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FLUORESCENCE AND LIFETIMES OF EXCITED STATES OF Pr^{+3} IN PHOSPHOROUS OXYCHLORIDE

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Depopulation of excited states of praseodymium in aprotic solvent phosphorous oxychloride was analysed using the results of fluorescence and lifetime measurements. The presented results and previously reported data indicate that the coupling between the fluorescing ion and the solvent vibrations, leading to nonradiative relaxations, is similar to the ion-phonon coupling in the solid state phosphate hosts. Attempts to calculate the quantum efficiencies of fluorescing states within the framework of the Judd-Ofelt theory were however unsuccessful.

1. Introduction

The spectroscopic properties of praseodymium ions in inorganic matrices are certainly less investigated than other rare earth ions. This is due mainly to the difficulties in interpretation of the experimental data in the framework of the existing theories. Reported attempts to analyse the absorption spectra of Pr^{+3} in various matrices, using the Judd-Ofelt theory, yielded rather unsatisfactory results. In most cases there was no agreement between the calculated and measured oscillator strengths [1, 2], frequently, a negative value of the Ω_2 parameter was obtained, which is incompatible with the Judd-Ofelt theory. In addition, the calculated radiative lifetimes of excited states were not in agreement with experiment [3, 4]. All the above listed discrepancies are rather discouraging and prevent the extensive study of praseodymium doped materials, which are nevertheless of practical interest. Laser action in $PrCl_3$ and in PrB_3 was observed [5], also very recently lasing in PrP_5O_{14} was reported [6]. Quantum yields exceeding unity in the conversion of UV-excitation into visible emission in YF_3Pr^{+3} [7], prove that the praseodymium doped materials are also attractive for application as the UV-to-visible light converters.

In this paper we present the results of investigation of electronic transitions within the $4f^2$ configuration of Pr^{+3} in solution. We have chosen the phosphorous oxychloride as a solvent for several reasons: first, the lack of high energy vibrational modes of the sol-

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vent makes possible measurements of fluorescence, which is absent in a proton containing hosts; secondly, owing to the chemical composition and properties, the solvent is a liquid counterpart of the solid state phosphate hosts: crystals and glasses. We believe that the experimental results presented in this work will, together with other published data, contribute to the elucidation of the exceptional behaviour of praseodymium.

2. *Experimental*

The solutions were obtained by dissolving the anhydrous praseodymium trifluoroacetate in an anhydrous mixture $POCl_3 : ZrCl_4$. The details of preparation were essentially the same as in our previous works [8, 9]. The absorption spectra were measured with a Cary 14 spectrophotometer and the fluorescence spectra were measured with a spectrophotometer constructed in our laboratory using a Carl Zeiss GDM 1000 grating monochromator and a phase sensitive detection system. The fluorescence was excited by radiation of a XBO 1600 high pressure xenon lamp filtered by a prism monochromator and detected by a cooled photomultiplier with S-1 response. In lifetime measurements a pulsed tunable dye laser was used for selective excitation into the desired energy levels. Short exciting pulses (10 ns full width) and fast detection system TRW Decay Time Fluorometer Model 75A made measurements of lifetimes as short as 100 ns possible. All measurements were made at room temperature.

3. *Results*

3.1. Deexcitation of excited levels of Pr^{+3}

Fluorescence was excited by optical pumping into the $^3P_2$, $^1I_6$, $^3P_1$ group of levels lying at about $21–22 \cdot 10^3$ cm^{-1} (see Fig. 1). Strong absorption bands corresponding to transitions to these levels assure efficient excitation. The $^3P_2$, $^1I_6$ and $^3P_1$ levels are connected with the $^3P_0$ level by fast nonradiative transitions the rates of which are certainly higher than about 10^7 s^{-1} (beyond the upper speed limit of our detection system) as determined by measurements of a rising portion of transient fluorescence originating from the $^3P_0$ level when exciting to the $^3P_2$ level. As a consequence no fluorescence originating from these levels was observed, except for traces of weak emission attributed to transitions from thermalized lowest components of the $^3P_1$ level. This emission gives the measurable background seen in the fluorescence spectrum presented in Fig. 2.

The $^3P_0$ level is spaced from the next lower lying level $^1D_2$ by about 3500 cm^{-1}, whereas the highest energy of P–O stretching vibrations is equal to 1100 cm^{-1}. The experimental works on radiative and nonradiative transitions of rare earth ions in the phosphorous compounds: phosphate glasses [10], pentaphosphate crystals [11] and also phosphorous oxychloride [12], have shown that the rates of multiphonon relaxations of excited levels are negligible for energy gaps ranging from 5000–6000 cm^{-1}, but they are of the order of 10^5–10^6 s^{-1} for energy gaps equal to 3000–3500 cm^{-1}. Thus the nonradiative relaxations are expected to play an important role in the depopulation of the $^3P_0$ level. The calculation of quantum efficiency of the $^3P_0$ level is quite complicated. However,

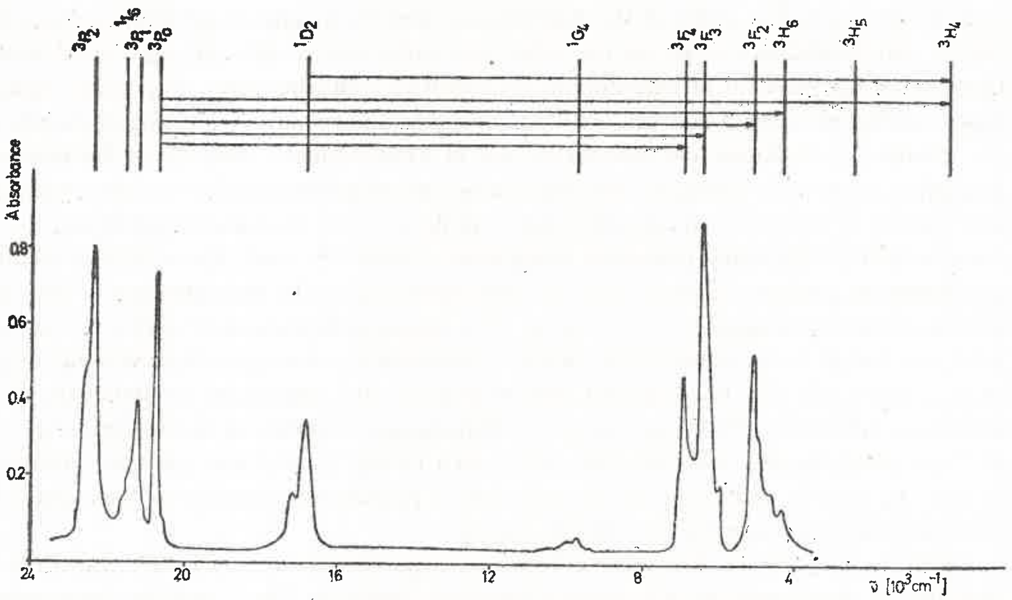

Fig. 1. Room temperature absorption spectrum of Pr^{+3} in phosphorous oxychloride. Praseodymium concentration was 0.3 mole/l. Arrows indicate the observed fluorescence transitions

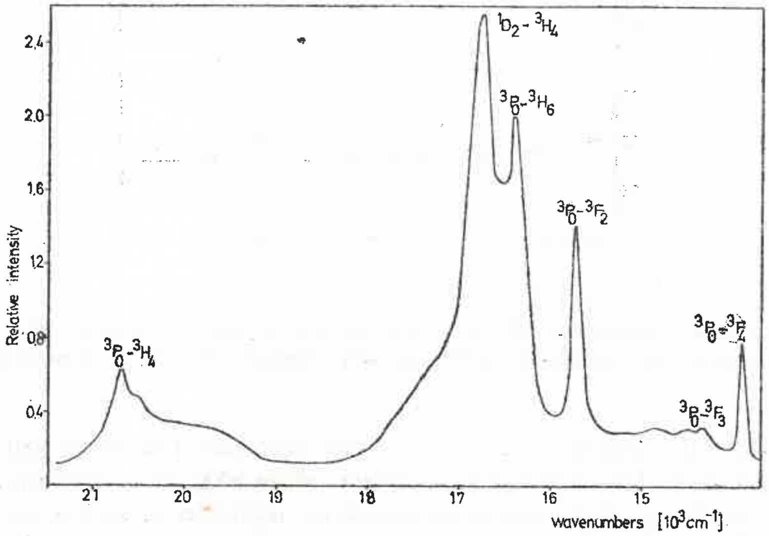

Fig. 2. Room temperature fluorescence spectrum of Pr^{+3} in phosphorous oxychloride

even if we assume the order of the nonradiative transitions rate as determined from the energy gap dependence observed for other rare earth ions in phosphorous based hosts, there exists the problem of determining the radiative transition rates. The usual method based on the relationship between oscillator strengths and radiative transition probabilities for resonance transitions and subsequent use of experimentally determined fluorescence branching ratios is not applicable here because of unresolved properly fluorescence spectrum and because of difficulties in extracting the weak fluorescence background attributed to the transitions from thermally populated components of the $^3P_1$ level. The results of lifetime measurements indicate however that the dominant role in the depopulation of the $^3P_0$ level is played by nonradiative relaxations. The measured fluorescence lifetime of the $^3P_0$ level was found to be independent on Pr^{+3} concentration and the obtained value equal to 1 μs conforms with the expected rate of nonradiative relaxations involving the P–O stretching vibrations. The dependences of fluorescence lifetimes of fluorescing levels of Pr^{+3} on praseodymium concentration are shown in Fig. 3. The low quantum efficiency of the $^3P_0$ level is confirmed by the presence of fluorescence originating from the $^1D_2$ level when exciting into the $^3P_1$ or $^3P_0$ levels.

The position of the fluorescence band corresponding to the $^1D_2$–$^3H_4$ transition is indicated in the composite fluorescence spectrum shown in Fig. 2 and the dependence of the fluorescence lifetime of this level on Pr^{+3} concentration is shown in Fig. 3. In contrast to the $^3P_0$ level, the decrease of lifetime with increasing praseodymium concentration was observed, indicating the presence of ion-pair processes. The energy gap between the $^1D_2$ level and the next lower lying level is equal to about 6000 cm^{-1}, hence the nonradiative relaxations involving solvent vibrations should be negligible. In such a case, the extrapolation of fluorescence lifetime to zero concentration limit, so as to minimize the ion-pair

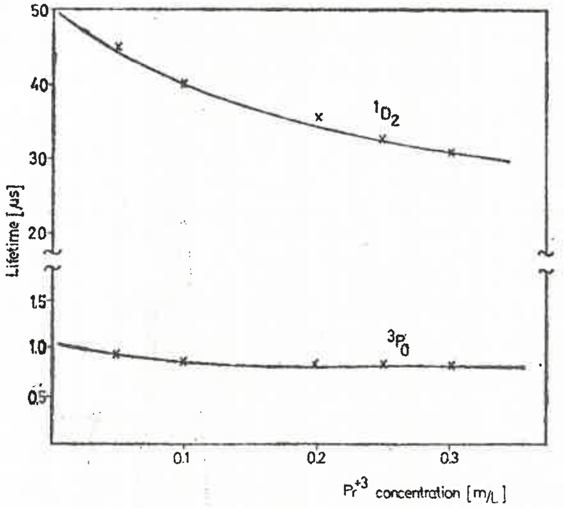

Fig. 3. Dependence of fluorescence lifetimes of the $^3P_0$ and $^1D_2$ levels on praseodymium concentration. Error associated with the determination of lifetimes was estimated to be within 5 percent of the measured value

processes should give the radiative lifetime of the level. The value so obtained is equal to 50 μs. The high quantum efficiency of the $^1D_2$ level is confirmed by lack of measurable fluorescence originating from the $^1G_4$ level, when exciting into the $^1D_2$ level.

3.2. Calculation of radiative transition probabilities

In this section we present the results of attempts to analyse the spectroscopic behaviour of Pr^{+3} in the framework of the Judd-Ofelt theory. The main aspects of the theory are presented in a variety of published works, so we limit ourselves to basic relations only.

The oscillator strength P of an electric dipole transition between the initial $\langle 4f^n[S, L]J|$ level and final $|4f^n[S', L']J'\rangle$ level of the rare earth ion is given by

$$P = \frac{8\pi^2 mc(n^2+2)^2}{3h(2J+1)\lambda 9n} \sum_t \Omega_t |\langle 4f^n[S, L]J \| U^t \| 4f^n[S', L']J'\rangle|^2, \tag{1}$$

where λ is the mean wavelength of the transition, n is the material's index of refraction at the mean wavelength of the transition, $\langle \| U^t \| \rangle$ are the doubly reduced unit tensor operators calculated in the intermediate coupling approximation. The three coefficients Ω_2, Ω_4, and Ω_6 contain implicitly the odd crystal field terms, radial integrals, and perturbation energy denominators. These quantities are regarded as the empirical parameters, which are determined by a least squares fit between the oscillator strengths measured in the absorption spectrum, and calculated using Eq. (1). Similarly, the spontaneous emission probability A for an electric dipole transition between the excited level $\langle 4f^n[S, L]J|$ and lower lying level $|4f^n[S', L']J'\rangle$ is

$$A = \frac{64\pi^4 e^2 n^2(n^2+2)^2}{3h(2J+1)\lambda^3 9n} \sum_t \Omega_t |\langle 4f^n[S, L]J \| U^t \| 4f^n[S', L']J'\rangle|^2. \tag{2}$$

The sum of the transition probabilities from the initial excited level to all lower lying levels is defined as the total radiative transition probability A_{tot} from the initial excited level. The results of calculation are presented in Table I. As can be seen, the calculation is rather rough since the exclusion of the $^3P_2$ level does not influence the value of the obtained parameters, giving only a lower RMS deviation, but even in this case the calculated values of the oscillator strengths for transitions to the $^1D_2$ and $^1G_4$ levels are seriously underestimated and the error associated with the determined Ω parameters is still high. This is due primarily to the paucity of experimental data: the absorption spectra yielded only two strong data groups, one corresponding to transitions to high energy levels assigned as the $^3P_{2,\,1,\,0}$, $^1I_6$, and the second one corresponding to low energy levels assigned as the $^3F_{4,\,3,\,2}$, $^3H_6$. The transition to the $^1G_4$ level is very weak. The absorption bands in both groups are not resolved properly and in addition the degree of J-mixing is not known. On the other hand, the Ω_2 parameter does not seem to have any meaning since only the $\langle ^3H_4 \| U^2 \| ^3F_2\rangle$ matrix element has significant value. Moreover, the calculated oscillator strengths of the $^3H_4$–$^3P_{1,\,0}$ transitions depend on the U^4 term only. The other possible

TABLE I

Calculated and experimental oscillator strengths for Pr^{+3} in phosphorous oxychloride and resulting Ω parameters

Transition	P_{exp}	a	b
		$P_{calc} \times 10^6$	P_{calc}
$^3P_2 \rightarrow {}^1H_4$	13.55	5.72	—
$^3P_1, {}^1I_6$	5.20	5.72	5.73
$^3P_0$	4.41	3.69	3.74
$^1D_2$	3.66	2.17	1.79
$^1G_4$	0.46	0.25	0.25
$^3F_4, {}^3F_3$	13.67	16.71	13.90
$^3F_2, {}^3H_6$	5.17	4.53	5.12

a

$\Omega_2 = (0.21 \pm 11.62) \cdot 10^{-20}\ \mathrm{cm}^2$
$\Omega_4 = (6.53 \pm 4.19) \cdot 10^{-20}\ \mathrm{cm}^2$ RMS $= 4.3\ 10^{-6}$
$\Omega_6 = (11.28 \pm 3.68) \cdot 10^{-20}\ \mathrm{cm}^2$

b

$\Omega_2 = (2.71 \pm 3.27) \cdot 10^{-20}\ \mathrm{cm}^2$
$\Omega_4 = (6.69 \pm 1.34) \cdot 10^{-20}\ \mathrm{cm}^2$ RMS $= 1.2\ 10^{-6}$
$\Omega_6 = (8.79 \pm 1.08) \cdot 10^{-20}\ \mathrm{cm}^2$

a — calculated including the $^3H_4$ — $^3P_2$ transition
b — calculated excluding the $^3H_4$ — $^3P_2$ transition.

reasons for so called "breakdown" of the Judd-Ofelt theory in the case of praseodymium are discussed by Peacock [13].

The calculated Ω parameters (b case in Table I) were next used to calculate the radiative transition probabilities for the two fluorescing levels $^3P_0$ and $^1D_2$

$$A(^3P_0) = (43.51\Omega_2 + 74.46\Omega_4 + 12.41\Omega_6) \cdot 10^{22} s^{-1} = 554300\ s^{-1}$$

$$A(^1D_2) = (4.97\Omega_2 + 2.96\Omega_4 + 2.52\Omega_6) \cdot 10^{22} s^{-1} = 72400\ s^{-1}$$

In the above equations all transitions to the lower lying levels are included.

Whereas the calculated value of radiative transition probability for the $^3P_0$ level is not contradictory to measured fluorescence lifetime, the value for the $^1D_2$ level is considerably higher than inverse of the measured fluorescence lifetime.

4. *Conclusions*

The use of an aprotic solvent $POCl_3$ made fluorescence and lifetimes measurements of the $^3P_0$ and $^1D_2$ levels of Pr^{+3} possible. Based on previously reported data on non-radiative relaxations of excited levels of other rare earth ions in this solvent and on those presented in this work experimental results we can estimate the quantum efficiency of the

$^1D_2$ level as being close to unity. Similarly, we can conclude that the nonradiative relaxations play a dominant role in the depopulation of the $^3P_0$ level.

The attempts to calculate the radiative transition probabilities in the framework of the Judd-Ofelt theory were however unsuccesful. Among possible reasons for the discrepancy observed, the paucity of experimental data used for the determination of the parameters seems to be most important.

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