ANALYSIS OF SPECTRAL LINE INTENSITIES OF Nd^{3+} IONS IN NEODYMIUM PENTAPHOSPHATE*

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The Judd-Ofelt Ω_λ parameters were determined from quantitative measurements of the absorption spectra intensities for NdP_5O_{14} system. Emission intensities between the $^4F_{3/2}$ and ^4IJ levels were calculated together with the radiative lifetime and fluorescence branching ratios.

Recently Auzel [1] has reported the oscillator strength measurements of Nd^{3+} in $Nd_xLa_{1-x}P_5O_{14}$ for a wide range of neodymium concentrations in order to test Danielmeyer's hypothesis [2] concerning neighbouring ion overlap in the so-called "stechiometric laser material". The main result of this work was the statement that the oscillator strengths are practically constant with respect to concentration. Unfortunately, Auzel [1] has limited his analysis only to a few observed bands. For this reason we would like to present a detailed study of the radiative transition probabilities for pure neodymium pentaphosphate (NdP_5O_{14}).

The single crystal of NdP_5O_{14} under investigation was grown by the method described by Danielmeyer [3]. The crystal has a length of 0.68 mm along the optical axis. The room temperature absorption spectra of this sample were recorded on the Cary Model 14 spectrophotometer from 3200 Å to 10 000 Å. The experimental oscillator strengths were calculated by the graphical integration method by means of the computer programme. These data were used for evaluating the Judd–Ofelt parameters [4], according to the equation

$$P = \frac{8\pi^2 mc}{3h}\chi \sum_{\lambda=2,4,6} \Omega_\lambda |\langle f^n SLJ \| U^{(\lambda)} \| f^n S'L'J' \rangle|^2 (2J+1)^{-1}, \tag{1}$$

where $\langle f^n SLJ || U^{(\lambda)} || f^n S'L'J' \rangle$ are the matrix elements of the unit tensor operator calculated for Nd^{3+} by Judd [4]. σ is the wavenumber, and χ is the Lorentz field correction for the refractivity of the medium, $\chi = n(n^2+2)^2/9$, calculated for $n = 1.62$ [5].

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The Ω_λ parameters were evaluated using the least-squares method, from the set of experimental oscillator values. These values of Ω_λ were used again for calculating the oscillator strengths (P_{cal}) and for determining the mean square error (Table I).

TABLE I

Oscillator strengths for Nd^{3+} ions in NdP_5O_{14}

$S'L'J'$	σ [cm^{-1}]	$P\times 10^6$	
		exp	calc
$^2L_{15/2}$	29429		
$^4D_{1/2}$	28777	7.53	7.94
$^2I_{11/2}$	28555		
$^4D_{5/2}$	28137		
$^4D_{3/2}$	28029		
$^2D_{5/2}$	23742	0.0612	0.0313
$^2P_{1/2}$	23255	0.387	0.378
$^4G_{11/2}$	21708		
$(^2D, ^2F)_{3/2}$	21585	2.09	0.87
$^2G_{9/2}$	21299		
$^2K_{15/2}$	20945		
$^4G_{9/2}$	19342		
$^4G_{7/2}$	19160	5.38	3.38
$^2K_{15/2}$	19000		
$^2G_{7/2}$	17461	6.48	6.62
$^4G_{5/2}$	17241		
$^2H_{11/2}$	15924	0.130	0.116
$^4F_{9/2}$	14611	0.693	0.417
$^4S_{3/2}$	13531	4.78	5.47
$^4F_{7/2}$	13378		
$^2H_{9/2}, ^4F_{5/2}$	12453	5.27	5.13
$^4F_{3/2}$	11460	2.11	1.53

rms dev. $= 6.98 \cdot 10^{-8}$

The transition probabilities for emission from the initial manifold $|S'L'J'\rangle$ to the terminal manifold $|SLJ\rangle$ is given by the expression

$$A[S'L'J'; SLJ] = \frac{64\pi^4 e^2}{3h(2J'+1)} \lambda^{-3} \chi \sum_{\lambda=2,4,6} \Omega_\lambda |\langle SLJ \| U^{(\lambda)} \| S'L'J' \rangle|^2. \tag{2}$$

The fluorescence branching ratios, for the transition originating on a specific initial manifold $|S'L'J'\rangle$, are defined by

$$\beta(S'L'J'; SLJ) = A[SLJ; S'L'J'] \{\sum_{SLJ} A[S'L'J'; SLJ]\}^{-1}, \tag{3}$$

where the sum over all possible terminal manifolds SLJ represents the total transition probabilities for the radiative decay from the initial manifolds and is equal to the reciprocal of the radiative lifetime

$$\tau_{\mathrm{rad}}^{c} = \Big(\sum_{SLJ} A[S'L'J'; SLJ]\Big)^{-1}. \tag{4}$$

The calculated transition probabilities from the $^4F_{3/2}$ to the $^4I\,J$ manifold for NdP_5O_{14} and suitable branching ratios are given in Table II.

TABLE II

The fluorescence intensities $^4F_{3/2} \rightarrow {}^4IJ$ manifold for NdP_5O_{14}

$S'L'J'$	$\lambda(u)$	$U^{(4)}$	$U^{(6)}$	A (sec^{-1})	β_c
$^4I_{9/2}$	0.88	0.230	0.056	855	0.38
$^4I_{11/2}$	1.05	0.142	0.407	1128	0.51
$^4I_{13/2}$	1.33	0	0.212	228	0.10
$^4I_{15/2}$	1.8	0	0.027	12	0.005

The branching ratios for NdP_5O_{14} have been measured by [6, 9]. Among others Weber et al. [9] have measured the branching ratios for the transition from $^4F_{3/2}$ to $^4I_{9/2}$ and $^4I_{11/2}$ neglecting the transitions to $^4I_{13/2}$ and $^4I_{15/2}$. They have obtained $\beta_{9/2} = 0.38 \pm 0.04$ and $\beta_{11/2} = 0.62 \pm 0.04$. Huber et al. [6] have shown that the branching ratio for $^4F_{3/2} \rightarrow {}^4I_{13/2}$ cannot be neglected. They have determined the relative branching ratios contained in $\beta_{9/2}+\beta_{11/2} = 0.93$ and $\beta_{13/2} = 0.07$. The branching ratio for the transition $^4F_{3/2} \rightarrow {}^4I_{15/2}$ is of the order of 10^{-4} at room temperature. The agreement between the calculated and the measured branching ratios is within the accuracy of the Judd–Ofelt method. Similar accuracy in the branching ratio calculation for Nd:YAG was reported by Krupke [4]. The calculated radiative lifetime was found to be $\tau_{\mathrm{rad}}^{c} = 448\ \mu\mathrm{sec} \pm 42\ \mu\mathrm{sec}$.

Since the multiphonon relaxation in NdP_5O_{14} is practically negligible [7] we can interpret the lifetime measured in the limit of zero neodymium concentration as the real radiative lifetime. The zero concentration lifetime for $Nd_xLa_{1-x}P_5O_{14}$ has been measured as 310 μsec [7]. The fluorescence lifetime τ_f is related to the radiative and nonradiative transition as, $\tau_f^{-1} = A + k_{\mathrm{nr}}$. In the low concentration region for $x < 0.1$ the measured lifetime is constant and the nonradiative quenching can result only from the multiphonon processes.

The multiphonon decay rate k_{nr} is given as [8]

$$k_{\mathrm{nr}}(T) = k_{\mathrm{nr}}(0)\,[1-\exp(-\hbar\omega_M/kT)]^{-\Delta E/\hbar\omega_M} \exp(-\beta\Delta E), \tag{5}$$

where ΔE is the effective energy gap, ω_M is the phonon cut-off frequency, $k_{\mathrm{nr}}(0)$ and β are characteristics of the host material. In NdP_5O_{14} the high phonon cutoff energy of 1300 cm^{-1} makes a low-order multiphonon decay possible, which could be revealed in the temperature dependence of the fluorescence lifetime. Weber et al. [9] have measured the temper-

ature dependence of the fluorescence lifetime for $x < 0.1$ which is interesting for us. They have not found the temperature dependence in such a concentration region. It means that the multiphonon decay rate is negligible in comparision to the radiative rate constant. The quenching efficiency estimated by Weber [9] was found to be $0 < \eta_q < 0.2$. This value does not allow the precise determination of the radiative lifetime value, 310 μsec $< \tau_r <$ 362 μsec. It should be noted that the calculated radiative lifetime significantly exceeds the experimentally determined error assigned on the basis of the rms fitting error. This discrepancy may be attributed to inadequacy of the local field correction χ used in calculations for electrons in the ground $^4I_{9/2}$ and excited $^4F_{3/2}$ states which was assumed to be identical.

In this place we would like to pay attention — in view of the recent results obtained by Singh et al. [10] for the fluorescent lifetime measurements for Nd:YAG and Nd:Y_2O_3 — to the connection between the observed lifetime in neodymium pentaphosphate crystals and the quality of the crystal used in the experiment. Singh [10] has shown that the unproper way of growing crystals creates defects at high temperatures which can act as quenching centers. For the Nd:YAG crystals obtained by the new method the experimental fluorescent lifetime of the $^4F_{3/2}$ state was found as 420 μsec, i. e. much higher in comparison to the previously measured radiative lifetime (280 μsec). In their results the authors have paid attention to the disagreement between the measured radiative lifetime and that predicted by the Judd-Ofelt method which for Nd:YAG was lower than the experimental one.

In our case for the NdP_5O_{14} system the situation was quite different, the calculated lifetime was higher than the experimental one. It was reported by [7] that the observed lifetime of the $^4F_{3/2}$ state is strongly dependent on the hydrogen contamination in a crystal. Nevertheless taking the recent result of Singh's [10] into account it seems likely that the real fluorescent lifetime in NdP_5O_{14} may be higher than reported up to now.

REFERENCES

[1] F. Auzel, *IEEE J. Quantum Electron.* **QE-12**, 779 (1976).
[2] H. G. Danielmeyer, *J. Lumin.* **12/13**, 715 (1976).
[3] H. G. Danielmeyer, J. P. Jeser, E. Schönherr, W. Stelter, *J. Cryst. Growth* **22**, 298 (1974).
[4] B. Judd, *Phys. Rev.* **127**, 750 (1962); G. S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962); W. F. Krupke, *IEEE J Quantum Electron.* **QE-7**, 153 (1971).
[5] H. G. Danielmeyer, H. P. Weber, *IEEE J. Quantum Electron.* **QE-8**, 805 (1972).
[6] G. Hubert, W. W. Krühler, W. Bludau, H. G. Danielmeyer, *J. Appl. Phys.* **46**, 3580 (1975).
[7] B. C. Tofield, H. P. Weber, T. C. Damen, P. F. Liao, *J. Solid State Chem.* **12**, 207 (1975).
[8] L. A. Riseberg, H. W. Moos, *Phys. Rev.* **174**, 429 (1968).
[9] H. P. Weber, P. F. Liao, B. C. Tofield, *IEEE J. Quantum Electron.* **QE-10**, 563 (1974).
[10] S. Singh, W. A. Bonner, W. H. Grodkiewicz, M. Grasso, L. G. Van Uitert, *Appl. Phys. Lett.* **29**, 343 (1976).