Brief Reports

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Interference effects in the degenerate-wave-mixing spectroscopy of alexandrite

T. Catunda and L. A. O. Nunes
Instituto de Física e Química de São Carlos, Universidade de São Paulo–São Carlos, Caixa Postal 369, 13560 São Carlos, São Paulo, Brasil
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The degenerate-multiwave-mixing spectroscopy of alexandrite at 77 K using a pulsed dye laser in resonance with the R_{1m} line was studied in this work. Unusual asymmetric line shapes that can be explained by an interference effect between resonant and nonresonant contributions of the media susceptibility were observed. The resonant effect is caused by the saturation of the two-level system susceptibility and the nonresonant contribution comes from the linear polarizability difference between excited and ground states. The present work shows an observation of this kind of interference phenomena in degenerate-wave-mixing experiments. Furthermore, we note that it is an observation of saturation line splitting in degenerate wave mixing in a narrow line in solids.

Most of the degenerate four-wave mixing (DFWM) experiments in resonant gas media have been explained by two- or three-level models where it was observed that the DFWM lines shape broadens and splits (symmetrically in relation to the line center) due to the nonlinearity dispersive character in the saturation regime.[1] In the present work we observed the line splitting with remarkable asymmetric features in degenerate-multiwave-mixing (DMWM) spectroscopy by performing a self-diffraction experiment in resonance with the alexandrite ($BeAl_2O_3:Cr^{3+}$) R_{1m} line. This asymmetric behavior can be explained by an interference effect resulting from the simultaneous contribution of two different nonlinear mechanisms: a resonant two-level system interaction and the difference between the linear polarizabilities of these two levels (the ground and excited states). Although the importance of the linear polarizability difference in resonant interactions was theoretically pointed out earlier by Butylkin, Kaplan, and Khronopulo,[2] and DMWM spectroscopy[3] has been extensively studied, this is the first experimental evidence of this effect, as far as we know. In ion-doped materials the effect of the polarizability difference[4] is well known, but in this work the effect of the resonant interaction with a sharp line was also observed.

In the self-diffraction experiment (also called self-induced grating or coherent scattering) a focused laser beam is split in two parts that are recombined in a small angle in the crystal. The interference of these two beams in the nonlinear media produces a spatial modulation of the polarization that generates waves into directions $\mathbf{k}_n^{\pm}=\mathbf{k}_0^{\pm}\pm n(\mathbf{k}_0^{+}-\mathbf{k}_0^{-})$, where $\mathbf{k}_0^{\pm}$ are the wave vectors of the incident beams. An oxazine 720 dye laser, pumped by the second harmonic of a $\tau_p=5$ nsec pulsed Nd:YAG laser, with $\sim 0.2\text{-cm}^{-1}$ line width and 400-kW peak

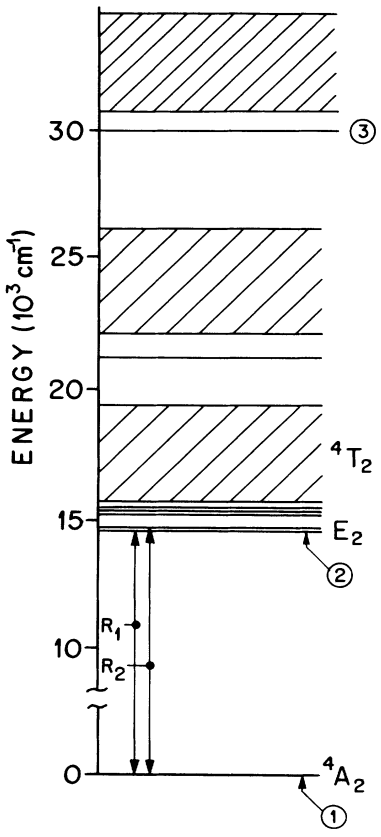

FIG. 1. Energy level diagram of alexandrite with the levels important to this experiment. The levels 2 and 3 correspond to energies directed pumped by the laser (multiples of the R_{1m} energy).

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power was used. The crystal was cooled to 77 K to increase the R_{1m} cross section, its thickness was $L=0.085$ cm, and the laser was linearly polarized in the direction of alexandrite b axis. Sintonizing the laser at $\lambda \sim 680$ nm in resonance with the R_{1m} line (shown in Fig. 1) four orders of the scattered field could be observed with the naked eye. Figure 2 shows the spectra measured of the first three orders ($n=1$, 2, and 3) obtained with several laser powers. We also observed scattered field in resonance with the alexandrite R_{2m} line, with the same kind of line shape as for the R_{1m} line, but a lower efficiency because the R_{2m} cross section is ~ 0.2 of the R_{1m} one. The maximum scattering efficiency, defined as the ratio between the generated and incident beams intensity, varies in the range $10^{-3}-10^{-4}$ for all the Fig. 2 spectra. In the low-intensity regime one should have expected the intensity of the n order field I_n to be proportional to the $(2n+1)$ power of the incident beams intensity, which is clearly not the experimental behavior for all the Fig. 2 spectra due to saturation effects. The double peak struc-

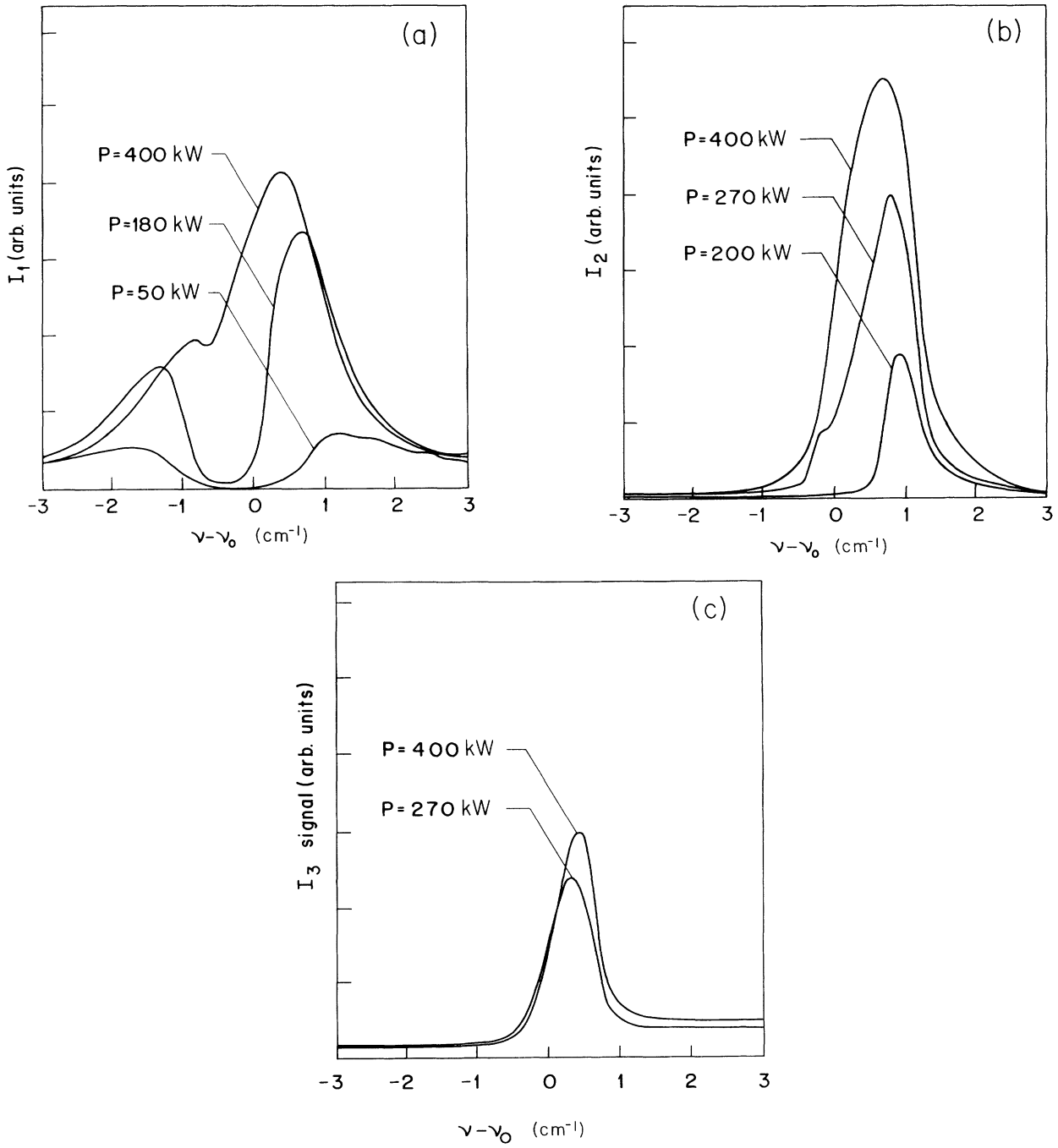

FIG. 2. Experimental data with the scattered field spectrum in the self-diffraction experiment for the first three orders $n=1$, 2, and 3 in parts (a), (b), and (c), respectively. The laser frequency ν_0 was scanned over the alexandrite R_{1m} line.

ture shown in Fig. 2(a) is a saturation splitting as observed in resonant interactions in atomic and molecular gases.[1,3] However, unlike most of the previous experiments, all spectra measured in this work are asymmetric and shifted in relation to the absorption line center. We should remark that in some atomic vapor experiments,[5] the spectrum asymmetric is justified by self-focusing effects that do not appear in this experiment.

The main features observed in this experiment can be explained by the susceptibility given by

$$\chi=-\frac{\alpha_0}{2\pi k}\frac{i+\delta}{1+\delta^2+s}+\chi_m+\frac{1}{N_0}(N_1\chi_1+N_2\chi_2+N_3\chi_3)\ , \tag{1}$$

where the first term is the two-level susceptibility with α_0 the line center small-signal-field attenuation coefficient, k the wave-number magnitude at the frequency ω, $\delta=(\omega-\omega_0)T_2$ the detuning parameter, and s the saturation parameter of the first transition (the transition between levels 1 and 2 shown in Fig. 1). The nonresonant terms are the host matrix susceptibility χ_m, and χ_i is the Cr^{3+} ion susceptibility in state i ($i=1$, 2, and 3 are the energy levels shown in Fig. 1). The total Cr^{3+} ion concentration is $N_0=4\times10^{19}$ cm^{-3} and N_i is the Cr^{3+} concentration in state i. We sintonized the laser near the R_{1m} line, the transition between the ground state $^4A_2$ and first excited state ^2E (levels 1 and 2, respectively) for the Cr ion in the alexandrite mirror site. This transition is strongly saturated ($s\sim100$ for maximum laser power) due to its high absorption cross section σ_1. Although level 2 is metastable ($\tau_2=1.3$ msec) in the calculation of the parameter s we have to consider that the pumping is limited by the laser pulse duration $\tau_p\ll\tau_2$. The second transition, between levels 2 and 3, is not saturated because of its lower cross section $\sigma_2\sim2\times10^{-3}\sigma_1$ (Ref. 6) and lifetime $\tau_3\ll\tau_p$ (τ_3 should be in the order of 10^{-12} sec) resulting in a very high saturation intensity $I_{s2}\gg I_{s1}$. Therefore, we should have $N_3\ll N_1,N_2$ so we can consider $N_3=N_2I/I_{s2}$. Taking N_2 from the two-level model and using Eq. (1) we obtain

$$\chi=-\frac{\alpha_0}{2\pi k}\frac{i+\delta-As-Bs^2}{1+\delta^2+s}\ , \tag{2a}$$

with

$$A=\frac{\pi k}{\alpha_0}(\chi_2-\chi_1)\ , \tag{2b}$$

$$B=\frac{\pi k}{\alpha}(\chi_3-\chi_1)\frac{I_{s1}}{I_{s2}}\ , \tag{2c}$$

where A (B) account for the contribution of level 2 (level 3) susceptibility. The real part of A (B) is proportional to the linear polarizability difference $\alpha_2-\alpha_1$ ($\alpha_3-\alpha_2$) between levels 2 and 1 (3 and 1). The imaginary part of A (B) is proportional to the absorption cross section σ_2 (σ_3) of level 2 (level 3). In the case $B=0$, which is equivalent to disregarding the presence of the second excited state, Eqs. (2) are equivalent to the susceptibility calculated in Ref. 2 for the case $T_2\ll\tau_1$, which would correspond to our experiment.

In order to compare our theoretical model with the experimental data, several features of our nonlinear media must be considered. The alexandrite R_{1m} line is inhomogeneously broadened at low temperatures, with 2.15-cm^{-1} inhomogeneous linewidth. The R_{1m} homogeneous

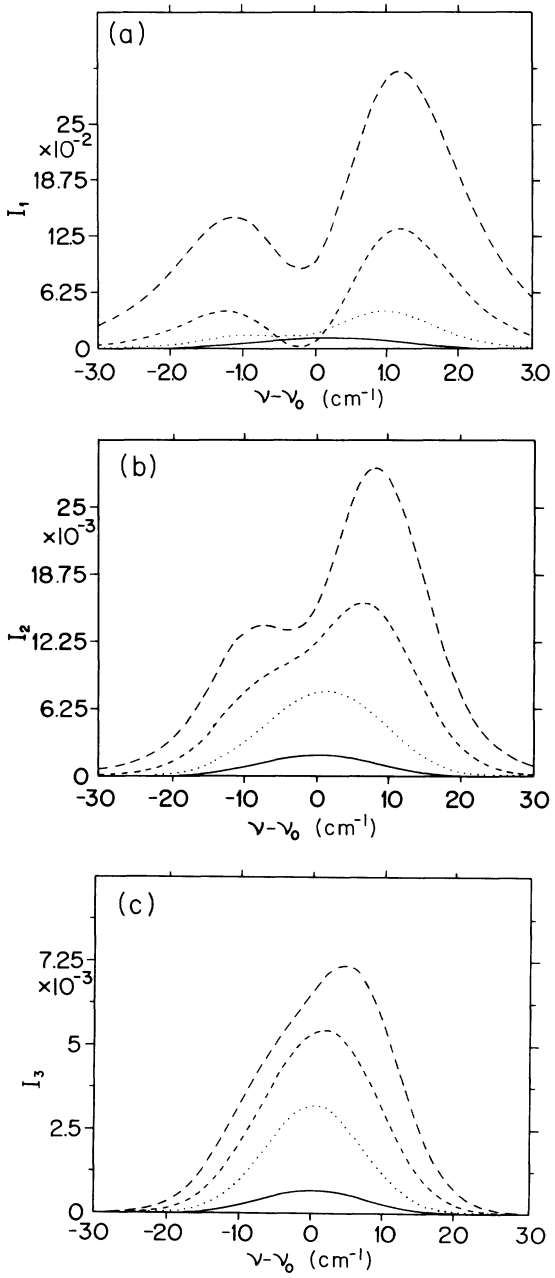

FIG. 3. Spectra calculated considering the inhomogeneous broadening of the alexandrite R_{1m} line with inhomogeneous linewidth 2.15 cm^{-1}. Parts (a), (b), and (c) show the $n=1$, 2, and 3 spectra, respectively, for several saturation parameters s: $s=10$ for solid lines, $s=30$ for dotted lines, $s=70$ for short-dashed lines, and $s=110$ for long-dashed lines. All the curves were calculated with $A=0.027$, $B=i2\times10^{-4}$, and a homogeneous linewidth ten times narrower than the inhomogeneous one. The y axis gives the intensity in units of saturation intensity I_s, and the x axis the laser frequency with $\nu=\nu_0$ at R_{1m} line center.

linewidth is estimated by Powell *et al.*[6] to be $\sim .05\ cm^{-1}$ at 77 K (due to phonon broadening) so in this experiment the homogeneous linewidth is determined by the laser linewidth $\sim 0.2\ cm^{-1}$. We calculate the spectra line shape by making a Fourier expansion of the susceptibility as done in Ref. 7. The curves shown in Fig. 3 were obtained by making the convolution of the spectrum of a homogeneously broadened system with a Gaussian that represents the inhomogeneous distribution of the Cr^{3+} ions. We do not have a precise value for the polarizability difference of the Cr^{3+} in the alexandrite mirror site but four-wave mixing experiments[8] indicate that this value should be similar to the ruby value $\alpha_2-\alpha_1=0.025\ Å^3$ measured by Catunda, Andreeta, and Castro.[4] With this $(\alpha_2-\alpha_1)$ value and the absorption cross section of Walling *et al.*[6] from Eq. (3b) we calculated $A=0.027$. Using the excited-state absorption cross section of Shand and Walling,[6] we calculated that, like other Cr^{3+} doped systems,[4] for alexandrite the imaginary part of A is one order of magnitude smaller than its real part, so its contribution can be neglected. Figure 2(a) shows that the splitting magnitude tends to vanish at higher laser power. This behavior can only be explained by the effect of a second population grating [given by the factor B in Eq. (2)] once for $B=0$ the splitting always increases with s. Although $N_3 \ll N_2$, the effect of this second grating is significant because both the polarizability and absorption cross section of level 3 should be larger than that of level 2 due to its proximity to the charge transfer band at energy $\sim 50\,000\ cm^{-1}$. There is no data available for the calculation of the parameter B so we choose $B=-i2\times 10^{-4}$ as an adjustable parameter which indicates that this grating is absorptive. The spectrum line shape is similar for all the orders investigated but the higher n orders saturate at higher intensities.[3,7] For the parameters in Fig. 3, the line splitting appears at $s\sim 30$ for $n=1$, $s\sim 100$ for $n=2$, and $s\sim 200$ for $n=3$. Comparing this behavior with the experimental data we can infer that all the measured $n=1$ spectra correspond to the saturation regime $(s\geq 30)$ because we have broadened line shapes with splitting. On the other hand, in the $n=3$ experimental spectra narrow lines were obtained (without splitting) because the saturation regime for $n=3$ was not reached. The $n=2$ case is an intermediate case; a narrow line at lower power and broadened lines at higher power were obtained. We also considered the effect of the pump beams absorption in calculations of Fig. 3 (where $\alpha_0 L\sim 0.9$), but it did not change line shapes significantly. The maximum scattering efficiencies calculated for Fig. 3 are $\sim 10^{-4}$; so both the spectra line shape and the scattering efficiencies are in relatively good agreement with the experimental data.

In this work we showed that DMWM line shape of a resonant transition can be significantly changed from the two-level system due to nonresonant contributions to the nonlinearity and the population of higher excited states. This line-shape modification is made evident by the interference process between the real parts of two different contributions to the media susceptibility. Therefore, this DMWM experiment provided spectroscopic information that would not be evident by saturated absorption techniques. Although this interference process is similar to the one observed in coherent antistokes Raman spectroscopy (CARS), in CARS the interference occurs between a Raman transition and the nonresonant χ^3, and in this work we have a resonant single-photon transition and the difference between the linear polarizabilities of ground and excited states. We should remark that in this kind of ion-doped crystal the resonant transition has a very weak oscillator strength $\sim 10^{-6}$ (which is the typical value for the Cr^{3+} R lines) compared with oscillator strength $\sim 10^{-2}$ of the charge-transfer band which, according to Powell and Payne,[4] gives the most important contribution to the Cr^{3+} polarizability. The results present in this work show that these peculiar characteristics of ion-doped laser materials are very important for the understanding of their nonlinear properties.

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