PHYSICAL REVIEW B VOLUME 8, NUMBER 11 1 DECEMBER 1973

Excitation of uv Fluorescence in LaF_3 Doped with Trivalent Cerium and Praseodymium*

L. R. Elias†, Wm. S. Heaps, and W. M. Yen

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

(Received 18 June 1973)

We have investigated the excitation of uv and visible fluorescences in LaF_3:Ce^{3+} and LaF_3:Pr^{3+} pumped through the 5*d* and 6*s* bands of the impurity ion. We have also investigated the pumping bands in absorption. Several Stark components of the 5*d* bands of Ce^{3+} and of Pr^{3+} in LaF_3 have been identified. We report uv and visible emissions originating from the $^1S_0$ state of the Pr^{3+} ion at 2500, 2700, and 4000 Å and a broad-band fluorescence (2700–4500 Å) in Ce^{3+} with bandwidth dependent on doping. Using the Judd-Ofelt theory we have calculated the line strengths and transition probabilities for the $^1S_0$ emissions, obtaining a lifetime for that state of 3.6 μsec. Measurement of the lifetime yielded a value of 720 nsec. The lifetime for the cerium emissions was found to be 20 nsec. The threshold for stimulated emission in the transitions of LaF_3:Pr^{3+} has been calculated and the possibility of uv lasing is discussed.

I. INTRODUCTION

The optical properties of trivalent rare-earth (4*f*) ions doped into a variety of host lattices have been extensively studied and the general features of their spectra are now well understood. The majority of the transitions that have been studied occur between Stark manifolds belonging to the same $4f^n$ electronic configuration and fall in the infrared and visible portions of the spectrum. In most cases the strong ultraviolet (uv) absorption of the host-lattice materials has limited the uv spectral study of the rare-earth ions. Such studies are now possible using the intense uv radiation of synchrotron-storage-ring sources.

We present in this paper results of absorption and fluorescence studies of LaF_3: Pr^{3+}, LaF_3: Ce^{3+}, and CeF_3 conducted in the 1200–4000-Å spectral range. We report the existence of sharp-line fluorescences in LaF_3: Pr^{3+} at 2500, 2700, and 4000 Å originating from the $^1S_0$ state. Selective excitation spectra of these fluorescences indicate that the pumping bands occur in the 1200–2100-Å region and correspond to interconfigurational transitions of the impurity ion involving the promotion of one of the two 4*f* electrons to either the 5*d* or 6*s* bands. We also present the absorption spectrum of LaF_3: Pr^{3+} in this region and show that the observed absorption bands correspond to these pumping bands. We have calculated the line strengths and transition probabilities for transitions from the $^1S_0$ state. A value of 3.6 μsec for the fluorescent lifetime is obtained. This compares to a measured value of 720 nsec.

A broad-band fluorescence in LaF_3: Ce^{3+} and CeF_3 in the region 2700–4500 Å is observed. This fluorescence corresponds to transitions originating from the 5*d* states of Ce^{3+} and terminating on the 4*f* states. The temperature and concentration dependences of this fluorescence are discussed. The absorption spectrum of LaF_3: Ce^{3+} is investigated and four Stark components of the 5*d* bands lying in the range 2000–2700 Å are identified. We have measured the lifetime of the cerium fluorescence obtaining a value of 20 nsec.

II. EXPERIMENTAL DETAILS

The absorption spectra of Pr^{3+} and Ce^{3+} ions doped into LaF_3 were obtained utilizing uv synchrotron radiation from the 240-MeV electron-storage-ring facility of the University of Wisconsin Physical Science Laboratories. Light from the storage ring was passed through a $\frac{1}{2}$-m McPherson vacuum monochromator with scanning capabilities between 0 and 3000 Å. A 1-mm-thick LiF filter eliminated unwanted second-order radiation and provided a normalization intensity for the absorption spectra in the region 1100–2000 Å. For normalization at longer wavelengths a suprasil-quartz filter was used.

The samples consisted of disk-shaped crystals of LaF_3 10 mm diameter × 1 mm thick, doped with various concentrations of Pr^{3+} and Ce^{3+}. The *c* axes of the crystals were oriented parallel to the faces of the disks. The samples were mounted with GE-7031 varnish to a cold-finger tip in thermal contact with a liquid-nitrogen or liquid-helium reservoir. The ultimate pressure in the monochromator and sample chamber was 10^{-7} Torr.

The uv light transmitted by the sample was converted to 4000 Å by a layer of sodium salicylate deposited on a quartz window and detected by an EMI 9558Q photomultiplier. Transmission data were digitized and stored in the first half of the memory of a Nuclear Data ND800 Enhancetron. Simultaneously, the changing electron-beam current was monitored and stored in the second half of the Enhancetron memory. This permitted point-by-point normalization of the transmitted uv light with respect to the time-decaying incident intensity.

Ultraviolet and visible fluorescences were monitored with a $\frac{1}{4}$-m Jarrell-Ash monochromator with grating blazed at 3000 Å, located at a right angle to the excitation. Excitation spectra were obtained by scanning the $\frac{1}{2}$-m McPherson while monitoring the intensity of one of the observed fluorescences with the Jarrell-Ash or with narrow-band filters, again at a right angle to the exciting beam. Both absorption spectra and the selective excitation spectra were stored permanently in punched paper tape for subsequent digital processing as well as in analog form with a Hewlett-Packard X-Y recorder.

The lifetime measurement on praseodymium was made with the same $\frac{1}{4}$-m monochromator and photomultiplier, but the fluorescence was produced with a high-pressure N_2 flash lamp.[1] The decaying signal was monitored with a photon counting apparatus built in this laboratory. Photon pulses from the PM tube were amplified and sent to a discriminator coupled to a one-shot multivibrator. This generated pulses of uniform height and duration. From the one shot the pulses went to our analyzer. The analyzer consisted of 10 sixteen-bit binary counters, which could be sequentially addressed by clock pulses from a crystal-controlled oscillator. The chan nel widths (counter—on time) could be varied from 62.5 nsec to 5 sec. The count could be delayed by as much as 63 channel widths before counting commenced. For our measurement 500-nsec channels were used with one-channel delay. The flash-lamp frequency was 1 kHz. The cerium lifetime was measured utilizing the synchrotron as a very fast pulsed source. Details of the measurement technique will appear elsewhere.[2]

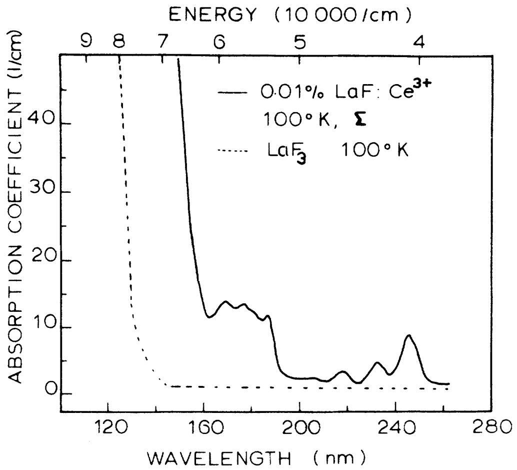

FIG. 1. Absorption spectrum of $LaF_3:Ce^{3+}$ (0.1 at.%). The dashed line represents the approximate behavior of the absorption coefficient of LaF_3.

III. RESULTS

A. Cerium

The free-ion spectrum of trivalent cerium has been studied in detail by Lang[3] in 1936. This is the simplest ion of the trivalent rare-earth series having only a single $4f$ electron. Spin-orbit interaction splits the ground configuration with a $^2F_{7/2}$ level 2253 cm^{-1} above the $^2F_{5/2}$ ground level. The first-excited configuration consists of an electron in the $5d$ shell. Spin-orbit interaction splits this configuration into $^2D_{3/2}$ and $^2D_{5/2}$ levels, which lie at 49 737 and 52 226 cm^{-1}, respectively, above the ground state. The $6s$ state has been located at 86 600 cm^{-1}. We have investigated the absorption spectrum for Ce^{3+} ions doped into single crystals of LaF_3 at several concentrations (see Fig. 1). The band edge of LaF_3 has been located at about 1250 Å.[4] The features peaking at about 1800 Å belong to trace impurities of Pr^{3+} and appeared in all our absorption traces. The onset of absorption at 1600 Å arises from the $6s$ band of Ce^{3+} as well as charge-transfer mechanisms. At 0.01-at.% concentration, the large oscillator strength of this band prevented the determination of the regions of maximum absorption. However, Ce^{3+} appeared as a trace impurity at lower concentrations in other crystals of LaF_3. Here the peak of the absorption was observed to occur at about 68 000 cm^{-1}. The structures occurring in the region 2000–2700 Å belong to the $5d$ bands of Ce^{3+}. We have identified four Stark components peaking at 40 600, 43 800, 46 000, and 48 500 cm^{-1}. At higher concentrations of Ce^{3+} the $5d$ and $6s$ bands broaden and increase in strength. At 100-at.% concentration (CeF_3) the $5d$ and $6s$ bands overlap at room temperature, but below 150 °K a transmission region between the bands emerges. This peculiar behavior allows the system to be used as a variable-bandwidth uv filter centered at 1760 Å. A discussion of this filter has been presented elsewhere.[5]

The fluorescence spectra of the Ce^{3+} ion were taken at four different doping levels (see Fig. 2) and at several temperatures (see Fig. 3). We identify two broad bands centered at 2850 and 3050 Å in the low-doping samples. In the higher-concentration samples (5 and 100 at.%) the two peaks become less distinct and shift to lower energy. At lower temperatures the peaks are more easily resolved. Traces taken with broad-band excitation (undispersed synchrotron radiation) are qualitatively similar. The lifetime measurement for these emissions was made on the 5-at.%-doped sample at 3050 Å at room and liquid-nitrogen temperatures. The emissions arise from allowed electric dipole transitions: hence the very short lifetime of 20 nsec was not surprising. No temperature dependence for the lifetime was observed.

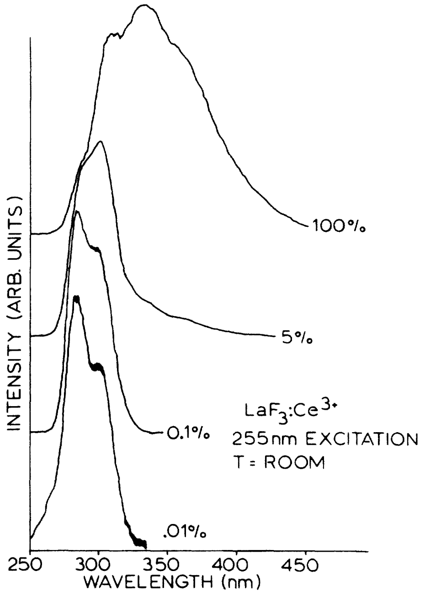

FIG. 2. $5d \rightarrow 4f$ fluorescence of LaF$_3$: Ce^{3+} as a function of impurity doping concentration at room temperature. Excitation was at 2500 Å. The traces are not to the same scale. All concentrations are in at.%.

B. Praseodymium

The trivalent free-ion spectrum of Pr has been studied in detail by Sugar[6] and Crosswhite.[7] The $4f5d$ configuration lies between 61 170 and 78 776 cm^{-1}. The $4f6s$ configuration has been located at about 100 000 cm^{-1}. The $4f^2$ configuration of Pr^{3+} has 13 levels, all of which have been observed in absorption, fluorescence, or both. Wong[8] has observed most of the absorptions and emissions of Pr^{3+} doped into various hosts—including LaF$_3$. However, the position of $^1S_0$ has been in some dispute. Carnall[9] has made a careful determination of the position of the $^1S_0$ state in LaF$_3$ and has placed it at 46 896 cm^{-1} above the ground state. In absorption we have located three Stark components of the 5d band in LaF$_3$: Pr^{3+} at 53 200, 56 000, and 59 000 cm^{-1} (see Fig. 4). The 6s band was obscured by the onset of the LaF$_3$ band edge and was

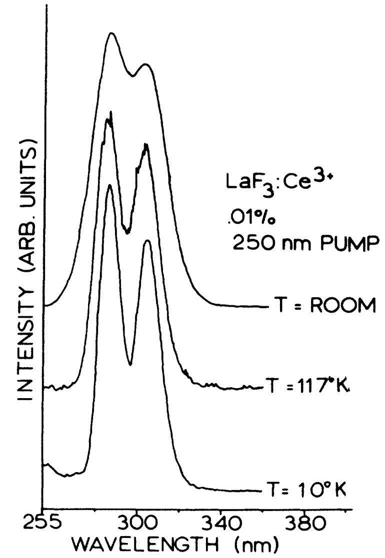

FIG. 3. $5d \rightarrow 4f$ fluorescence of LaF$_3$: Ce^{3+} as a function of temperature for 0.01-at.% concentration sample. Excitation was at 2550 Å.

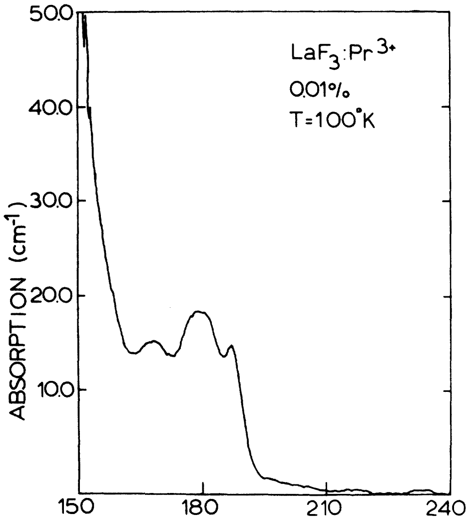

FIG. 4. Absorption spectrum of LaF$_3$: Pr^{3+} (0.01 at.%). The temperature was 100 °K and the polarization was π.

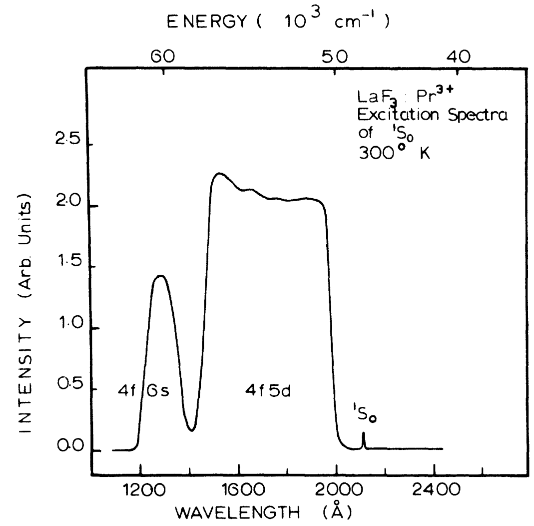

FIG. 5. Selective excitation spectrum of uv and visible fluorescences in LaF$_3$: Pr^{3+}. The 6S peak position may be distorted by LaF$_3$ absorption.

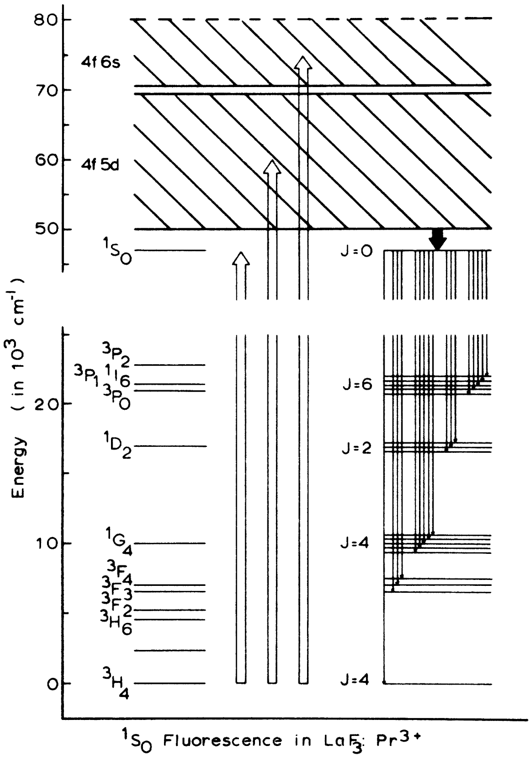

FIG. 6. The transitions involved in Pr^{3+} fluorescences.

not observed in absorption.

We have obtained the excitation spectra for the $LaF_3:Pr^{3+}$ fluorescences (see Fig. 5). Three distinct pumping bands are evident. The first peak, at about 2100 Å, corresponds to the direct excitation of the $^1S_0$ state. The energy of this transition is in good agreement with the value measured in absorption by Carnall. The pumping band in the region 1400–2000 Å has been identified as transitions from the ground state to Stark components of the $4f\,5d$ states. The region below 1400 Å has been assigned to the onset of absorption by the 6*s* band of Pr^{3+}. As previously mentioned, this band was not observed in absorption. Hence, through selective excitation we are able to extend our observations deeper into the band edge of the host lattice. Also, the effect of impurities is minimized, since

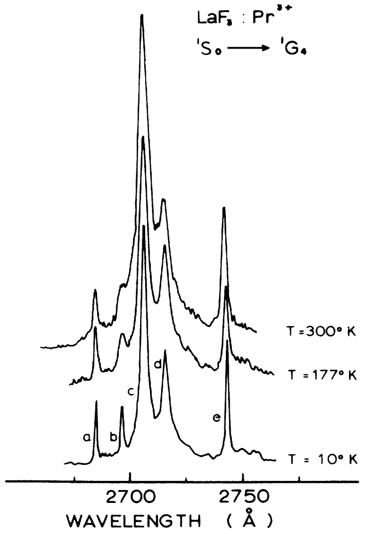

FIG. 8. $^1S_0 \rightarrow {}^1G_4$ fluorescence of $LaF_3:Pr^{3+}$ as a function of temperature. Excitation was at 1850 Å.

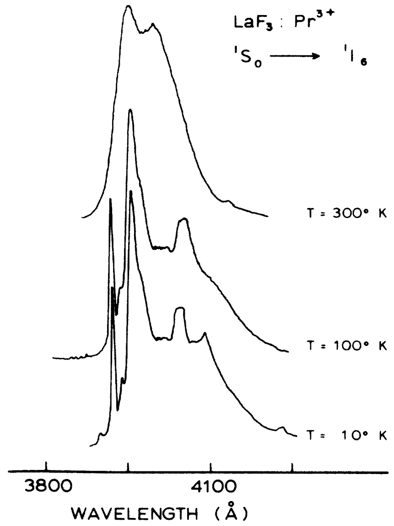

FIG. 7. $^1S_0 \rightarrow {}^1I_6$ fluorescence of $LaF_3:Pr^{3+}$ as a function of temperature. Excitation was at 1850 Å.

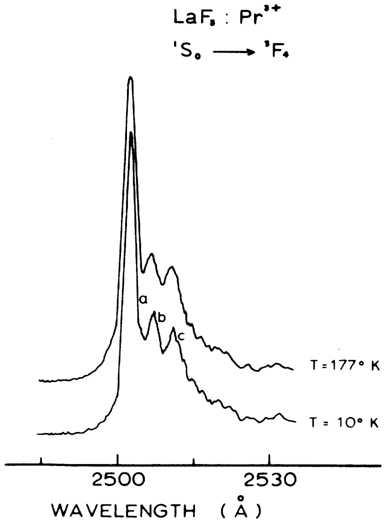

FIG. 9. $^1S_0 \rightarrow {}^3F_4$ fluorescence of $LaF_3:Pr^{3+}$ as a function of temperature. Excitation was at 1850 Å.

we are monitoring the fluorescence corresponding to unique radiative transitions in the Pr^{3+} ion.

Figure 6 gives the transitions involved in uv and visible emissions in $LaF_3:Pr^{3+}$. Figures 7, 8, and 9 show the fluorescences from $^1S_0$ to the $^1I_6$, $^1G_4$, and $^3F_4$ states of the ground configuration of Pr^{3+}, respectively. We have also observed weaker emissions to the $^1D_2$ and $^3H_4$ states at 3350 and 2150 Å, respectively. The energies and wavelengths of the strongest lines have been tabulated on Table I.

IV. INTERPRETATION

A. Cerium

The energy levels of the ground configurations of the rare-earth ions in crystals are normally treated in the weak-field approximation. The approximation is justified in that the $4f$ orbitals lie well within the $5s$, $5p$, and $6s$ shells of the atom and are prevented from interacting strongly with the host-lattice ions. Typical crystal-field splittings for lanthanide ions are ~ 100 cm^{-1}, which are small compared to the spin-orbit interactions (~ 1000 cm^{-1}) and much smaller than the electronic repulsion term splittings (~ 10 000 cm^{-1}). This situation is understandably changed when we deal with configurations involving $5d$ or $6s$ electrons, which have orbitals of considerably larger radii. Our data indicate that for Ce^{3+} the LaF_3 crystal field depresses the $6s$ states by about 18 000 cm^{-1} and the $5d$ states by about 10 000 cm^{-1}. The crystal-field parameters of LaF_3 are not known, which makes it difficult to estimate the crystal-field contribution to the $5d$ splitting. The site symmetry is very low, C_2,[10] which should split the $5d$ states into five Kramers degenerate states. Our data for Ce^{3+} show only four peaks; the fifth is either unresolved or obscured by the onset of the Pr^{3+} impurity absorption. The fluorescence spectra for Ce^{3+} show two peaks, which we identify as transitions from the bottom of the $5d$ band to the two components of the $4f$ configuration. For the low-concentration samples the Stokes shift is about 4100 cm^{-1}. The more-strongly-doped samples are broader and show a larger Stokes shift, 9800 cm^{-1} for the CeF_3. This is consistent with a larger radius for the $5d$ orbital in CeF_3 than in LaF_3.

TABLE I. Strongest emissions from the $^1S_0$ state of $LaF_3:Pr^{3+}$ (letters refer to illustrations).

$L'S'J'$		Wavelength (Å)	Energy (cm^{-1})
$^1I_6$	a	3892	25 693
	b	3900	25 641
	c	3939	25 387
	d	3988	25 075
$^1G_4$	a	2686	37 235
	b	2697	37 074
	c	2707	36 944
	d	2716	36 823
	e	2741	36 487
$^3F_4$	a	2503	39 957
	b	2507	39 893
	c	2508	39 882

The lifetime of the Ce^{3+} fluorescence is 20 nsec. This is much shorter than the lifetimes for rare-earth fluorescences occurring within $4f^n$ configurations, because the Ce^{3+} transition is an allowed electric dipole transition which is not dependent upon crystal-field mixing of states for its dipole nature. Although the ion-lattice coupling is greater for a $5d$ configuration than for a $4f$ configuration, nonradiative decay involving multiphonon emissions is impossible because of the great separation between the $5d$ band and the nearest $4f$ level.[11] Therefore no temperature dependence for the lifetime should be expected.

B. Praseodymium

The same difficulties apply to the interpretation of the $5d$ bands of Pr^{3+} as to Ce^{3+}. This case is further complicated by the presence of the Coulomb interaction between the $4f$ and the $5d$ electrons. We have identified the absorption and selective excitation peaks in the 1400–2000-Å region as Stark components of the $5d$ band. The peak at 1250 Å, seen only in the selective excitation spectrum, involves transitions to the $6s$ band possibly altered by charge-transfer mechanisms. The strong Ce^{3+} impurity absorption, beginning at 1600 Å, prevented location of other Pr^{3+} levels.

No broad-band interconfigurational fluorescence was observed in Pr^{3+} because of the proximity of the $^1S_0$ state of the $4f^2$ configuration to the $4f\,5d$ band (3000 cm^{-1}). The large separation between the $^1S_0$ and the next-lower state of the $4f^2$ configuration (24 000 cm^{-1}) prevents relaxation by multiphonon emission. Therefore the $^1S_0$ is the origin of several narrow uv and visible fluorescences which can be pumped by the strong $5d$ and $6s$ absorption bands. We have used the Judd-Ofelt[12,13] theory to calculate the radiative transition probabilities from the $^1S_0$ to all other states of the ground configuration of $LaF_3:Pr^{3+}$. According to this theory the line strength S for electric dipole transitions between SLJ states is expressed as follows:

$$S=e^2\sum_{\lambda=2,4,6}\Omega_\lambda$$

$$\times\,|\langle 4f^n[S,L]J\,||U^{(\lambda)}||\,4f^n[S',L']J'\rangle^2 .$$

The intensity parameters Ω_λ have been measured by Krupke.[14] Weber[15] has calculated the matrix elements of the tensor operator $U^{(\lambda)}$. The index of refraction of LaF_3, needed to calculate life-

TABLE II. Transition probabilities of electric dipole transitions originating from the $^1S_0$ state of $LaF_3:Pr^{3+}$.

$L'S'J'$	ν (cm^{-1})	λ (Å)	n	χ	S	A (sec^{-1})
$^3H_4$	46 786	2137	1.67	4.25	0.0113	353 9
$^3H_5$	44 623	2241	1.67	4.25	0	0
$^3H_6$	42 499	2353	1.67	4.25	0.0015	337
$^3F_2$	41 771	2394	1.66	4.17	0.495×10^{-3}	108
$^3F_3$	40 418	2474	1.66	4.17	0	0
$^3F_4$	39 955	2503	1.66	4.17	0.224	427 29
$^1G_4$	36 985	2704	1.64	4.00	0.773	112 612
$^1D_2$	29 939	3340	1.62	3.84	0.060	445 1
$^3P_0$	26 059	3837	1.62	3.84	0	0
$^1I_6$	25 472	3926	1.61	3.77	2.71	119 220
$^3P_1$	25 472	3926	1.61	3.77	0	0
$^3P_2$	24 240	4125	1.61	3.77	0.0076	238

Lifetime of the $^1S_0$ state of LaF_3 doped with $Pr^{3+} = 3.6$ μsec.

times from line strengths, was obtained from Hass.[16] We show in Table II the results of our calculations.

Our observations of the relative intensities of the various fluorescence agree well with the calculations. However, our calculated value of the radiative lifetime of 3.6 μsec for the $^1S_0$ state in $LaF_3:Pr^{3+}$ is five times the measured value of 721 ± 10 nsec. This discrepancy is not too surprising when one examines the approximations of the Judd-Ofelt theory. The theory assumes that the perturbing configuration is completely degenerate and has an energy large compared to that of the $4f^n$ term under consideration. Examination of the excitation spectrum shows that these approximations are particularly bad for the case of the $^1S_0$ state perturbed by the $4f\,5d$ configuration. The good agreement observed for the relative line intensities is not surprising, because the $5d$ admixing into the $^1S_0$ state affects all the lines equally.

Although the Pr^{3+} fluorescences have high energy and are short lived, they may still be useful in producing stimulated emission in the uv. This is due to the following characteristics of these lines. First, the pumping mechanism consists of a strong broad-band absorption, which rapidly populates the upper ($^1S_0$) level of the laser. Second, the lines are rather narrow even at room temperature (95 cm^{-1} at 2710 Å, 55 cm^{-1} at 2500 Å). A calculation of thresholds for four-levels operation of such a system yields an energy of 8.13×10^{-2} J/cm^3 for the 2710-Å line, 4.03×10^{-2} J/cm^3 for the 4000-Å line, and 1.0×10^{-1} J/cm^3 for the line at 2500 Å. These values were calculated for a rod 3.6 cm long with 2% cavity losses. The quantum efficiencies were estimated for each line and ranged from 7% to 10%. Because the lifetime is so short, the energy must be delivered in a very short time—perhaps on the order of 250 nsec. For flash-lamp pumping this means that the lamp must deliver power on the order of 0.5 MW in the absorption band. We believe such powers are attainable, particularly through the use of double pulsed flash lamps as described by Emmett and Schawlow.[17] Such lamps have two advantages for pumping the Pr^{3+} laser. They produced the very short pulses required and they produce a great deal of light in the uv spectral range.

V. CONCLUSION

The results presented here demonstrate the usefulness of synchrotron radiation as a source of uv for spectroscopic studies. In the rare earths this radiation should be of use in finding the $5d$ and $6s$ bands in a variety of host materials. The short light pulse is useful for measuring very short lifetimes characteristic of fluorescences from these states. We intend to extend these measurements to other rare-earth fluorescences in the near future. It is hoped that this research will lead to increased understanding of the crystal-field interaction with higher configurations of the rare earths. We also look forward to the development of new solid-state lasers operating in the ultraviolet.

ACKNOWLEDGMENTS

We would like to thank T. K. Bergstresser for many helpful discussions. We also thank the staff of the Physical Science Laboratory and particularly Roger Otte for their aid and advice.

[*] Work supported by the U. S. Air Force Office of Scientific Research under Grant No. AFOSR-70-1953, Project No. 9763. Physical Sciences Laboratory work supported by the AFOSR under Contract No. F44620-70-C-0029.

[†] Present address: Dept. of Physics, Stanford University, Stanford, Calif. 94305.

[1] D. H. McMahan, A. R. Franklin, and H. R. Carleton, Rev. Sci. Instrum. **137**, 1142 (1966).

[2] Wm. S. Heaps, D. S. Hamilton, and W. M. Yen (unpublished).

[3] R. L. Lang, Can. J. Res. A **14**, 127 (1936).

[4] W. R. Hunter and S. A. Malo, J. Phys. Chem. Solids **30**, 2739 (1969).

[5] L. Elias, W. M. Yen, and R. Flach, Appl. Opt. **12**, 138 (1973).

[6] J. Sugar, J. Opt. Soc. Am. **55**, 1058 (1965).

[7] H. M. Crosswhite, A. H. Dieke, and W. J. Carter, J. Chem. Phys. **43**, 2047 (1965).

[8] E. Y. Wong, O. Staefsudd, and D. Johnson, J. Chem. Phys. **51**, 2587 (1969).

[9] W. T. Carnall, P. R. Fields, and R. Sarup, J. Chem. Phys. **51**, 2587 (1969).

[10] A. Zalkin, D. H. Templeton, and T. E. Hopkins, Inorg. Chem. **5**, 1466 (1966).

[11] M. J. Weber, Solid State Commun. **12**, 741 (1973).

[12] B. R. Judd, Phys. Rev. **127**, 750 (1962).

[13] G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

[14] W. F. Krupke, Phys. Rev. **145**, 325 (1966).

[15] M. J. Weber, J. Chem. Phys. **48**, 4774 (1968).

[16] G. Hass, J. B. Ramsey, and R. Thun, J. Opt. Soc. Am. **49**, 120 (1959).

[17] J. L. Emmett and A. L. Schawlow, Appl. Phys. Lett. **2**, 204 (1963).