Absorption and Emission Analysis of Pr^{3+} in Yttrium Aluminium Garnet*

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Praseodymium doped yttrium aluminium garnet (YAG) has been studied previously by Hooge [1] and Gourley [2]. Hooge undertook experiments between 16–20 K and up to room temperature. His absorption and fluorescence measurements are in fair agreement with ours, the difference coming from our helium absorption spectra. The $^3P_0$ level at 4.2 K must be unique for a single crystallographic site. Hooge effectively attributes a level at 20 533 cm^{-1} to $^3P_0$. We detect a complex structure for the $^3P_0$ level, seen only at 4.2 K, with three distinct lines at 20 546, 20 536 and 20 518 cm^{-1}. The most intense is at 20 536 cm^{-1} (Fig. 1). (Two Pr^{3+}-doped at the 1% level YAG crystals, one from France, the other from the U.S.A., exhibit the same absorption spectra at 4.2 K.)

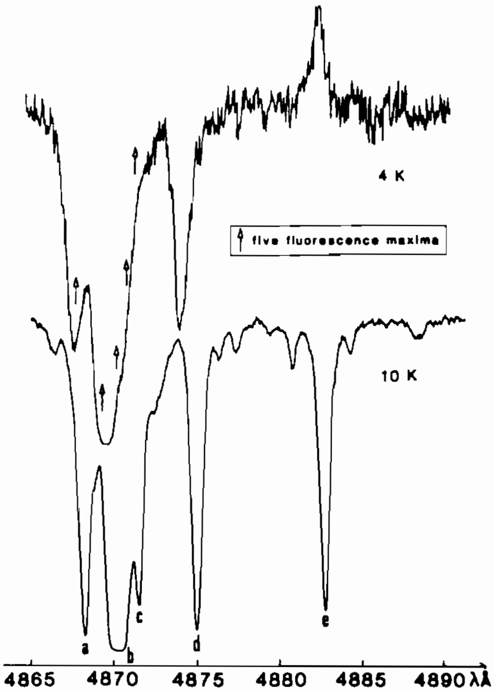

Fig. 1. Absorption spectra at 4.2 K and *ca.* 10 K for the transition $^3H_4 \rightarrow {}^3P_0$.

Results

The $^3P_0$ Level

In Fig. 1 are represented the absorption spectra of the $^3H_4 \rightarrow {}^3P_0$ transition at 4.2 K and about 10 K (4.2 K measurement: the sample is embedded in helium; 10 K measurement: the sample is not in direct contact with helium and the temperature measurement may be not exact).

The 4.2 K absorption spectrum for the $^3H_4 \rightarrow {}^3P_0$ transition is a puzzle. Three intense lines are observed; one of them must correspond to the $^3P_0$ YAG level. We choose the most intense line at 20 536 cm^{-1} (line (b)). A 20 518 cm^{-1} line (line (d)), 18 cm^{-1} from the 20 536 cm^{-1} line has also been observed by Hooge at a higher temperature, but it was still present at 4.2 K in our experiment. It may be one of the upper Stark components of the $^3H_4$ level. In the 300 and 77 K absorption spectra we found some electronic lines differing from the main ones by 18 and 50 cm^{-1}, but in the fluorescence spectra excited by a dye laser excitation at 4.2 K or at 10 K, or by various argon laser excitation frequencies at 77 K, the $^3H_4$ Stark component at 18 cm^{-1} is never seen as a ground level for fluorescence lines from $^3P_0$. This 18 cm^{-1} Stark component is observed by dye laser excitation for fluorescence lines from the $^1D_2$ level at 300 K, 77 K and 4.2 K (at 4.2 K the selective excitation of the lowest $^1D_2$ level is very complex).

If this line at 20 518 cm^{-1} is effectively a $^3H_4$ Stark component at 18 cm^{-1}, it is difficult to explain its presence in absorption at 4.2 K, because an 18 cm^{-1} level is not populated at 4.2 K. We propose the following explanation: the transition from $^3P_0$ to the Stark level of $^3H_4$ at 50 cm^{-1} (20 486 cm^{-1}), which is very intense and seen even as an emission line in the absorption spectrum in white light (upper spectrum, Fig. 1), populates an 18 cm^{-1} Stark level by non-radiative de-excitation. The scheme is given in Fig. 2. The third line in the $^3P_0$ group, at 20 546 cm^{-1} (line (a)), seems to be associated with another crystallographic 'site'.

Line (c) (20 527 cm^{-1}) disappears at 4.2 K. This means that it is one of the upper Stark components of the ground level. If this is true, and if this line is associated with the (b) line at 20 536 cm^{-1}, then for the main site $^3H_4$ four lower Stark components exist at 0–6–18–50 cm^{-1}. This is not in agreement with the crystal-field calculation in D_2 symmetry using B^k_q parameters for Pr^{3+}:YAG from ref. 3.

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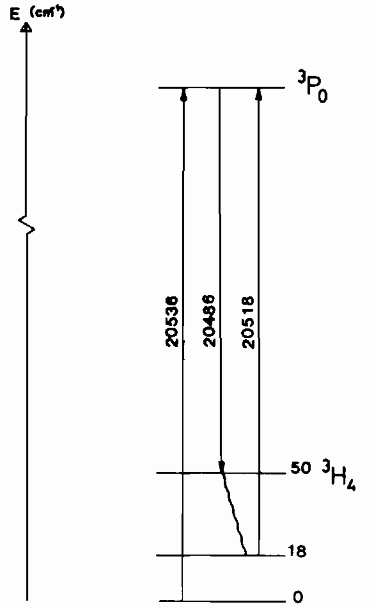

Fig. 2. Energy level scheme for the $^3P_0$ level in absorption at 4.2 K.

TABLE I. Lifetime Measurements of the $^3P_0$ level at 4.2 K

Energy (cm^{-1})	20546.5 line (a)	20535.2 line (b)	20533.9 ?	20527.5 line (c)	20523.7 ?
Life-time (μs)	3.15	10.3	5.5	10.1	2.9

Selective Laser Excitation of the $^3P_0$ Level

For the excitation of the (a, b) group at 4.2 K, five fluorescence maxima are observed and five lifetime measurements recorded (Table I), one for line (a) and four for line (b). One of these fluorescence maxima corresponds to the residue of the (c) line. Excitation of the (d) line (20 518 cm^{-1}) yields no fluorescence at 4.2 K, as opposed to 10 K when it was observed.

The energy sequences for the ground level and the excited levels observed by selective excitation of the $^3P_0$ level are the same for the four highest in energy fluorescence maxima; the lowest (at 20 523.7 cm^{-1}) situated at the side of the (b) line corresponds to a different $^3H_4$ sequence.

In Figs. 3 and 4 are shown the spectra for the $^3P_0 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_6$ transitions associated with excitations of the lines (a), (b) and the residue of (c), and two other fluorescence maxima (those only for $^3P_0 \rightarrow {}^3H_4$; $^3P_0 \rightarrow {}^3H_6$ is weak). We see that the splittings are the same, but the absolute positions are slightly different corresponding to the shift in position of the associated $^3P_0$. This suggests that the praseodymium ions experience identical crystal fields, but are associated with slightly different free-atom parameters.

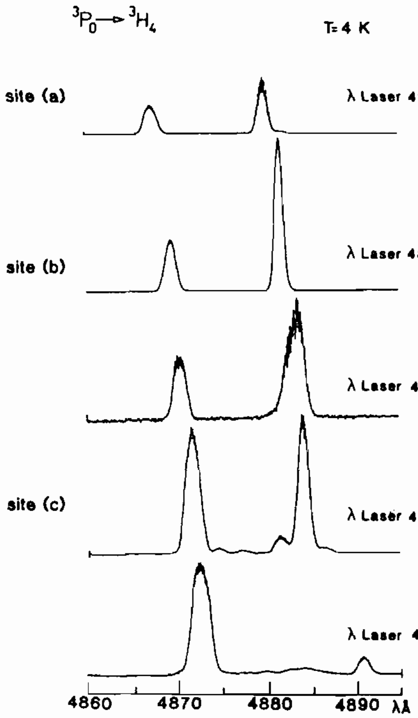

Fig. 3. Selective excitation at 4.2 K of the $^3P_0$ level: $^3P_0 \rightarrow {}^3H_4$ transition observed.

A dye laser excitation of the (d) line at 10 K exhibits the same $^3H_5$, $^3H_6$ and $^3F_2$ levels; for the $^3H_4$ level we observed one component at 32 cm^{-1} from this line, that is at 50 cm^{-1} from the (b) line at 20 536 cm^{-1}. Then, the (d) line is effectively at 18 cm^{-1} from 20 536 cm^{-1}. The lifetime measurements are very different for the (a) and (b) lines, but for the (b) and (c) lines they are very close, 10.3 μs and 10.1 μs respectively. In our previous study on up-conversion processes in Pr^{3+}:YAG, the lifetime of the $^3P_0$ level at 300 K was found to be 8 μs [4]. The mystery persists for the 20 533.9 cm^{-1} fluorescence maximum, just near the (b) line, and for the 20 523.7 cm^{-1} maximum situated at the side of the (b) line.

Excitation Spectra in the $^3P_1$–$^1I_6$ Area

The excitation spectra in the $^3P_1$–$^1I_6$ area of the five $^3P_0$ dye laser selected fluorescences (Fig. 3) are represented in Fig. 5 and the energy values are given in Table II. We will try to extract the $^3P_1$ energy level sequences from the data. If there is a single site, the computation (with D_2 parameters) predicts the following splitting: 39 cm^{-1} for the two lower levels, and the third one 131 cm^{-1} above the second one. We may then expect two close $^3P_1$ components in our data. Differences exist between the four upper spectra and the last one, monitored at 4890 Å (20 450 cm^{-1}). It is the most simple spectrum. But there is also some difference between the (a) spectrum and the others. The very intense line at 21 053 cm^{-1} in the (a)

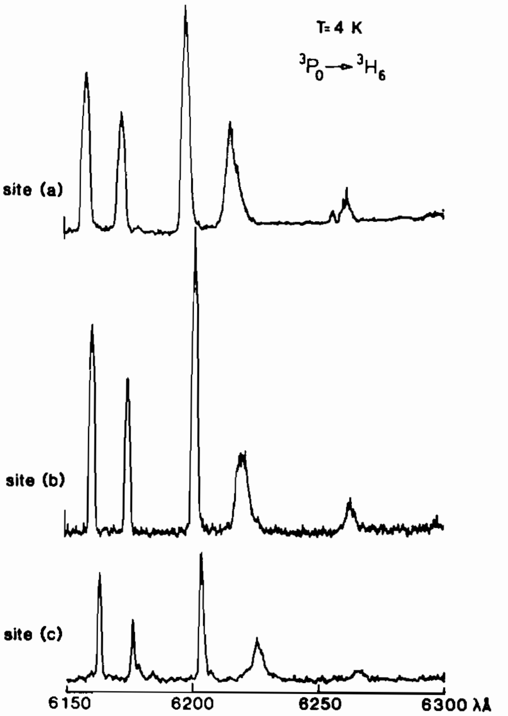

Fig. 4. Selective excitation at 4.2 K of the $^3P_0$ level: $^3P_0 \rightarrow {}^3H_6$ transition observed.

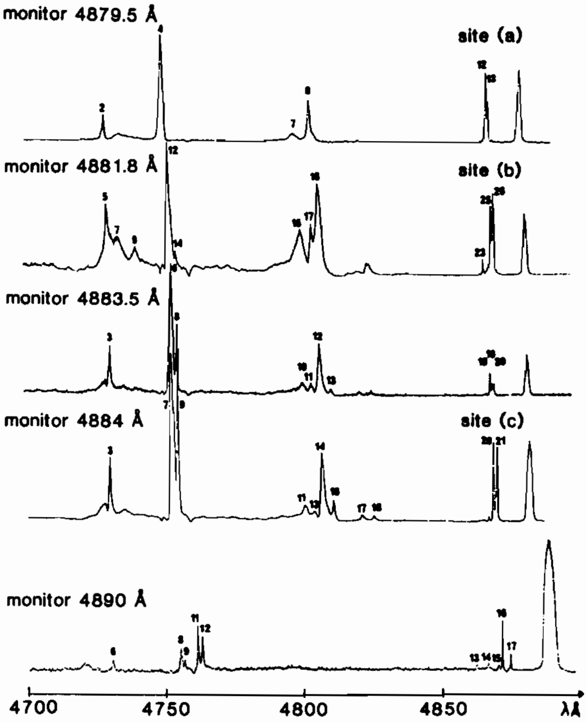

Fig. 5. Excitation spectra at 4.2 K for different emission lines.

TABLE II. Excitation Spectra of Several $^3P_0 \rightarrow {}^3H_4$ Emissions at 4.2 K (The numbers correspond to Fig. 5)

Monitor 4879.5 Å site (a)	Monitor 4881.8 Å site (b)	Monitor 4883.5 Å	Monitor 4884.0 Å site (c)	Monitor 4890.0 Å
	21202.2*			
	21182.9*			21183.7*
21177.2*				21177.2*
	21170.9*			
				21162.1*
				21158.8*
21146.2(2)	21147.7*	21147.7*		
		21144.3*	21144.3*	21143.7*
	21140.3(5)		21141.6	
		21136.9(3)	21136.9(3)	21136.6(6)
	21132.4*			
			21124.4*	
	21122.8(7)			
21120.5*		21114.3*		
	21100.2*			
	21094.0(9)			
	21082.1*			
21052.9(4)	21053.1**	21053.4**	21053.2**	
21048.9				
	21040.5(12)			
	21037.2*	21038.5(6)	21037.4(7)	
		21033.8	21033.5	
	21028.8(14)	21027.5(8)		21028.2
			21026.3(9)	21026.1(8)
				21020.3(9)
21008.0**	21006.9**	21008.0**	21007.1**	21006.9**

(continued)

TABLE II. *(continued)*

Monitor 4879.8 Å site (a)	Monitor 4881.8 Å site (b)	Monitor 4883.5 Å	Monitor 4884.0 Å site (c)	Monitor 4890.0 Å
				20999.5(11)
				20992.3(12)
20842.7(7)				
	20830.5(16)			
		20827.2(10)		
			20825.9(11)	
			20823.2*	
20818.5(8)				
	20813.6(17)	20813.4(11)		
20810.8*			20810.5(13)	
	20802.5(18)			
		20801.0(12)		
			20799.0(14)	
			20790.6*	
	20782.2*	20782.2(13)		
			20780.8(16)	
20741.8*				
		20737.4*		
			20736.5(17)	
	20728.7			
		20727.0*		
	20725.5			
		20719.9*		
			20717.5(18)	
20564.2*				20564.4(13)
	20553.8*			
	20548.1(23)			
20544.2(12)				20545.9(14)
20540.4(13)	20539.0	20541.0*	20540.0*	
	20535.6(25)	20536.1(18)		
20533.5*		20532.3(19)	20533.4(20)	
	20530.4(26)	20529.5(20)		20530.1(15)
			20527.5(21)	
20522.8*				20524.6(16)
20514.0*				20511.3(17)

All values are in cm^{-1}; *very weak line; **absorption line.

spectrum (line 4 in Fig. 5) is observed as an absorption line in the other spectra, and a line at 21 007 cm^{-1} (4760 Å) is observed only as an absorption line for all spectra. The intense line at 21 038–21 040 cm^{-1} for (b)–(c) spectra is not present in the (a) spectrum. In the absorption spectrum at 4.2 K three intense lines are observed for the $^3P_1$–$^1I_6$ area at 21 011, 21 045 and 21 055 cm^{-1}. We have three lines instead of the two lower $^3P_1$ expected. According to our results we believe that the 21 055 cm^{-1} line should be connected with the $^3P_0$ absorption at 20 542 cm^{-1} ((a) line). The two other lines, 21 011 and 21 045 cm^{-1}, may be transitions to the two components of $^3P_1$ associated with the 'main' garnet site ($^3P_0$ (b)) absorption. Hooge observed only a line at 21 040 cm^{-1} in his 77 K absorption spectrum. In our 77 and 300 K absorption spectra this line exists. One would expect two lines at 21 040 and 20 989 cm^{-1} from the thermal population of the 50 cm^{-1}, $^3H_4$ upper Stark component. We observed, in fact, lines at 21 041, 21 025, 21 008 and 20 994 cm^{-1}. The lines at 21 041, 21 025 and 20 994 can be related to the 0, 18 and 50 cm^{-1} Stark components of $^3H_4$ associated with the (b) absorption line of $^3P_0$, but the absorption at 21 008 cm^{-1} is a supplementary one. This line becomes 21 011 cm^{-1} at 4.2 K, (21 041 at 77 K becomes 21 045 cm^{-1} at 4.2 K). We believe that the two $^3P_1$ levels are at 21 029 and 21 045 cm^{-1} at 4.2 K. The line at 21 011 cm^{-1} in the absorption spectrum corresponds to a transition from the first excited Stark level of $^3H_4$ at 18 cm^{-1} to the lower $^3P_1$.

Discussion

The complexity of the absorption and fluorescence spectra for 1% Pr-doped crystal YAG is evident.

TABLE III. Energy Levels of 1% Pr^{3+}:YAG at 4.2 K

$^3H_4$	$^3H_5$	$^3H_6$	$^3F_2$	$^3F_3$	$^3F_4$	$^1G_4$	$^1D_2$	$^3P_0$	$^1I_6$, $^3P_1$	$^3P_2$
0	2275 ?	4304	5369	6499	7101	9716	16401	20518[a]	20707**	22104
18	2297	4314	5432	6530 ?	7134	9798 ?	16414	20536	20727	22156
50	2404	4340	5452	6560	7158	9827	16884	20542[b]	20770	22295
528*	2573	4358	5534	6797	7299	10115	17084		20807	22384 +
546	2583	4411		6831	7420	10167 ?	17216		20834	22596 +
575	2604	4459		6860		10261			21029 ($^3P_1$)	
737*	2618	4579		6995		10337			21045($^3P_1$)	
751*	2842	4658							21055	
	2866	4842 ?							21122	
		4856							21142	
		4882							21171($^3P_1$)	
		5045 +							21230**	
		5143							21322**	
									21508 ++	
									21547 ++	
									21588 ++	
									21672	
									21829	
									21875	
Barycenter										
401	2562	4629	5446	6724	7222	10031	16799	20536	21082, $^3P_1$	22307

All values in cm^{-1}; *from $^1D_2$ level; ?, uncertain lines; **observed under magnetic field; +, weak broad band, ++, weak lines.
[a]From $^3H_4$ (18 cm^{-1}). [b]Probably from another site.

Asano and Koningstein worked [5] on europium-doped YAG, a crystal for which they found two distinct sites with rather different crystallographic surroundings. For the four fluorescence maxima at 4.2 K in the 20 527–20 546 cm^{-1} region, all observed transitions in our case have quite the same aspect and the crystal field parameters expected must be of the same order of magnitude. One of us has suggested a perturbation of the ground state level by an electron–phonon interaction which may induce some Stark level energy shifts of about 10–20 cm^{-1} [6]. If the ground state Stark level is affected by such a phenomenon, with different couplings, it will translate as several spectra showing only a small apparent change in free atom parameters.

A tentative energy level scheme for Pr^{3+} in YAG is given in Table III. The $^3H_4$ data are simplified to the 'site' corresponding to line (b) as ground state. The difficulties in the establishment of this scheme are mostly linked to transitions from absorption or fluorescence involving the $^3H_4$ ground state. However fluorescence transitions between excited levels (see Fig. 4) yield a pattern corresponding apparently to a single site.

References

1 F. N. Hooge, *J. Chem. Phys., 45,* 4504 (1966).
2 J. T. Gourley, *Phys. Rev. B, 5,* 22 (1972).
3 G. A. Morrison and R. P. Leavitt, 'Handbook on the Physics and Chemistry of Rare Earths', Vol. 5, North-Holland, Amsterdam, 1982, p. 632.
4 O. L. Malta, E. Antic-Fidancev, M. Lemaître-Blaise, J. Dexpert-Ghys and B. Piriou, *Chem. Phys. Lett., 129,* 557 (1986).
5 M. Asano and J. A. Koningstein, *Chem. Phys., 42,* 369 (1979).
6 P. Caro, *J. Less-Common Met., 126,* 239 (1956).