E. Kholodenkov and A. K. Makhanek, Phys. Status Solidi **125**, 365 (1984).
[24]L. E. Kholodenkov, A. K. Makhanek, and A. A. Kaminskii, Phys. Status Solidi **126**, 659 (1984).
[25]U. Fritzler and G. Schaack, J. Phys. C **9**, L23 (1976).
[26]U. Fritzler, Z. Phys. B **27**, 289 (1977).
[27]C. D. Cordero-Montalvo, Phys. Rev. B **31**, 5433 (1985).
[28]R. Mahiou, B. Jacquier, and R. L. Cone, J. Phys. (Paris) **46**, C7-119 (1985).
[29]B. Jacquier, Y. Salem, C. Linares, J. C. Gacon, R. Mahiou, and R. L. Cone, J. Lumin. **38**, 258 (1987).
[30]B. Jacquier, J. C. Gacon, J. F. Marcerou, M. F. Joubert, and R. L. Cone, J. Lumin. **40&41**, 517 (1987).
[31]P. A. Apanasevich, R. I. Gintoft, V. S. Korolkov, A. G. Makhanek, and G. A. Skripko, Phys. Status Solidi **58**, 745 (1973).
[32]D. N. Rao, J. Prasad, and P. N. Prasad, Phys. Rev. B **28**, 20 (1983).
[33]R. I. Gintoft and G. A. Skripko, Zh. Prikl. Spektrosk. **17**, 885 (1972) [J. Appl. Spectrosc. (USSR) **17**, 1480 (1972)].
[34]K. C. Bleijenberg, F. A. Kellendonk, and C. W. Struck, J. Chem. Phys. **73**, 3586 (1980).
[35]J. E. Bjorkholm and P. F. Liao, Phys. Rev. Lett. **33**, 128 (1974).
[36]Reviews have been given by J. B. Grun, B. Hönerlage, and R. Levy, in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), pp. 459–504, and E. S. Koteles, *ibid.,* pp. 83–140.
[37]R. L. Cone, D. A. Ender, M. S. Otteson, P. L. Fisher, J. M. Friedman, and H. J. Guggenheim, in *Laser Techniques for Extreme Ultraviolet Spectroscopy, (Boulder, CO),* Proceedings of the Conference on Laser Techniques for Extreme Ultraviolet Spectroscopy, AIP Conf. Proc. No. 90, edited by T. J. McIlrath and R. R. Freeman (AIP, New York, 1982), pp. 471–477.
[38]R. L. Cone, D. A. Ender, M. S. Otteson, P. L. Fisher, J. M. Friedman, and H. J. Guggenheim, Appl. Phys. B **28**, 143 (1982).
[39]D. A. Ender, M. S. Otteson, R. L. Cone, M. B. Ritter, and H. J. Guggenheim, Opt. Lett. **7**, 611 (1982).
[40]D. A. Ender, M. S. Otteson, Jin Huang, R. L. Cone, J. M. Friedman, and H. J. Guggenheim (unpublished).
[41]Jin Huang, R. L. Cone, J. M. Friedman, H. J. Guggenheim, and B. Jacquier (unpublished).
[42]A. Kiel, *Light Scattering Spectra of Solids,* edited by G. B. Wright (Springer-Verlag, 1969), pp. 245–253.
[43]D. Nicollin and J. A. Konigstein, Chem. Phys. **49**, 377 (1980); P. Myslynski and J. A. Konigstein, *ibid.* **114**, 137 (1987); J. A. Konigstein, Chem. Phys. Lett. **146**, 576 (1988).
[44]R. L. Cone, T. W. Scott, J. M. Friedman, and H. J. Guggenheim (unpublished).
[45]P. C. Becker, G. M. Williams, R. E. Russo, N. Edelstein, J. A. Konigstein, L. A. Boatner, and M. M. Abraham, Opt. Lett. **11**, 282 (1986).
[46]P. C. Becker, N. Edelstein, G. M. Williams, J. J. Bucher, R. E. Russo, J. A. Konigstein, L. A. Boatner, and M. M. Abraham, Phys. Rev. B **31**, 8102 (1985).
[47]P. C. Becker, N. Edelstein, B. R. Judd, R. C. Leavitt, and G. M. S. Lister, J. Phys. C **18**, L1063 (1985).
[48]R. L. Cone, T. W. Scott, J. M. Friedman, H. J. Guggenheim, Hannah Crosswhite, Jin Huang, and Liu Guokui (unpublished).
[49]H. P. Christensen, Phys. Rev. B **17**, 4060 (1978).
[50]W. Hayes and R. Loudon, *Scattering of Light by Crystals* (Wiley, New York, 1978), pp. 43–49.
[51]B. R. Judd, Phys. Rev. **127**, 750 (1962); G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).
[52]For a recent review of ion-ion interactions including upconversion phenomena see R. L Cone and R. S. Meltzer, in *Spectroscopy of Solids Containing Rare Earth Ions,* edited by A. A. Kaplyanskii and R. M. Macfarlane (North-Holland, Amsterdam, 1987), pp. 481–556.
[53]F. Auzel, Phys. Rev. B **13**, 2809 (1976).
[54]G. M. Williams, P. C. Becker, N. Edelstein, L. A. Boatner, and M. M. Abraham (unpublished); G. M. Williams, Ph.D. thesis, University of California, Berkeley, 1988.