Ultranarrow Nonlinear Optical Resonances in Solids

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Using a method for nonlinear laser spectroscopy which eliminates the effects of laser jitter in nearly degenerate four-wave mixing, we present the first direct measurement of the ground-state relaxation rate of optically excited Cr^{3+} ions in $Cr:YAlO_3$. The Lorentzian linewidth of the emission resonance is 9.8 Hz (FWHM). The mechanism of ground-state relaxation is established to be fluorescent decay of the ^2E metastable level.

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In this paper, we present a measurement of the frequency-domain spectrum of the backward-wave resonance in $Cr:YAlO_3$ using a technique which eliminates the effects of laser jitter in nearly degenerate four-wave mixing (NDFWM). An emission-resonance linewidth of 9.8 Hz (FWHM) is measured at room temperature and provides the first direct measurement of the ground-state relaxation rate. These results are explained quantitatively on the basis of the third-order nonlinear optical polarization obtained by a solution of the equation of motion for the density matrix. The observations are entirely distinct from narrow linewidths observed previously on first-order coherences in low-temperature solids.[1] We show that $Cr:YAlO_3$ is an open two-level quantum mechanical system due to the excited-state decay channel to the ^2E level. This interpretation is analogous to earlier work where atomic sodium was shown to evolve from a closed two-level system to an open two-level system[2,3] in the presence of state-specific[4] buffer-gas collisions.

Earlier measurements of NDFWM resonant structure were limited by laser jitter and transit-time effects. In this work, we present a new technique which eliminates the adverse effects of laser-frequency jitter and apply it to a system in which there are no transit-time effects, namely, $Cr:YAlO_3$. These measurements show that the resonant structure is a Lorentzian profile with a width determined by the ground-state relaxation of the Cr^{3+} ion involving a single process: fluorescent decay of the ^2E level. The frequency-domain measurements are in excellent agreement with time-domain measurements of the fluorescence decay. Similar results are obtained for ruby.

NDFWM emission resonances arise from the third-order nonlinear optical interaction[5] of two counterpropagating pump beams at frequency ω and an independently tunable probe beam at frequency $\omega+\delta$. Energy conservation gives the signal frequency at $\omega-\delta$. Phase matching insures that if the two pumps are counterpropagating, then the signal wave is counterpropagating with respect to the probe beam. For our measurements the resonance of interest occurs at $\delta=0$ and is observed by sweeping δ and observing the backward-wave signal. The nonlinearity responsible for the mixing is due to spatial hole burning in the Cr^{3+}-doped materials. In this paper, we demonstrate that if the two frequencies ω and $\omega+\delta$ are derived from the same source, then the source jitter does not contribute to the observed linewidth.

Our measurements were performed with a 3.9-mm-thick sample of room-temperature $Cr:YAlO_3$ doped with approximately 0.05% Cr and exhibiting an optical density of 0.29 at 570 nm. The crystal was positioned with the *c* axis parallel to the two counterpropagating pump beams. The experimental configuration is shown in Fig. 1. The probe beam was nearly collinear with the forward pump beam and intersected the pump beams in the sample at an angle of 0.3°. As shown in the figure, two acousto-optic modulators were used to synthesize the appropriate wavelengths for the pump and probe beams and to permit tuning through zero offset frequency. The intensities were in the range of 1–20 W/cm^2. The measurements were confirmed to be independent of pump intensity. The acousto-optic modulators were driven by two frequency synthesizers at ω_1 and ω_2, respectively. The two synthesizers were phase locked together and stable to better than 1 Hz throughout the duration of each experiment. Typically, ω_1 was held fixed at 40 MHz, and ω_2 was scanned over a 200-Hz range centered at 40 MHz. The fundamental laser frequency was tuned near 570 nm for peak signal from the sample. As we show below, the

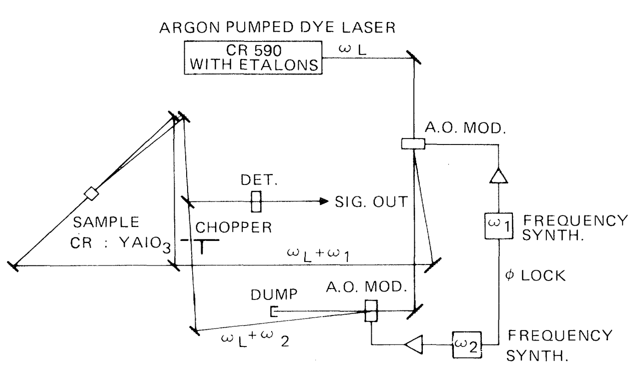

FIG. 1. Experimental configuration for NDFWM using synthesized frequencies for the three input beams.

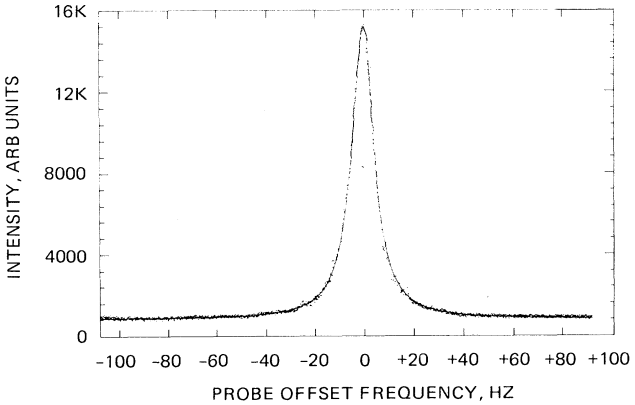

FIG. 2. NDFWM signal as a function of pump-probing detuning, δ.

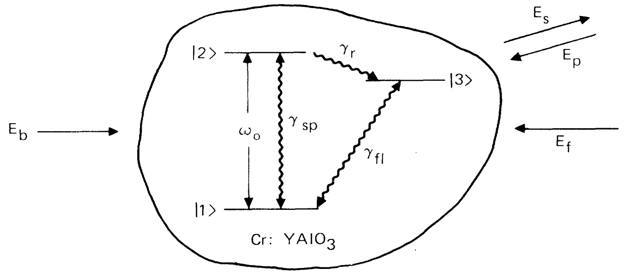

FIG. 3. Three-level model for Cr:YAlO$_3$ and geometry for calculating the NDFWM response.

40-MHz time-averaged bandwidth of this laser does not contribute to the observed linewidth as long as the jitter is small compared to the absorption linewidth of the sample. This is certainly the case in Cr:YAlO$_3$ where the ^4A-^4T absorption profile has a homogeneous width of approximately 65 nm centered at 560 nm.

For weak signals, the probe beam was chopped at a low frequency and the signal was phase-sensitively detected with a lock-in amplifier. The signal was recorded on a signal averager and then sent to a VAX 11-780 computer for analysis. Figure 2 shows a 200-Hz scan over the resonance. The smooth curve is the result of a least-squares fit with a Lorentzian function. The observed width is 9.8 Hz (FWHM). It should be noted that the observed width is not instrument limited since other measurements on LiF color centers have shown temperature-dependent linewidths as small as 3 Hz and measurements on BaTiO$_3$ have shown intensity-dependent widths as small as 2.5 Hz.

To interpret the spectrum shown in Fig. 2, we consider the three-level model for Cr:YAlO$_3$ and the four-wave mixing geometry shown in Fig. 3. The frequencies of the input optical beams (two pump beams, E_f and E_b, and the probe beam, E_p) are assumed to be close to the resonant frequency ω_0. A chromium atom excited from the ground state, $|1\rangle$, to the excited state, $|2\rangle$, can decay by spontaneous emission back to the ground state. State $|2\rangle$ can also decay by a nonradiative transition to the metastable state $|3\rangle$. This state decays by fluorescence back to the ground state, emitting a photon in the region of 694 nm.

The equation of motion for the density matrix describing this system is given by[6]

$$i\hbar\frac{\partial\rho}{\partial t}=[H,\rho]+[V,\rho]-\frac{i\hbar}{2}[\Gamma,\rho]_{+}-i\hbar\left.\frac{\partial\rho}{\partial t}\right|_{\text{deph.}}+i\hbar\left.\frac{\partial\rho}{\partial t}\right|_{\text{sp.tr.}}, \tag{1}$$

where H represents the Hamiltonian for the system in the absence of radiation. H is assumed to be diagonalized. V represents the electromagnetic interaction term and is of the form $-\boldsymbol{\mu}\cdot\mathbf{E}$. Γ is the decay term of populations. $i\hbar\,\partial\rho/\partial t|_{\text{sp.tr.}}$ is a source term for decay into a state (diagonal terms, only), and $i\hbar\,\partial\rho/\partial t|_{\text{deph.}}$ describes dephasing of off-diagonal terms. It is assumed that the electromagnetic interaction is significant only for the transition between states $|1\rangle$ and $|2\rangle$. The equation for ρ is solved in the steady state by use of perturbation theory and the assumption that all zero-order coherences (e.g., ρ_{12}) are zero. We also assume the rotating-wave approximation. The polarization is calculated from $P=\mathrm{Tr}\mu\rho$, where ρ is third order in the electromagnetic fields. We have kept only those terms which are phase matched in the direction of interest: i.e., k_s, the signal wave vector, is given such that $k_f+k_b-k_p-k_s\sim 0$. The polarization of interest is given by

$$P=2\mu_{12}\rho_{11}^{(0)}\Omega_f\Omega_b\Omega_p^{*}e^{i(\omega-\delta)t+ik_px}\left[\frac{1}{\delta+i\gamma_T}+\frac{1}{\gamma_T-\gamma_{\mathrm{fl}}}\left(\frac{\gamma_r}{\delta+i\gamma_{\mathrm{fl}}}+\frac{\gamma_{\mathrm{sp}}-\gamma_{\mathrm{fl}}}{\delta+i\gamma_T}\right)\right]$$
$$\times\left\{\frac{1}{-\Delta+\delta+i\gamma_{\mathrm{ph}}}\left(\frac{1}{-\Delta-\delta-i\gamma_{\mathrm{ph}}}-\frac{1}{-\Delta+i\gamma_{\mathrm{ph}}}\right)\right\}, \tag{2}$$

where $\Omega_i=\mu_{12}E_i/2\hbar$, $\Delta=\omega_1-\omega_0$, $\delta=\omega_2-\omega_1$, $\gamma_T=\gamma_{\mathrm{sp}}+\gamma_r$, and γ_{ph} represents dephasing due to the crystal and is related to the absorption linewidth (for a Lorenztian profile) by $1/\pi\gamma_{\mathrm{ph}}$ (FWHM in hertz).

In spectroscopy, by NDFWM, the signal wave, E_s, arises from a coupled-mode analysis between the probe wave and the signal wave. In the limit of weak coupling, the signal intensity, I_s, is proportional to the square of the polarization and is given by

$$I_s = C\frac{\gamma_r^2}{(\gamma_T-\gamma_{\rm fl})^2}\left\{1+2\left(1+\frac{\gamma_{\rm sp}-\gamma_{\rm fl}}{\gamma_T-\gamma_{\rm fl}}\right)\frac{\gamma_{\rm fl}\gamma_T}{\gamma_r(\gamma_T+\gamma_{\rm fl})}\right\}\frac{1}{\delta^2+\gamma_{\rm fl}^2}+\left(1+\frac{\gamma_{\rm sp}-\gamma_{\rm fl}}{\gamma_T-\gamma_{\rm fl}}\right)^2$$
$$\times\left\{1-2\frac{\gamma_r\gamma_T\gamma_{\rm fl}}{(\gamma_T+\gamma_{\rm sp}-2\gamma_{\rm fl})(\gamma_T^2-\gamma_{\rm fl}^2)}\right\}\frac{1}{\delta^2+\gamma_T^2}+\frac{2\gamma_r}{(\gamma_T-\gamma_{\rm fl})(\gamma_T^2-\gamma_{\rm fl}^2)}\left(1+\frac{\gamma_{\rm sp}-\gamma_{\rm fl}}{\gamma_T-\gamma_{\rm fl}}\right)\left(\frac{\delta^2}{\delta^2+\gamma_{\rm fl}^2}-\frac{\delta^2}{\delta^2+\gamma_T^2}\right). \tag{3}$$

In this expression, we have assumed that $\gamma_{\rm ph} >> \gamma_{\rm fl}$ and γ_T and have ignored resonances associated with $\Delta \pm \delta = 0$ which are included in the parameter C. In this description, we see that the polarization is the sum of three resonant denominators: two Lorentzians and a non-Lorentzian. In chromium, $\gamma_T = \gamma_{\rm sp} + \gamma_r >> \gamma_{\rm fl}$. Hence, the only term that contributes is the first Lorentzian, proportional to $(\delta^2 + \gamma_{\rm fl}^2)^{-1}$.

This resonant term originates explicitly in the equation of motion for the second-order contribution to the ground-state term, $\rho_{11}^{(2)}$. It contains a contribution from the fluorescent decay of the metastable state, ρ_{33}, generated by nonradiative transitions from the upper laser-excited population, ρ_{22}. This term describes the relaxation of the ground state and in general is in contrast to a time-domain measurement of fluorescent decay which measures the relaxation time of ρ_{33}. However, in the three-level system considered here, the frequency-domain measurement of the third-order polarization does measure the same parameter as the time-domain measurement of fluorescence. It is clear from the expression given above for the polarization that these two measurements coincide in this case only because of the relative magnitude of the different decay rates. To confirm this interpretation, a separate measurement of the fluorescent decay rate was made and shown to be $\gamma_{\rm fl}^{-1} = 33 \pm 1$ ms corresponding to a linewidth of 9.65 Hz, in excellent agreement with the observed linewidth of 9.8 Hz. In ruby also, the fluorescent decay rate $\gamma_{\rm fl}^{-1} = 2.6$ ms agreed well with the observed NDFWM spectral width of 138 Hz.

It is interesting to note that the contribution to the signal intensity from the ground states goes to zero if the rate, γ_r, of the excited-state decay channel to ^2E goes to zero. In this limit, Cr:YAlO$_3$ would behave as a closed two-level system in which the spectral response is determined by the excited-state relaxation. This would lead to a broad NDFWM spectral response with a width given by γ_T.

From the above data, it is clear that this new spectroscopy technique is not sensitive to laser jitter. An analytical description of this is beyond the scope of this paper and will be the subject of a separate publication. However, we note here that dye-laser noise can be described by an electric field of the form $E = \frac{1}{2}Ee^{i[\omega t + kx + \phi(t)]} + \text{c.c.}$, where $\phi(t)$ is a time-dependent random phase, assumed to be a Gaussian random variable. An expansion of this phase in time gives rise to frequency slewing of the monochromatic laser output. Preliminary calculations of the nonlinear optical polarization with driving fields modulated in this way indicate that fast frequency fluctuations do not broaden the resonance, which depends on the difference between the pump and probe frequencies and not the absolute frequency. This effect was noticed earlier for quite a different optical resonance in a Ramsey-fringe experiment with an atomic beam,[7] but the linewidth was limited to the kilohertz level by transit-time effects. It was also pointed out earlier[8] that optical Hanle experiments can be made jitter free in systems exhibiting the Zeeman effect. However, our experiments show that laser jitter can be eliminated in four-wave mixing experiments in *any* system in which the resonance in $\chi^{(3)}$ is associated with terms which first appear in the second-order computation of the ground-state elements of the density matrix and depend on the difference of two laser frequencies. This will prove very useful in ultrahigh-resolution frequency-domain spectroscopy studies of inverted *V*-type transitions where the linewidth is determined by the relaxation between states of identical parity. It may also be possible to adapt the results described here for integrated atomic clock applications.

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