

Inhomogeneity study of Pr³⁺-doped yttrium aluminium garnet using time-resolved spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 6469

(<http://iopscience.iop.org/0953-8984/5/35/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 14:23

Please note that [terms and conditions apply](#).

Inhomogeneity studies of Pr³⁺-doped yttrium aluminium garnet using time-resolved spectroscopy

M Malinowski†, P Szczepański†, W Woliński†, R Wolski† and Z Frukacz‡

† Institute of Microelectronics and Optoelectronics PW, ulitsa Koszykowa 75, 00-662 Warsaw, Poland

‡ Institute of Electronic Materials Technology, ulitsa Wólczyńska 133, 01-919 Warsaw, Poland

Received 14 December 1992, in final form 13 May 1993

Abstract. The temporal behaviour of the excitation lineshape of the ¹D₂(1) level of YAG:Pr³⁺ for three different concentrations of Pr³⁺ (0.08, 0.24 and 0.6 at.%) is investigated. The satellite line structure in the vicinity of the main inhomogeneously broadened transition is related to ions in different crystal-field sites. Studies of the selectively excited decay curves of the ¹D₂ luminescence reveal an almost exponential decay only for the 0.08 at.% sample after excitation of the absorption line centre. A non-exponential decay from the 0.24 and 0.6 at.% crystals is interpreted in terms of direct donor–acceptor energy transfer by cross relaxation. The technique of fluorescence line narrowing is used to analyse the effect of phonon-assisted spectral diffusion. Anti-Stokes emission from the ³P₀ level following excitation of the ¹D₂ state is studied as a function of Pr³⁺ concentration. It is concluded that the anti-Stokes fluorescence in the diluted YAG:0.08 at.% Pr³⁺ system results from the excited-state absorption process while in YAG:0.6 at.% Pr³⁺ this anti-Stokes emission is attributed to up-conversion by energy transfer.

1. Introduction

Recently, there has been a revival of interest in the optical properties of trivalent rare-earth ions (R³⁺) in yttrium aluminium garnet (YAG) owing to advances in development of new solid state lasers operating in the near infrared [1–3]. Also a new class of visible up-conversion lasers pumped in the near infrared has received much attention and has stimulated new studies of the multi-photon and multi-ion processes responsible for the up-conversion [4, 5].

Trivalent-neodymium(Nd³⁺)-doped YAG is the most successful solid state laser material and it has been extensively studied during the last decade. A considerable amount of work has been undertaken to explain the effect of concentration-dependent fluorescence quenching and quantum efficiency variation [6]. It was shown that cross relaxation via the intermediate ⁴I_{5/2} and ⁴I_{13/2} levels plays the dominant role in relaxing the ⁴F_{3/2} Nd³⁺ state [7, 8]. Recently Devor and co-workers [9–11] and Lupei *et al* [12, 13] pointed out the role of non-equivalent crystal field sites, line broadening and lattice–defect interactions in quenching the Nd³⁺ fluorescence.

Praseodymium-doped YAG crystals exhibit interesting luminescence properties. Room-temperature emission of Pr³⁺ ions can originate from three metastable states: ³P₀, ³P₁ and ¹D₂. Recently, laser action at λ = 690 nm was observed on the ³P₀ → ³F₆ transition [14] and a detailed understanding of the physics of this system is essential to further improvement of its lasing properties.

This paper deals with the spectroscopic investigation of the microscopic disorder in praseodymium(Pr^{3+})-doped YAG crystals. In YAG the R^{3+} impurity substitutes predominantly for Y^{3+} ions in dodecahedral sites; the degree of lattice perturbation is strictly related to the difference between the ionic radii of the two ions. It is known that ions from the beginning of the lanthanide group such as Ce^{3+} and Pr^{3+} have larger ionic radii than Nd^{3+} and Y^{3+} itself. As a consequence we would expect that the crystal-field distortion due to the presence of a Pr^{3+} neighbour is larger than that produced by a Nd^{3+} neighbour in the YAG lattice. This also explains the fact that Pr^{3+} -doped garnet crystals do not exist for all Pr^{3+} concentrations [15]. Thus, this system seems to be a good choice for studying inhomogeneity effects.

Recently, the complex structure of the absorption and emission spectra of Pr-doped garnet crystals YAG, GGG and YGG was investigated by Antic-Fidancev *et al* [16, 17]. They concentrated on analysing the fluorescence from different ion sites after selective excitation of the $^3\text{P}_0$ state. Antic-Fidancev *et al* [18] have also studied this system using a CW laser to excite the $^1\text{D}_2$ fluorescence. They showed that at least three different sites were responsible for the observed emission. It is known that, in all Pr^{3+} systems investigated [19–21], the $^1\text{D}_2$ level emission is affected much more strongly by quenching than is $^3\text{P}_0$. Hence, to study the ion–ion interaction we focus our attention on the $^1\text{D}_2$ level and its fluorescence dynamics. From our previous studies of YAG: Pr^{3+} [22] it is known that the $^1\text{D}_2$ emission is much stronger and that its lifetime is about one order of magnitude larger than that of the $^3\text{P}_0$ state. In this paper we present and reanalyse site-selective spectra obtained in a series of Pr-doped YAG crystals. The influence of concentration on the absorption and emission spectra and on the excited-state kinetics has been investigated and is presented below. The nature of the inhomogeneous broadening of the lowest component of the $^1\text{D}_2$ state is studied. The energy levels involved in this study are shown in figure 1 [23]. Some additional information concerning the ion–ion interaction processes was obtained by means of time-resolved (TR) fluorescence line narrowing (FLN) spectroscopy [24] and by observations of the anti-Stokes (AS) $^3\text{P}_0$ fluorescence after selective excitation of the $^1\text{D}_2(1)$ level. Observation of AS emission, originating from cooperative energy transfer and multi-photon processes, has proven to be a powerful spectroscopic tool complementary to one-photon spectroscopy [25, 26]. Interest in studying these multi-photon processes is also motivated by the practical significance of up-conversion pumping of high-energy rare-earth excited states for use in blue and UV lasers.

2. Experimental methods

YAG: Pr^{3+} samples with concentrations of 0.08, 0.24 and 0.6 at.% as determined by x -ray fluorescence analysis were grown parallel to the (111) direction by the Czochralski technique at the Institute of Electronic Materials Technology laboratory in Warsaw. Most experiments were carried out with a Displex closed-cycle He cryostat. The Pr^{3+} ion luminescence was excited with a 500 kW nitrogen pumped Hansch-type dye laser, dispersed with a 1 m double-grating GDM 1000 monochromator and was detected with an RCA C 31034-02 cooled GaAs photomultiplier tube. The dye laser, equipped with a Jobin–Yvon holographic grating with 600 grooves mm^{-1} , provided pulses of 7 ns duration and 0.05 cm^{-1} linewidth. Data acquisition was carried out with a Stanford Research SR 400 gated photon counter controlled with a PC AT computer. Some decay curves were taken from the MCS II Multichannel Scaler Card from Oxford Tennelec/Nucleus.

3. Results

3.1. Absorption and excitation spectra

In most of the experiments the Pr³⁺ ions were excited through the ¹D₂ state centred at approximately 16 400 cm⁻¹. The Pr³⁺ ions that substitute for Y³⁺ have D₂ site symmetry and each of the free-ion levels $|JM\rangle$ is split into $2J + 1$ Stark components. The energies of the five components of the ¹D₂ level have been given by Gruber *et al* [23] and are shown in figure 1. To avoid additional broadening by spontaneous phonon emission, our linewidth studies concentrated on the lowest 16 399 cm⁻¹ Stark component of the ¹D₂ manifold. The next higher-lying level ¹D₂ is separated by 9 cm⁻¹ and at 10 K is thermally populated. Figure 2 shows the concentration-dependent and, in the case of the 0.6 at.% Pr³⁺ crystal, the temperature-dependent absorption spectra around the chosen transition. The inhomogeneous width of the ¹D₂(1) absorption line in the low-concentration YAG:0.08 at.% Pr³⁺ sample is 1.5 cm⁻¹; in the 0.6 at.% Pr crystal the lines are much broader and several additional lines appear. With increasing temperature, transitions from the thermally populated higher components of the ground ³H₄ state are clearly observed. In figure 3 the 10 K excitation spectra of the total ¹D₂ → ³H₆ non-resonant fluorescence in three investigated samples are presented. The laser was tuned through the ³H₄(1) → ¹D₂(1, 2) absorption lines. This configuration is favourable because of the large branching ratio for this transition [22], the wide spectral separation from the exciting radiation, and the absence of any reabsorption. From figure 3 it can be seen that the investigated absorption lines consist of four peaks c, d, f and g centred at about 16 400 cm⁻¹ and several less intense additional satellite lines. Two major lines at 16 399 cm⁻¹ and 16 408 cm⁻¹ (lines f and d) arise from the transitions of regular Pr³⁺ ions in D₂ sites. It is interesting to note that the character of the spectra changes with concentration. In the diluted YAG:0.08 at.% Pr³⁺ sample the two regular ion transitions d and f and line g at 16 390 cm⁻¹ dominate, but in the YAG:0.6 at.% Pr³⁺ crystal the lines became much broader and difficult to resolve and two strong additional transitions l and i at 16 338 cm⁻¹ and 16 355 cm⁻¹, respectively, appear. Line a at 16 478 cm⁻¹ is observed for all samples investigated but its relative intensity is concentration dependent. A weak satellite structure e is observed on the high-energy side of line d at 16 408 cm⁻¹ and for YAG:0.6 at.% Pr³⁺ at 16 381 cm⁻¹ (line h) and at around the 16 338 cm⁻¹ transition j, k and m. The half-width of the regular ion transition f at 16 399 cm⁻¹ is 1.8 cm⁻¹ for the 0.08 at.% Pr³⁺-doped sample.

3.2. Fluorescence spectra

In order to associate the observed excitation lines with corresponding fluorescence frequencies, the excitation spectra of monochromator-filtered emission transitions and the selectively excited fluorescence spectra were recorded. To avoid thermally activated fluorescence transitions starting from the ¹D₂(2) Stark level these measurements were performed at $T = 5$ K. The ¹D₂(1) → ³H₆(1-4) spectra as a function of excitation energy are presented in figure 4. After excitation of the centre of the absorption line at 16 399 cm⁻¹ the regular ion fluorescence dominates and several intense emission lines at 12 094, 12 060 and 11 840 cm⁻¹ are clearly observed. With the dye laser tuned to the satellite absorption a new set of fluorescence lines is observed, slightly shifted in energies from the intrinsic ion values. We have identified six characteristic fluorescence spectra resulting from excitation at lines a, be, cg, df, i and l from figure 3.

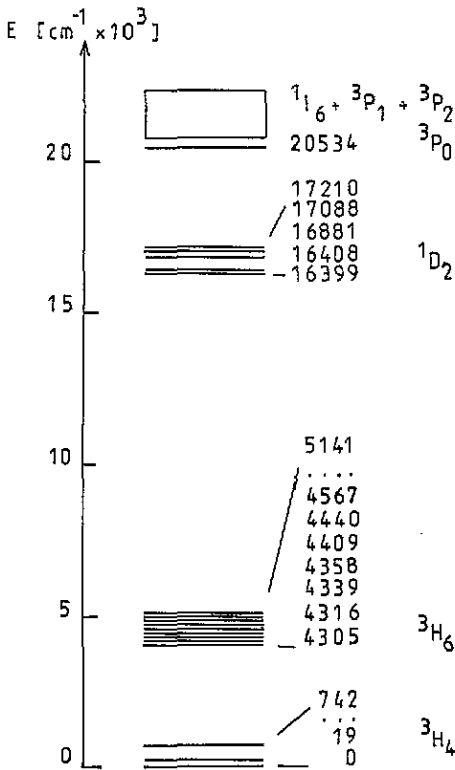


Figure 1. Schematic energy level diagram of Pr^{3+} ions in D_2 sites of YAG.

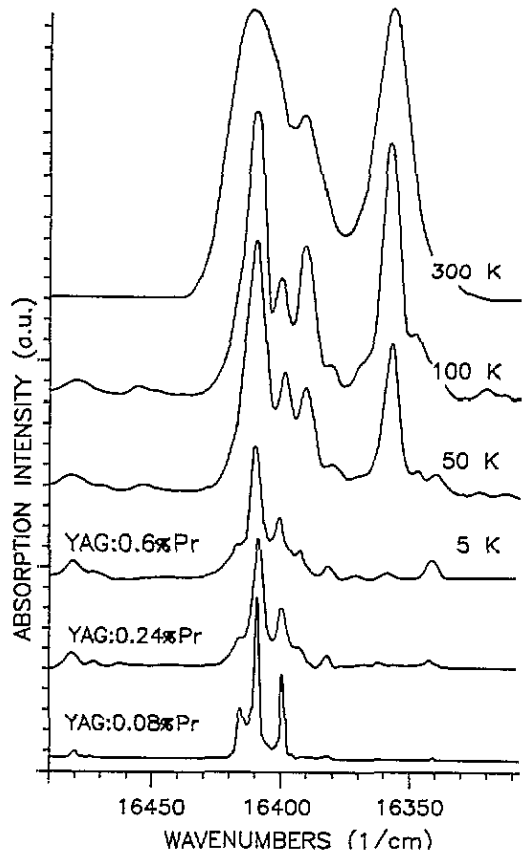


Figure 2. Concentration-dependent absorption spectra of YAG:Pr^{3+} around the ${}^3\text{H}_4(1) \rightarrow {}^1\text{D}_2(1, 2)$ transition (a.u., arbitrary units). The temperature dependence of the absorption of $\text{YAG:0.6 at.}\% \text{Pr}^{3+}$ is also shown.

3.3. Time-resolved spectra and fluorescence dynamics

The temporal variation in the ${}^1\text{D}_2$ fluorescence of $\text{YAG:0.08 at.}\% \text{Pr}^{3+}$ is shown in figure 5. Total ${}^3\text{H}_6$ fluorescence was detected for a fixed time window of $100\ \mu\text{s}$ while the wavelength excitation was scanned across the ${}^3\text{H}_4(1) \rightarrow {}^1\text{D}_2$ absorption lines. Thus, we had wavelength selectivity in excitation but not in emission. Excitation spectra recorded at a $500\ \mu\text{s}$ delay show a noticeable linewidth narrowing and contain only two lines representing the regular ion emission. A similar situation has been observed for 0.24 and 0.6 at.% Pr^{3+} -doped YAG crystals. This indicates that ions responsible for the additional transitions have a significantly shorter lifetime. This was also studied directly by monitoring the emission decay after selective excitation (figures 6 and 7). The temporal dependence of the emission was non-exponential for the 0.24 and 0.6 at.% samples. Only for the $\text{YAG:0.08 at.}\% \text{Pr}^{3+}$ sample did excitation of the regular ions at the line centre result in an almost exponential decay; the decay rate increased gradually at later times, indicating the isolated ion lifetime τ_0 of $245\ \mu\text{s}$. Satellite decay times were determined after subtraction of the isolated ion lifetime from the signal.

Finally, the broad-band excited ${}^1\text{D}_2$ fluorescence decay was measured. The results of

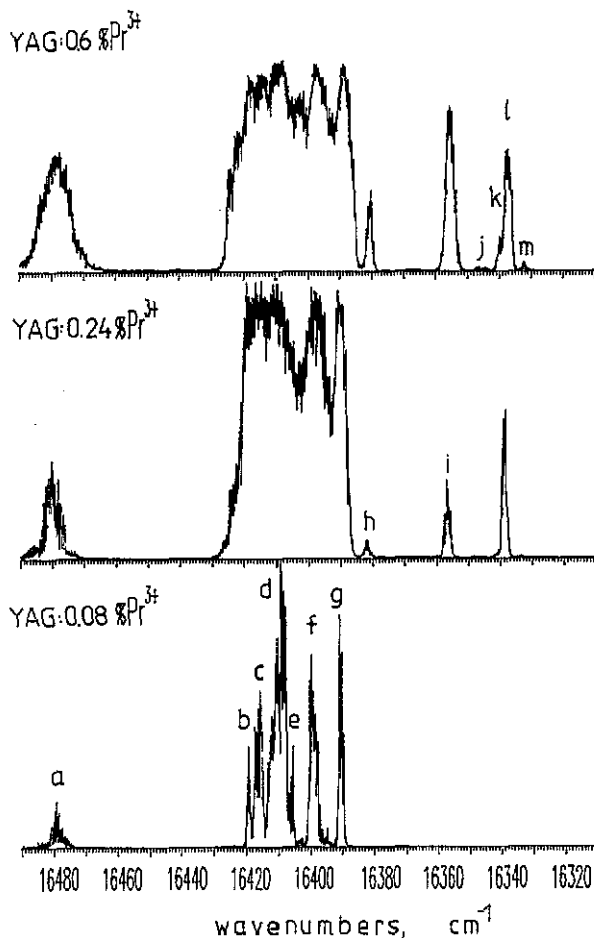


Figure 3. Excitation spectra of the $^1D_2(1)$ fluorescence observed in three samples of YAG:Pr³⁺ of different nominal concentrations. Well resolved lines are labelled by lower-case letters; $T = 10$ K.

the Pr³⁺ fluorescence decay experiments are presented in table 1.

3.4. Fluorescence line-narrowing studies

In order to study the microscopic disorder in YAG:Pr³⁺ crystals we used the technique of FLN within the inhomogeneously broadened $^1D_2(1)$ transition. The $^3H_4(1) \rightarrow ^1D_2(1)$ excitation line of the YAG:0.08 at.% Pr³⁺ crystal is presented in figure 8. For pumping the high-energy wing of the $^1D_2(1)$ line the non-resonant fluorescence corresponding to the $^1D_2(1) \rightarrow ^3H_5(1)$ radiative transition was successfully line narrowed and its spectral evolution as a function of time was measured at 15 K (see figure 8). The spectrum at $t = 0 \mu\text{s}$ shows a narrowed line shifted relative to the fluorescence centred at 12094 cm^{-1} . Later scans indicate a spread to the frequencies at the line centre and the broadening of the line. This reflects spectral diffusion from the initially excited ions to other ions across the crystal.

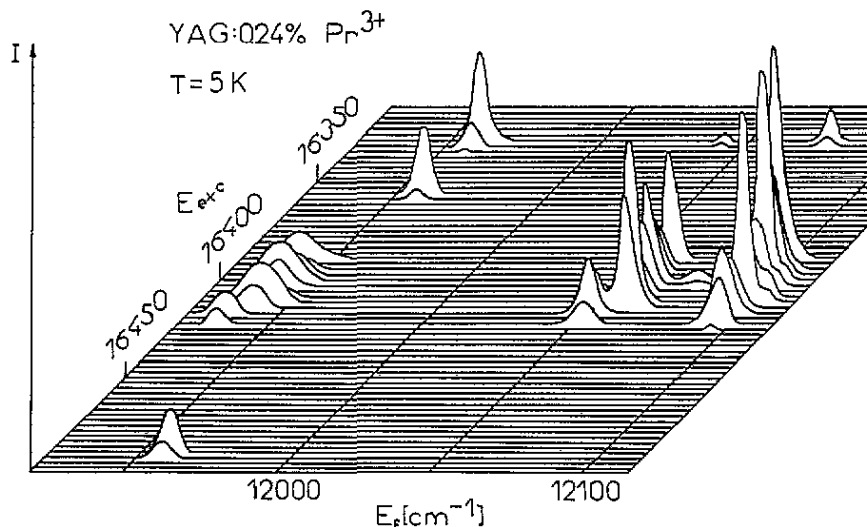


Figure 4. Fluorescence spectra of the $^1D_2(1) \rightarrow ^3H_6$ transition of YAG:Pr³⁺ after selective excitation at various wavelengths; $T = 5$ K.

3.5. Anti-Stokes fluorescence

It was found that the blue lines resulting from the $^3P_0 \rightarrow ^3H_4$ transitions were generated through the excitation of the 1D_2 state. A quadratic dependence of the blue fluorescence on the laser input power was determined. The excitation spectra of this blue AS emission were recorded when collecting the total 3P_0 ($20\,534\text{ cm}^{-1}$) fluorescence and tuning the laser frequency over the $^1D_2(1, 2)$ absorption band (figure 9). For comparison, an excitation spectrum of the yellow 1D_2 fluorescence is also shown. For YAG:0.08 at.% Pr³⁺ the time-integrated excitation spectra of the 3P_0 and 1D_2 fluorescence have the same form. The majority of the AS signal appears after excitation of the regular ions (lines d and f). Less intense AS emission results also from the excitation of two additional lines c and g. The effect of narrowing of the AS fluorescence could also be observed. The excitation spectrum of the blue emission of YAG:0.6 at.% Pr³⁺ exhibits different features; the AS signal is produced mainly by the wings and the satellites of the regular lines; the $^1D_2(1)$ is saturated or 'reversed'. The temporal evolution of the blue emission of YAG:0.08 at.% Pr³⁺ is non-exponential with an initial time constant of about $15\ \mu\text{s}$ and the lack of any observable rise time. For the 0.6 at.% Pr³⁺ sample the AS emission decay is also non-exponential but slower than under direct excitation and a fast rise time of about $1\ \mu\text{s}$ was observed (figure 10).

4. Discussion

From the complexity of the absorption spectra presented in figure 2 it is evident that the Pr³⁺ ions occupy several kinds of crystal site. The two strongest lines at $16\,399\text{ cm}^{-1}$ ($6098\ \text{\AA}$) and $16\,408\text{ cm}^{-1}$ ($6095\ \text{\AA}$) are assigned to transitions of Pr³⁺ ions occupying Y³⁺ sites of D₂ symmetry. Several weak peaks observed in the excitation spectra of the 1D_2 emission presented in figures 3, 5 and 8 are interpreted in terms of some perturbed ions whose energy is shifted from that of the intrinsic ions. The spectrum of these minority sites extends in

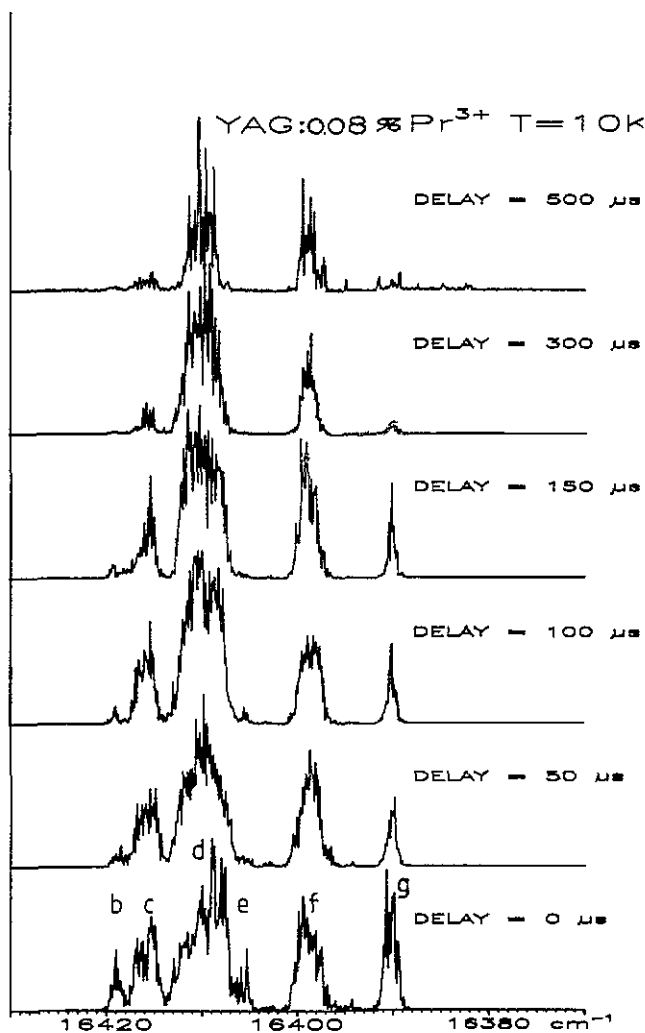


Figure 5. The TR excitation spectra of the $^1D_2(1)$ fluorescence of YAG:0.08 at.% Pr³⁺; $T = 10$ K. The excitation wavelength was scanned across the $^3H_4(1) \rightarrow ^1D_2(1, 2)$ absorption lines when detecting the total 3H_6 fluorescence for a fixed time delay.

YAG:0.6 at.% Pr³⁺ over 140 cm^{-1} , indicating that the crystal-field distortion is comparable in magnitude with the crystal field itself. A similar situation has been observed for other YAG:R³⁺ materials [27, 28]. The large inhomogeneous linewidths in the 0.6 at.% Pr³⁺ sample suggest a high degree of lattice strain. It is also observed that, with an increased doping level, several strong new lines h, i, j, l and m appear whose intensities are concentration dependent. We think that the main source of lattice distortion responsible for the large-scale shift in Pr³⁺ lines [11] lies in departures from stoichiometry; some of the Pr³⁺ ions enter the octahedral sites normally occupied by Al³⁺ ions and perturb the regular dodecahedral Y³⁺ sites. The microscopic lattice imperfections such as strains, dislocations and unintentional impurities result in a small-scale crystal-field perturbation of the order of 1 cm^{-1} , responsible for the irregular shape of the excitation spectral profile for the $^3H_4(1) \rightarrow ^1D_2(1)$ transition shown in figure 9. It is also observed that the spectral profile of this transition is nearly

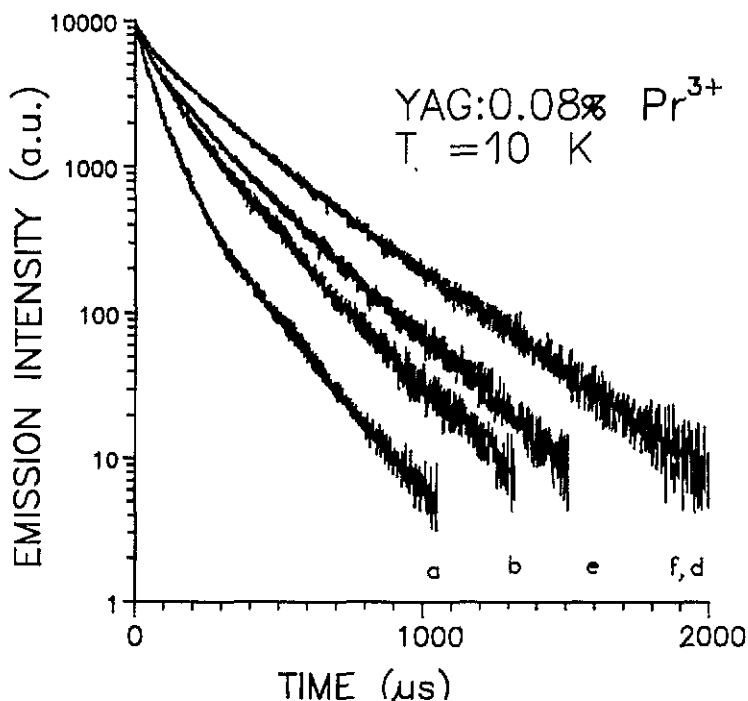


Figure 6. Fluorescence decay observed from the sample of 0.08 at.% Pr^{3+} -doped YAG after selective excitation around the ${}^3\text{H}_4(1) \rightarrow {}^1\text{D}_2(1, 2)$ transitions (a.u., arbitrary units). The lower-case letters refer to the lines from figures 3 and 5; $T = 10$ K.

time independent for the 0.08 at.% Pr^{3+} crystal, while it changes markedly with time for the 0.6 at.% Pr^{3+} sample. At longer delay times the ${}^3\text{H}_4(1) \rightarrow {}^1\text{D}_2(1)$ excitation spectrum reduces itself to that of the dilute crystal. An additional source of satellites comes from pairs or multi-ion complexes of activator ions. As shown by Lupei *et al* [13], the pair lines have been spectrally isolated for the YAG: Nd^{3+} system. On analysis of our spectra, the quadratic intensity dependence on Pr^{3+} concentration was found for the well resolved satellite h, suggesting its pair origin. However, the 18 cm^{-1} shift from the central line is unexpectedly large even for pairs of ions in the first-neighbour position.

Sets of fluorescence lines recorded after selective excitation (see figure 4), which represent the distinct spectra, are assumed to correspond to ions in different sites. Six such spectra were identified. This is consistent with observations of Lupei *et al* [13] and Devor and De Shazer [11] who observed four and five non-equivalent Nd^{3+} sites, respectively, in Czochralski-grown YAG crystals. Mares *et al* [29] reported nine Nd^{3+} crystal sites in doubly doped YAG: $\text{Nd}^{3+}+\text{Cr}^{3+}$.

Since electric-dipole transitions between Stark levels of the same symmetry are forbidden, the absence of radiative transitions from the ${}^1\text{D}_2(1)$ level which has Γ_1 symmetry to the ${}^3\text{H}_6(2, 4)$ Stark components is consistent with the assignments of Gruber *et al* [23]. However, the observation of regular ion emission at 11940 cm^{-1} leads to a Stark level at 4459 cm^{-1} (see figure 1) which is in good agreement with the work of Ryabchenkov [30] but was not observed by Gruber *et al* [23].

Figures 6 and 7 show the time evolution of the ${}^1\text{D}_2$ state emission. The fluorescence decay for YAG:0.08 at.% Pr^{3+} observed in this work is faster than reported for YAG:0.12 at.% Pr^{3+} [31] at 77 K. This could result from some energy transfer processes induced by the

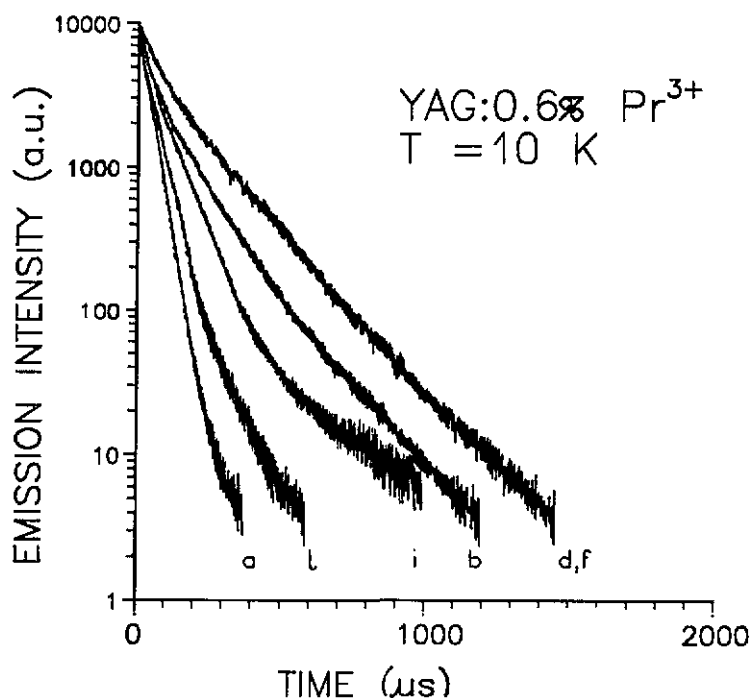


Figure 7. Fluorescence decay observed from a sample of 0.6 at. % Pr³⁺-doped YAG after selective excitation around the ³H₄(1) → ¹D₂(1, 2) transitions. The lower-case letters refer to lines from figures 3 and 5; T = 10 K.

Table 1. Summary of the fluorescence decay of the ¹D₂ state of Pr³⁺ ions in YAG after selective excitation at 10 K.

Satellite	Energy <i>E</i> (cm ⁻¹)	Energy shift ΔE (cm ⁻¹)	Lifetime τ (μ s) at the following Pr ³⁺ concentrations		
			0.6 at. %	0.24 at. %	0.08 at. %
a	16 478	79	57	72	80+200
b	16 420	21	75+200	90	130
c	16 417	18	100	115	175
d	16 408	9	130	160	200+245
e	16 406	7	86	94	140
f	16 399	0	130	160	200+245
g	16 390	-9	115	126	188
h	16 381	-18	1	1.2	—
i	16 355	-44	70	100	—
l	16 338	-61	62	90	—

unintentional Nd³⁺ impurity detected in the 0.12 at. % Pr³⁺-doped crystal.

From figures 6 and 7 it is seen that the ¹D₂ decay depends on the excitation wavelength and is generally non-exponential especially for higher Pr³⁺ concentrations. When the less intense additional lines were pumped, the emission decay was faster and non-exponential at an early time; at later times it approached the value for isolated regular ions. Since the radiative decay rates are assumed to be the same for ions in all major types of site, the observed fluorescence dynamics are an indication of fast energy transfer by cross relaxation.

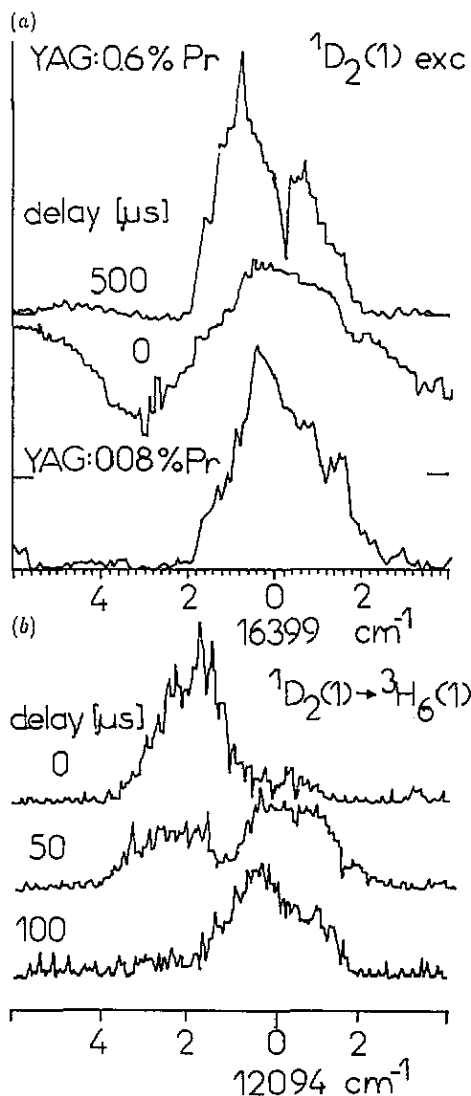


Figure 8. (a) The excitation spectral profile of the 1D_2 emission, $T = 15$ K. (b) Temporal evolution of an FLN signal for YAG:0.08 at.% Pr^{3+} .

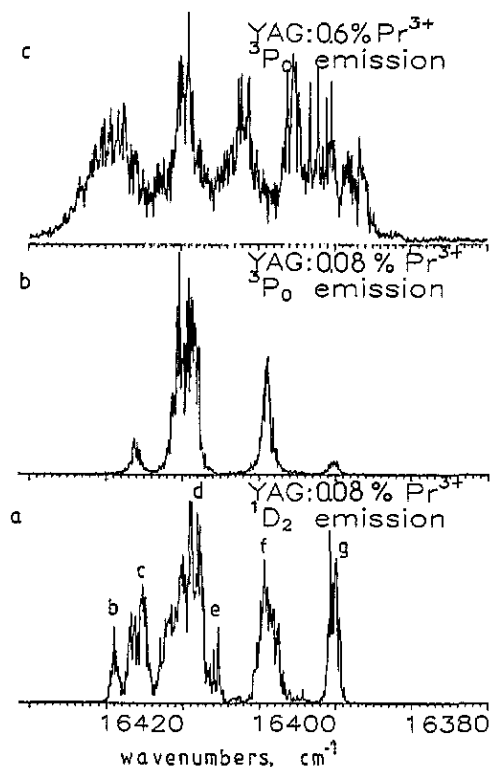


Figure 9. Excitation spectra of the (a) 1D_2 emission, (b) as 3P_0 emission in YAG:0.08 at.% Pr^{3+} , (c) as 3P_0 emission of YAG:0.6 at.% Pr^{3+} . The laser was scanned across the $^3H_4(1) \rightarrow ^1D_2(1, 2)$ absorption transitions; $T = 10$ K.

As shown by our FLN studies, energy diffusion is absent at 10 K in the investigated system. From figures 6 and 7 it can also be seen that the excitation of line a at 16478 cm^{-1} results in a fast non-exponential decay and the strongest selectivity of the fluorescence (see figure 4). This is evidence for the presence of strongly perturbed ion sites in YAG: Pr^{3+} . From table 1 it also follows that excitation of line h at 16381 cm^{-1} produces a very fast (of the order of $1\text{ }\mu\text{s}$) decay. As discussed earlier, this line could be related to some ion complex. On the assumption that the reduction in its lifetime is due to cross relaxation between an excited and unexcited ion, the transfer rate for such an ion pair is given by $X_h = 1/\tau_h - \gamma_0$, where $\gamma_0 = 4.1 \times 10^3\text{ s}^{-1}$ is the isolated ion decay rate ($\gamma_0 = 1/\tau_0$) measured for a low-

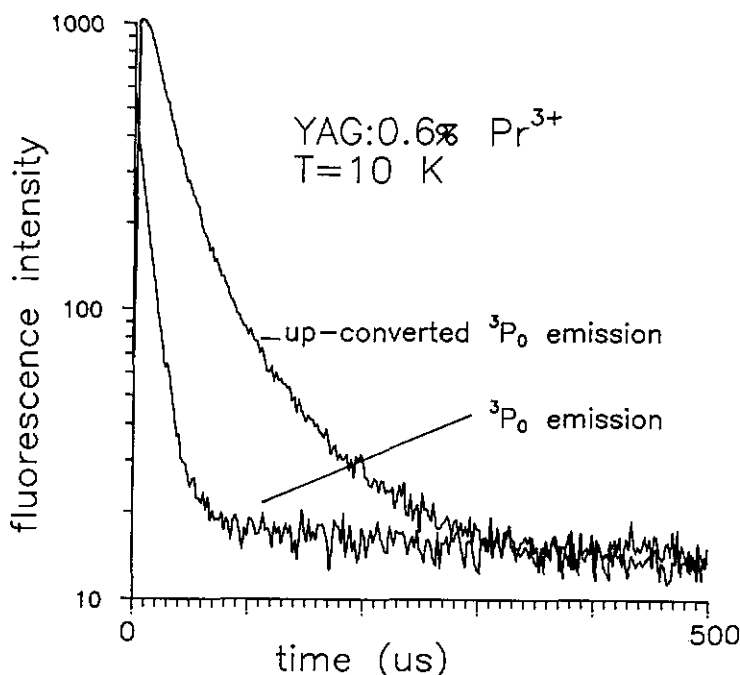


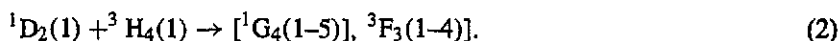
Figure 10. ³P₀ emission of 0.6 at.% Pr³⁺-doped YAG after resonant ³P₀ excitation and resulting from the up-conversion process after excitation of the ¹D₂(1) level.

concentration sample. When the measured value of τ_h was taken to be 1 μ s, X_h was found to be 9.96×10^5 s⁻¹.

Decay of the ¹D₂ state of Pr³⁺ in YAG measured under broad-band excitation was also analysed. Since at 10 K the donor-donor transfer is negligible, as confirmed by our FLN studies, the time dependence of the Pr³⁺ intensity $I(t)$ in the presence of Pr³⁺ traps can be described by the Inokuti-Hirayama [32] equation

$$I(t) = I_0 \exp[-t\gamma_0 - 4\pi/3 X_A R_{01}^3 (W_{01} t^{3/s})] \quad (1)$$

where X_A is the number of Pr³⁺ acceptors per unit volume, and R_{01} and W_{01} are the nearest-neighbour separation and transfer rate, respectively. s identifies the nature of interaction. We plotted $\ln I + t\gamma_0$ against $t^{1/2}$ putting $\tau_0 = 245$ μ s, $X_A = x_k \times 1.385 \times 10^{20}$ cm⁻³ ($x_1 = 0.006$, $x_2 = 0.0024$ and $x_3 = 0.0008$) and $R_{01} = 3.7$ Å. From figure 11 it is seen that for the 0.6 at.% Pr³⁺ crystal the plot can be best fitted for $s = 6$ by a straight line, confirming the validity of the Inokuti-Hirayama model and the electric dipole-dipole interaction mechanism. From the slope of the plot, 49 s^{-1/2}, and according to equation (1) we found the nearest-neighbour transfer rate to be $W_{01} \simeq 2.46 \times 10^6$ s⁻¹. This value is higher than the ¹D₂ quenching rates in most Pr³⁺-doped materials [33] but is in reasonable agreement with the transfer rate for line h determined earlier and confirms its pair origin. The dependence of W_{01} on Pr³⁺ concentration is presented in table 2. The high value of the nearest-neighbour quenching rate for ¹D₂ fluorescence of YAG:Pr³⁺ results probably from the quasi-resonant or phonon-assisted (less than 100 cm⁻¹ phonons) character of the cross-relaxation process which is attributed to the following transitions between two Pr³⁺ ions:



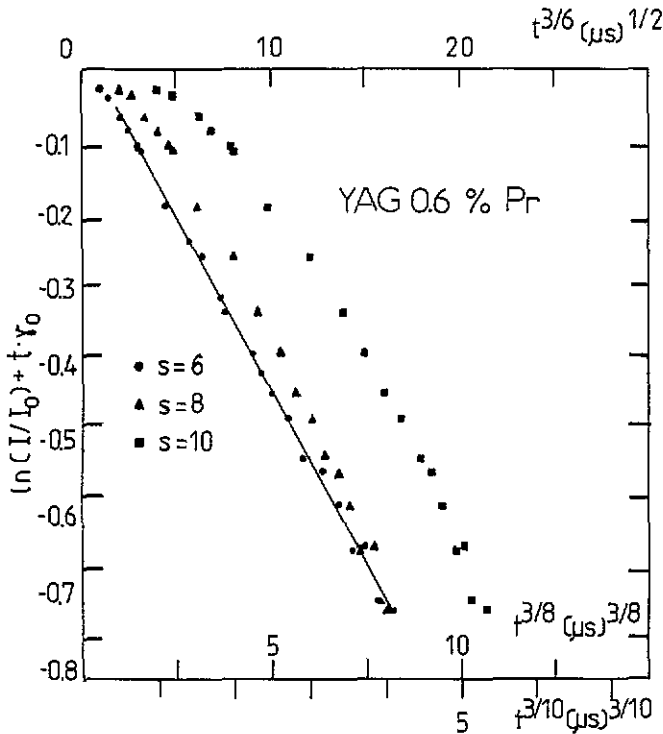


Figure 11. Plot of $\ln(I/I_0) + t\gamma_0$ against $t^{3/s}$ for $s = 6, 8$ and 10 for 0.6 at.% Pr^{3+} -doped YAG. The straight-line fit for $s = 6$ data indicates a near-neighbour transfer rate $W_{01} = 2.46 \times 10^6 \text{ s}^{-1}$.

Table 2. Energy transfer rates W_{01} as a function of Pr^{3+} ion concentration for YAG.

Pr concentration (at.%)	W_{01} (s^{-1})
0.08	3.5×10^5
0.24	1.8×10^6
0.6	2.46×10^6

Because of the quadratic dependence of the AS fluorescence on excitation energy it could be concluded that we are dealing with a second-order process. It is known that two $^1\text{D}_2$ ions which couple between themselves can also undergo an up-conversion process [19]



According to equation (3), only ion pairs can participate in the up-conversion transfer. This is consistent with our experimental data on YAG:0.6 at.% Pr^{3+} presented in figures 9 and 10. The ion pair character of the $^3\text{P}_0$ excitation spectrum measured as a function of $^1\text{D}_2(1)$ energy, the observed rise time of the $^3\text{P}_0$ signal and its longer lifetime than under direct excitation are indications that the energy transfer process is responsible for the AS fluorescence of YAG:0.6 at.% Pr^{3+} . The long part of the decay suggests that the lower levels of neighbour Pr^{3+} ions continually feed the $^3\text{P}_0$ level after the end of the excitation pulse.

A different situation has been observed for YAG:0.08 at.% Pr^{3+} where in figure 9 it appears that the AS signal is mainly associated with regular ion lines d and f and to a smaller

degree also with lines c and g, giving rise to a low emission. This is a clear indication that, for this very diluted Pr³⁺ system, the excited-state absorption (ESA) mechanism is responsible for populating the ³P₀ level. This is also consistent with the lack of any observable rise time of AS blue fluorescence. However, the observed 15 μs lifetime of the AS ³P₀ emission, which is slightly longer than the ³P₀ radiative lifetime of 12 μs, indicates that some energy transfer is still present. These observations are consistent with the work of Malta *et al* [34] who have proposed that the ESA process involving ³H₆ as the intermediate state is dominant in populating the ³P₀ level of YAG:Pr³⁺ at 300 K.

The TR FLN spectra presented in figure 8 show that the linewidth and spectral profile change with time, indicating the presence of donor–donor energy transfer in YAG:0.08 at.% Pr³⁺ at 15 K. It is known [35] that, owing to accidental coincidences with resonant transitions, this type of FLN has additional broadening and the observed linewidth does not represent the real homogeneous width of the transition. In our case, although the FLN resolution is monochromator limited, the FLN clearly demonstrates the crystal-field dependence on excitation energy.

The poor spectral isolation of the FLN component from the main line made the determination of the donor–donor transfer rate imprecise. Detailed studies of the donor–donor transfer in YAG:Pr³⁺ crystals are under way and will be presented in a separate paper.

5. Conclusions

The Pr³⁺-doped YAG crystals have been investigated by means of high-resolution pulsed-dye-laser spectroscopy. Our site-selective FLN and decay studies have enabled us to improve our knowledge of the Pr site distribution and energy transfer processes between Pr³⁺ ions. The non-equivalent crystal-field effects were observed on a large and on a small energy scale and six non-equivalent crystal-field sites have been spectrally resolved. Fluorescence dynamic studies provide evidence for the donor–acceptor energy transfer between ions. The results of preliminary FLN measurements on a YAG crystal with 0.08 at.% Pr³⁺ show a narrowing of the ¹D₂ → ³H₆ fluorescence and the absence of donor–donor transfer at 10 K; onset of spectral migration was observed at 15 K. We have observed the AS emission from the ³P₀ state after excitation of the ¹D₂ level. The concentration dependence of the ³P₀ excitation spectra and the temporal evolution of the blue fluorescence indicate that the AS emission results from the ESA process in the 0.08 at.% Pr³⁺-doped crystal. In the 0.6 at.% Pr³⁺ sample the non-exponential decay of this fluorescence and the observed rise time are indications of up-conversion by energy transfer.

Acknowledgments

The authors are indebted to Professor W Streck for many useful discussions. This work has been supported by the KBN grants 3 3706 91 02 and 3 1236 91 01.

References

- [1] Shi W Q, Bass M and Birbaum M 1990 *J. Opt. Soc. Am. B* **7** 1456
- [2] Gruber J B, Hills M E, Macfarlane R M, Morrison C A, Turner G A, Quarles G J, Kintz G J and Esterowitz L 1989 *Phys. Rev. B* **40** 9464
- [3] Armagan G, Buoncristiani A M and Di Bartolo B 1991 *J. Lumin.* **48–9** 171

- [4] Macfarlane R M, Tong T, Silversmith A J and Lenth W 1988 *Appl. Phys. Lett.* **52** 1300
- [5] Jacquier B, Malinowski M, Joubert M F and Macfarlane R M 1990 *J. Lumin.* **45** 357
- [6] Singh S, Smith R C and Van Uitert L G 1974 *Phys. Rev.* **10** 2566
- [7] Danielmeyer H G, Blatte M and Balmer P 1973 *Appl. Phys.* **1** 269
- [8] Voronko Yu K, Mamedov T G, Osiko V V, Timoschechkin M J and Scherbakow I A 1974 *Sov. Phys.-JETP* **38** 565
- [9] Devor D P and DeShazer L G 1983 *Opt. Commun.* **46** 97
- [10] Devor D P, Pastor R C and DeShazer L G 1984 *J. Chem. Phys.* **81** 4104
- [11] Devor D P and DeShazer L G 1989 *IEEE J. Quantum Electron.* **QE-25** 1863
- [12] Lupei V, Lupei A, Georgescu S and Ionescu C 1986 *Opt. Commun.* **60** 59
- [13] Lupei A, Lupei V, Georgescu S, Ionescu C and Yen W M 1987 *J. Lumin.* **39** 35
- [14] Wolinski W, Wolski R, Malinowski M and Mierczyk Z 1992 *Proc. 10th Int. Congr. on Laser Optoelectronics (Munich, June 1991)* ed W Waidelich (Berlin: Springer) p 611
- [15] Espinosa G P 1962 *J. Chem. Phys.* **37** 2344
- [16] Antic-Fidancev E, Lemaitre-Blaise M and Caro P 1987 *Inorg. Chim. Acta* **139** 281
- [17] Antic-Fidancev E, Lemaitre-Blaise M, Porcher P and Krupa J C 1991 *Eur. J. Solid State Inorg. Chem.* **28** 81
- [18] Antic-Fidancev E, Lemaitre-Blaise M, Krupa J C and Caro P 1988 *Czech. J. Phys. B* **38** 1268
- [19] Lai S T, Huang S and Yen W M 1982 *Phys. Rev. B* **26** 2349
- [20] Vial J C, Buisson R, Madeore F and Poirier M 1979 *J. Physique* **40** 913
- [21] Malinowski M 1990 *J. Phys.: Condens. Matter* **1** 4673
- [22] Malinowski M, Wolski R and Wolinski W 1990 *Solid State Commun.* **74** 17
- [23] Gruber J B, Hills M E, Macfarlane R M, Morrison C A and Turner G A 1989 *Chem. Phys.* **134** 241
- [24] Selzer P M 1981 *Laser Spectroscopy of Solids (Topics in Applied Physics 49)* ed W M Yen and P M Selzer (Berlin: Springer) p 113
- [25] Lezama A, Oria' M and de Araujo C B 1986 *Phys. Rev. B* **33** 4493
- [26] Malinowski M, Jacquier B, Bouazaoui M, Joubert M F and Linares C 1990 *Phys. Rev. B* **41** 31
- [27] Bayerer R, Huber J and Mateika D 1986 *Z. Phys. B* **64** 201
- [28] Popova M N 1989 *Proc. 1st Int. School on Excited States of Transition Elements (Ksiaz, June 1988)* ed B Jezowska-Trzebiatowska, J Legendziewicz and W Strek (Singapore: World Scientific) p 405
- [29] Mares J A, Nie W and Boulon G 1991 *J. Lumin.* **48-9** 227
- [30] Ryabchenkov V V 1988 *Sov. Phys.-Crystallogr.* **32** 855
- [31] Malinowski M, Wolinski W, Wolski R and Strek W 1991 *J. Lumin.* **48-9** 235
- [32] Inokuti M and Hirayama F 1965 *J. Chem. Phys.* **43** 1978
- [33] Pacheco E M and de Araujo C B 1988 *J. Lumin.* **42** 221
- [34] Malta O L, Antic-Fidancev E, Lemaitre-Blaise M, Dexper-Ghys J and Piriou B 1986 *Chem. Phys. Lett.* **129** 557
- [35] Flach F, Hamilton D S, Selzer P M and Yen W M 1977 *Phys. Rev. B* **15** 1248