PHYSICAL REVIEW B VOLUME 27, NUMBER 9 1 MAY 1983

Selective site excitation of europium-doped monoclinic Gd_2O_3

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(Received 1 December 1982)

Monoclinic crystals of Eu^{3+}:Gd_2O_3 were studied at 80 K with the use of fluorescence spectra to interpret the energy levels. A tunable dye laser was used to selectively excite levels of the ${}^5D_{0,1,2}$ manifolds. Three distinct crystallographic sites for Eu^{3+} ions were identified for a majority of the Stark levels of the ${}^7F_{0,1,2,3,4}$ and ${}^5D_{0,1}$ multiplets. Comparisons of the fluorescence spectra from different sites were used in this energy-level assignment. Several fluorescence-lifetime measurements were also recorded.

INTRODUCTION

Selective site excitation using a dye laser has been employed to aid in energy-level identification of rare-earth ions in crystals. Trivalent europium in monoclinic gadolinium oxide (Eu^{3+}:Gd_2O_3) has been investigated. The crystal field experienced by the Eu^{3+} ions manifests itself in three distinct crystallographic sites. Therefore the $2J+1$ splitting of the Russell-Saunder labeling scheme has an apparent

TABLE I. Fluorescence spectra of Eu^{3+}:Gd_2O_3 at 80 K from selective site excitation of the three sites of ${}^5D_0$.

		Site *A*			Site *B*			Site *C*	
Transition	λ (Å)	*E* (cm^{-1})	Δ*E* (cm^{-1})	λ (Å)	*E* (cm^{-1})	Δ*E* (cm^{-1})	λ (Å)	*E* (cm^{-1})	Δ*E* (cm^{-1})
${}^7F_0 \rightarrow {}^5D_0$	5785.0	17281		5822.0	17171		5824.0	17165	
${}^5D_0 \rightarrow {}^7F_1$	5838.0	17131	150	5911.3	16912	259	5940.5	16829	336
	5905.0	16931	350	5961.0	16770	401	5948.0	16807	358
	6013.5	16625	656	5969.0	16749	422	5951.0	16799	366
${}^5D_0 \rightarrow {}^7F_2$	6088.0	16421	860	6153.0	16248	923	6143.0	16274	891
	6166.5	16212	1069	6158.0	16235	936	6179.0	16179	986
	6238.0	16027	1254	6235.0	16034	1137	6261.0	15968	1197
	6278.0	15924	1357	6309.0	15846	1325			
				6327.5	15800	1371			
${}^5D_0 \rightarrow {}^7F_3$	6465.5	15462	1819	6520.0	15333	1838	6535.0	15298	1867
	6477.5	15433	1848	6537.5	15292	1879	6548.0	15268	1897
	6489.5	15405	1876	6542.0	15282	1889	6561.0	15238	1927
	6537.5	15292	1989	6563.0	15232	1939	6569.0	15219	1946
	6599.5	15148	2133	6577.0	15200	1971			
	6646.5	15041	2240	6617.5	15107	2064			
${}^5D_0 \rightarrow {}^7F_4$	6880.0	14531	2750	6877.0	14537	2634	6848.0	14599	2566
	6928.0	14430	2851	6947.0	14391	2780	6944.0	14397	2768
				6952.0	14381	2790	6969.0	14346	2819
				6963.0	14358	2813	7001.5	14279	2886
				7028.0	14224	2947	7023.0	14235	2930
	7088.0	14105	3176	7062.0	14156	3015	7083.0	14115	3050
	7134.0	14013	3268	7076.5	14127	3044			
	7142.0	13998	3283	7098.5	14084	3087			

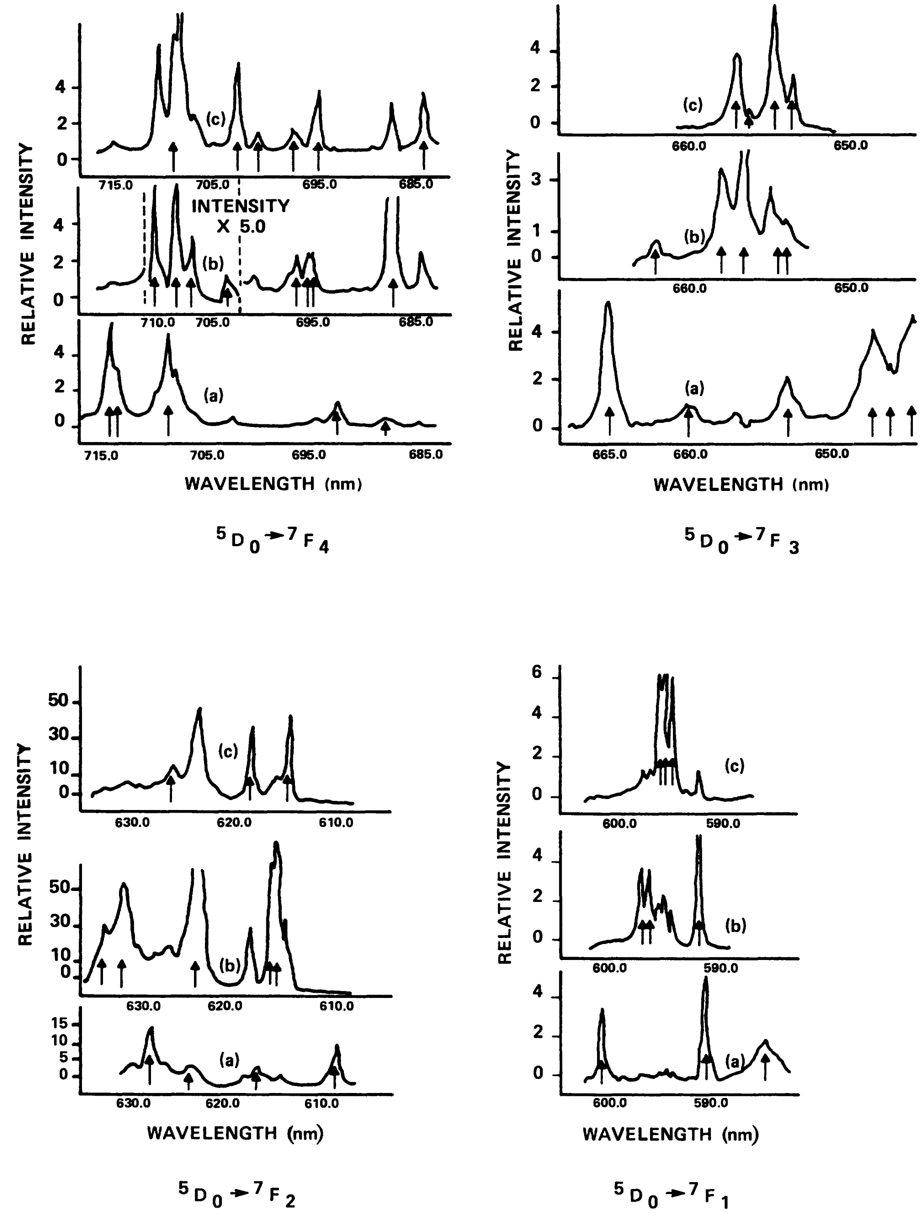

FIG. 1. Fluorescence spectra ($^5D_0 \rightarrow {}^7F_{1,2,3,4}$) of Eu^{3+}:Gd_2O_3 at 80 K from selective excitation of the three crystallographic sites of $^5D_0$: (a) 17281, (b) 17171, and (c) 17165 cm^{-1}.

threefold degeneracy. The resulting fluorescence spectra from broad-band excitation became too complex for accurate energy-level identification.

Rice and DeShazer[1] first investigated Eu^{3+}:Gd_2O_3 and made tentative ion-site determinations based on the absorption and fluorescence spectra of Eu^{3+} $4f^6$. A recent paper by Dexpert-Ghys *et al.*[2] reports the spectra of Eu^{3+}:Gd_2O_3 using selective site excitation. Our work[3] was done independently but concurrently with the Dexpert-Ghys study and extends their results to include fluorescence from $^5D_1$ and $^5D_2$ levels.

The technique of selective site laser excitation has been demonstrated to successfully identify previously obscure energy levels. All three crystallographic sites of the $^5D_0$ level of Eu^{3+} were excited and the fluorescence spectra were used in ^7F_J identification. Seven of the nine levels of the $^5D_1$ multiplet were

TABLE II. Fluorescence spectra of Eu^{3+}:Gd_2O_3 at 80 K from excitation of sites *A* and *B* of $^5D_0$. Spectra from excitation of site *B* and *C* were indistinguishable.

				Site *B* or *C*[a]			
		Site *A*				Site *B*	Site *C*[b]
Transition	λ (Å)	*E* (cm^{-1})	Δ*E* (cm^{-1})	λ (Å)	*E* (cm^{-1})	Δ*E* (cm^{-1})	Δ*E* (cm^{-1})
$^7F_0 \rightarrow {}^5D_0$	5785.0	17281		5822.0	17171		
$^5D_0 \rightarrow {}^7F_5$	7418.5	13476	3805				
	7432.0	13452	3829	7457.0	13407	3764	(3758)
	7461.0	13398	3883	7462.0	13398	3773	(3767)
	7478.0	13368	3913				
	7483.0	13350	3931				
	7486.0	13355	3926				
	7508.5	13315	3966	7487.0	13353	3818	(3812)
	7529.0	13279	4002	7516.0	13301	3870	(3864)
	7584.0	13182	4099	7525.0	13285	3886	(3878)
	7644.0	13078	4203				
	7748.0	12903	4378				
	7765.0	12874	4407				
	7815.0	12792	4489				
$^5D_0 \rightarrow {}^7F_6$	7989.5	12513	4768				
	8003.5	12491	4790	8151.0	12265	4906	(4900)
	8841.0	11308	5973	8161.0	12250	4921	(4915)
	8848.0	11299	5982	8445.0	11838	5333	(5327)
	8871.0	11270	6011				
	8879.0	11259	6022				
	8924.0	11202	6079				
	8936.5	11187	6094				
	9003.5	11104	6177				
	9045.0	11053	6228				

[a] Only transitions not observed in site-*A* excitation are listed.

[b] Parentheses show the $^7F_{5,6}$ levels possible for the *C* site.

similarly analyzed. Two stark levels of the $^5D_2$ manifold were excited but the fluorescence spectra became too complicated for accurate interpretation beyond this point. Also the fluorescence lifetimes were measured for transitions from the $^5D_0$ level for two different crystal sites.

EXPERIMENTAL SETUP

The pulsed-laser spectroscopic system used here was assembled specifically to perform selective site excitation of rare-earth crystals. This system was almost totally designed and constructed in our laboratory at North Dakota State University and has been described in detail elsewhere.[4]

A nitrogen-laser-pumped dye laser was chosen as the light source because of its fast energetic pulses and its wide tunability. The nitrogen laser typically operated at 5 Hz with a 700-kW, 10-nsec pulse at 337.1 nm. The 5-Hz rate allowed energy optimization and allowed the irradiated crystal to almost completely deexcite between pulses. Our organic dye inventory allowed complete tunability from 360 to 680 nm. Dye pulses were typically 30 kW with a duration of 5 nsec [full width at half maximum (FWHM)]. The crystals were mounted in a cryogenic Dewar with a conduction-type cold finger. This work was restricted to liquid-nitrogen temperatures (80 K). The excitation beam was focused vertically through the crystal so as to optically match the fluorescence with the entrance slit of the monochromator. A 0.5-m Bausch and Lomb monochromator was used with a first-order dispersion of 33 Å/mm. A thermoelectrically cooled photomultiplier tube (PMT) (RCA 31034B) was also used. A boxcar integrator of our own design signal-averaged the PMT

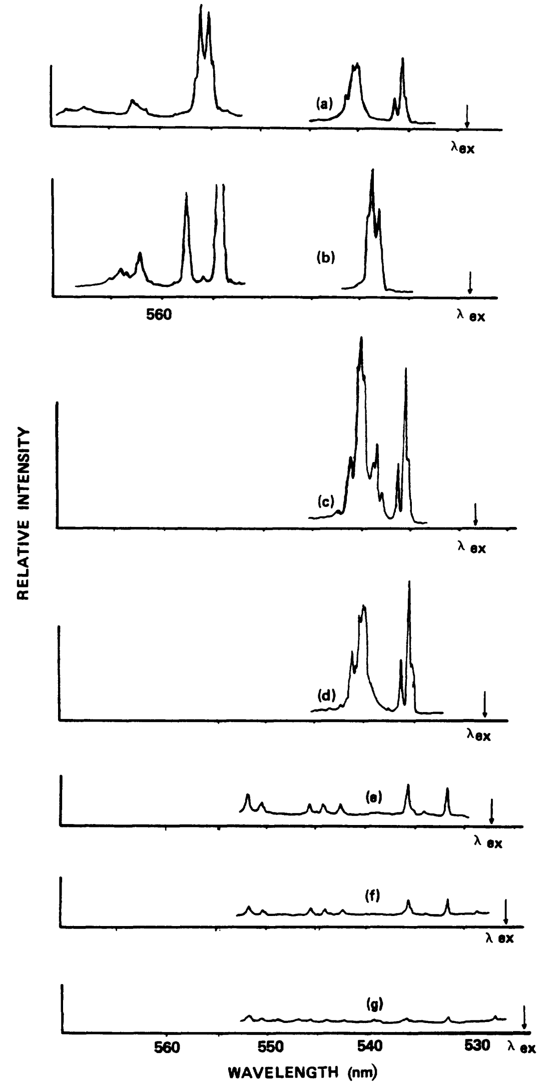

FIG. 2. Fluorescence spectra ($^5D_1 \rightarrow {}^7F_{1,2}$) of Eu^{3+}:Gd_2O_3 at 80 K from selective excitation of seven of the possible energy levels (and/or sites) of the $^5D_1$ manifold: (a) 18 900, (b) 18 918, (c) 18 934, (d) 18 942, (e) 18 979, (f) 19 024, and (g) 19 086 cm^{-1}.

output and interfaced with a strip chart recorder to complete our system.

Single crystals were grown using a flame-fusion technique by Johnson[5] under the supervision of Henderson at the McDonnell Douglas Corporation in Santa Monica, California, in the 1960s. The high temperatures used (>1670 K) ensure an irreversible transition from the cubic form to the monoclinic structure of this crystal (Gd_2O_3:Eu^{3+}), a consequence of this growing technique.

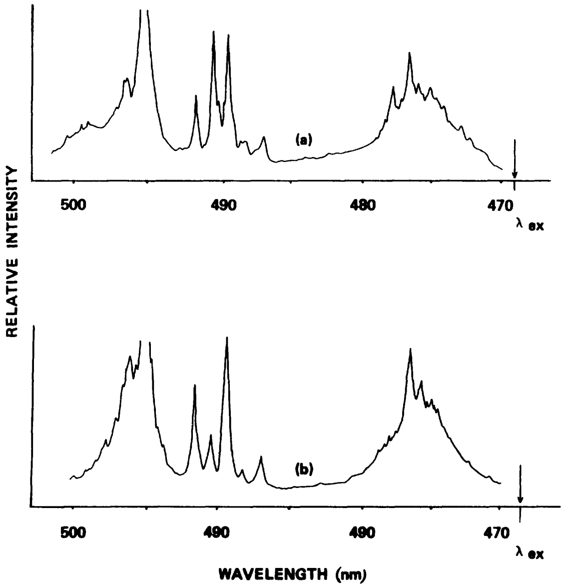

FIG. 3. Fluorescence spectra ($^5D_2 \rightarrow {}^7F_{1,2}$) of Eu^{3+}:Gd_2O_3 at 80 K from selective excitation of two of the levels of the $^5D_2$ manifold: (a) 21 335 and (b) 21 346 cm^{-1}.

RESULTS

The monoclinic structure of Gd_2O_3 is transparent for wavelengths greater than 300 nm. The crystal serves as a good lattice for the trivalent europium. In dilute concentrations, the Eu^{3+} ion fluoresces strongly. Our crystals of Eu^{3+}:Gd_2O_3 had a dopant concentration of 0.5 at. %. The excitation beam was projected along the crystallographic axis but since no polarization studies were undertaken its orientation is irrelevant.

The $^5D_0$ level offers an excellent test for selective site identification. Since $J=0$, there is no Stark splitting, but for the monoclinic crystal structure, three levels exist corresponding to the three distinct sites for Eu^{3+} in the Gd_2O_3 lattice. These three sites were identified as 17 281, 17 171, and 17 165 cm^{-1} and were separately excited ($^7F_0 \rightarrow {}^5D_0$) by tuning the dye laser (using Rhodamine 6G). Figure 1 shows the resulting fluorescence. By comparing the three sites for termination at the $^7F_{1,2,3,4}$ manifolds, the success of this technique is proven by the obvious differences in spectra for excitation of the three sites. Transfer from one site to another is also observable. Table I lists the prominent transitions of Fig. 1, and based on relative intensities assigns energies to the $^7F_{1,2,3,4}$ multiplets of all three sites.

Examination of the $^7F_{5,6}$ multiplets (involving

TABLE III. Tentative site assignment of the $^5D_1$ manifold from $^7F_1$ and $^7F_2$ identification of the $^5D_1 \rightarrow ^7F_{1,2}$ fluorescence spectra.

Fluorescence transition		Upper fluorescence level and energy of lower level (cm^{-1})						
λ (Å)	E (cm^{-1})	18 900	18 918	18 934	18 942	18 979	19 024	19 086
5268.5	18 975							a
5283.5	18 921						b	
5313.0	18 816					163		
5350.5	18 685				257			
5354.5	18 671			260				
5362.0	18 644	254						
5379.0	18 586		333					
5385.0	18 565		353					
5388.0	18 554		363					
5396.0	18 527			407				
5400.0	18 513			421				
5403.0	18 503	397						
5411.0	18 476	423						
5442.0	18 370						654	
5455.5	18 325				654			
5502.5	18 168						856	
5518.0	18 117				862			
5543.5	18 034		884					
5546.5	18 024				918			
5551.5	18 008				932			
5558.5	17 985	915						
5563.5	17 969	931						
5573.5	17 937		981					
5617.5	17 796			1138				
5623.5	17 777		1141					
5626.0	17 770	1130						
5641.5	17 721		1197					
5669.0	17 635			1299				
5676.0	17 613	1287						
5694.0	17 557			1377				

[a] Possible relaxation from $^5D_1$ (19 086) to $^5D_1$ (18 979), A site to A site, followed by $^5D_1 \rightarrow ^7F_0$ emission.

[b] Possible relaxation from $^5D_1$ (19 024) to $^5D_1$ (18 918), A site to C site, followed by $^5D_1 \rightarrow ^7F_0$ emission.

longer wavelengths) was inhibited by our detection apparatus. However, the fluorescence spectra from excitation of two sites of $^5D_0$ (17 281 and 17 171 cm^{-1}) were recorded. The spectra from excitation of $^5D_0$ at 17 165 cm^{-1} were indistinguishable from that of the 17 171-cm^{-1} level. Table II lists the more distinct transitions representing $^5D_0 \rightarrow ^7F_{5,6}$ and makes tentative assignment of the $^7F_{5,6}$ manifolds.

Of the nine Stark levels of the $^5D_1$ manifold in the three crystallographic sites, seven were selectively excited. Only the fluorescence spectra out to 570 nm were analyzed since at longer wavelengths spectra from the $^5D_0$ levels are present due to $^5D_1 \rightarrow ^5D_0$ relaxation processes. Figure 2 shows the fluorescence from these seven pumping schemes. The arrow in each spectrum shows the excitation wavelength, and comparison of the seven spectra aids in site determination, with association of each spectral line to a transition to the $^7F_{1,2}$ manifolds. Figure 3 extends the spectra of Figs. 2(a) and 2(b) to complete identification of transitions to the $^7F_2$ levels. Table III shows the identified transitions and permits site determination of these levels of the $^5D_1$ manifold.

Table IV lists the fluorescence ($^5D_2 \rightarrow ^7F_{1,2}$) from excitation to two Stark levels of $^5D_2$ at 21 332 and 21 346 cm^{-1}. These two sites correspond to the lowest and the third-lowest Stark levels. Associa-

TABLE IV. Fluorescence spectra from selective site excitation of two energy levels of the $^5D_2$ manifold at 21 332 and 21 346 cm^{-1}. See Fig. 3.

			ΔE (cm^{-1})		
Transition	λ (Å)	E (cm^{-1})	21 332	21 335	21 346
$^7F_0 \rightarrow {}^5D_2$	4683.5	21 346			
$^7F_0 \rightarrow {}^5D_2$	4686.5	21 332			
$^5D_2 \rightarrow {}^7F_1$	4743.5	21 075	257		
	4749.0	21 051			
	4757.0	21 016			
	4761.0	20 998		337	
	4764.5	20 983		352	
	4768.0	20 967		368	
	4776.0	20 932	400		
	4781.0	20 910	422		
$^5D_2 \rightarrow {}^7F_2$	4858.5	20 577			
	4878.0	20 494			
	4891.0	20 440		895	
	4897.5	20 413	919		
	4901.0	20 398	934		
	4913.5	20 346		989	
	4945.0	20 217			
	4949.0	20 200	1132		
	4951.0	20 192		1143	
	4956.5	20 170			
	4962.0	20 147		1188	
	4971.5	20 109			
	4977.0	20 087			
	4989.5	20 036	1296	1248	
	4995.0	20 014			
	5005.0	19 974			

tion of the observed transitions with the $^7F_{1,2}$ levels implies that the lowest level and its neighbor 3.0 cm^{-1} higher are well represented. However, the complexity of the observed spectra did not permit identification of the 21 346-cm^{-1} level.

Table V summarizes the results derivable from our data. The three distinct crystallographic sites have been labeled *A*, *B*, and *C*. The $^7F_1$ levels were completely identified. For $^7F_{2,3,4}$, some levels are missing. It is expected that many levels were not observed because of their near coincidence in wavelength with more intense transitions or in some cases because these transitions were too weak to detect. The data for $^7F_{5,6}$ was incomplete and therefore not included in this table. The $^5D_0$ and $^5D_1$ manifolds were nearly all identified, but the $^5D_2$ has only two levels labeled.

Several lifetime measurements of fluorescent transitions were made at 80 K. Table VI summarizes these data. From the relative intensities of fluorescence from *A*- and *C*-site excitation it can be concluded that the *A* site is dominant. Calculations of the predicted transition probabilities for the monoclinic lattice have not been performed. Gashurov[6] has made these determinations for hexagonal (D_{3h},C_{3h}) and tetragonal (D_{2d},S_4) sites. Continuation of this work to monoclinic sites will allow comparisons between the predicted and the observed lifetime. Differences between these two values gives insight into the competing nonradiative processes.

TABLE V. Tentative site assignments of the $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^5D_0$, $^5D_1$, and $^5D_2$ manifolds as interpreted from selective-site-excited fluorescence spectra.

Manifold	Site *A*	*B*	*C*
$^7F_1$	150	257	335
	350	401	354
	655	422	366
$^7F_2$	860	918	890
	1069	933	985
	1254	1134	1142
	1357	1325	1194
		1374	1248
$^7F_3$	1819	1838	1867
	1848	1879	1897
	1876	1889	1927
	1989	1939	1946
	2133	1971	
	2240	2064	
$^7F_4$	2750	2634	2566
	2851	2780	2768
	3176	2790	2819
	3268	2813	2886
	3283	2947	2930
		3015	3050
		3044	
		3087	
$^5D_0$	172 81	171 71	171 65
$^5D_1$	189 79	189 00	189 18
	190 24	189 34	
	190 86	189 42	
$^5D_2$		213 32	213 35

TABLE VI. Fluorescent lifetimes of Eu^{3+}:Gd_2O_3 at 80 K.

Transition	Wavelength λ (Å)	Fluorescent lifetime t (msec)
$^5D_0 \rightarrow {}^7F_1(A)$	6013.5	1.38
$^5D_0 \rightarrow {}^7F_2(A)$	6088.0	1.36
$^5D_0 \rightarrow {}^7F_1(C)$	5940.5	0.78
$^5D_0 \rightarrow {}^7F_2(C)$	6143.0	0.78

CONCLUSIONS

The partial determination of the crystal-field-splitting—induced energy-level scheme of the ^5D_J and ^7F_J manifolds should provide valuable comparison to theoretical crystal-field-splitting calculations of our colleagues. This technique was shown as a valuable tool in isolation of specific transitions. In crystals where the number of possible transitions becomes immense, with the relaxation and transfer mechanism contributing, this technique becomes invaluable.

To summarize, the investigations conducted on Eu^{3+}:Gd_2O_3 have identified energy levels of the trivalent europium in a monoclinic lattice not previously reported. The site assignment for the monoclinic host lattice constitutes the real success of our technique. Future studies should lend insight into the energy-transfer mechanisms not only from level to level but also from site to site. The reported fluorescent lifetime measurements show that there is a definite difference in transition probabilities from the different sites.

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