

## Application of the Judd-Ofelt theory to $\text{Pr}^{3+}$ ions in $\text{Y}_2\text{SiO}_5$ crystals

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The results of the Judd-Ofelt theory application to  $\text{Pr}^{3+}$  doped  $\text{Y}_2\text{SiO}_5$  are presented. For the first time for this matrix, the  $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$  parameters have been determined and radiative lifetimes of  ${}^3P_0$  and  ${}^1D_2$  multiplet states have been calculated basing on those parameters. The lifetimes obtained allow the significant influence of the channels of nonradiative quenching for the  ${}^3P_0$  state to be revealed. A more precise coincidence of calculated and observed spectroscopic characteristics can be obtained only when taking into account the influence of  $4f5d$  electron states on  $4f^2$  electron shell properties that is not considered in the framework of the Judd-Ofelt theory.

Представлены результаты применения теории Джарда-Офелта к иону празеодима, допированного в кристалл оксиортосиликата иттрия. Впервые определены параметры  $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$  для такой кристаллической структуры и на их основе проведены расчеты радиационного времени жизни  ${}^3P_0$  и  ${}^1D_2$  мультиплетных состояний. Полученные времена позволили установить существенное влияние каналов безызлучательного тушения для  ${}^3P_0$  состояния. Более точное совпадение расчетных спектроскопических характеристик с наблюдаемыми значениями возможно только при учете влияния  $4f5d$  электронных состояний на свойства  $4f^2$  электронной оболочки, которое в рамках теории Джарда-Офелта не рассматривается.

Trivalent praseodymium ion ( $\text{Pr}^{3+}$ ) in a solid matrix exhibits a complicated energy level scheme that results in emission within different spectral ranges. The features of spectral characteristics of  $\text{Pr}^{3+}$  promote its application in lasers [1], in memory cells of future optical computers [2], and in IR-visible up-converters. The spectral coincidence between one of the optical transitions of doped  $\text{Pr}^{3+}$  in a  $\text{Y}_2\text{SiO}_5$  crystal and an argon laser generation wavelength 488 nm. Optical properties of  $\text{Pr}^{3+}$  are governed by the inner well-screened  $4f^2$  electron shell. Electrostatic interaction between electrons in this shell forms  $LS$  terms  ${}^3H$ ,  ${}^3F$ ,  ${}^1G$ ,  ${}^1D$ ,  ${}^3P$ ,  ${}^1I$ , and  ${}^1S$ . Due to spin-orbit coupling,  $LS$  terms are split into  $J$  multiplets. The crystal field causes  $J$  multiplet splitting into Stark components. In a real experiment, we can observe as a rule the emission

from the Stark components. Symmetry and crystal field strength of a matrix doped with  $\text{Pr}^{3+}$  ions define the details of the energy levels scheme and metastability of different levels. Each crystal doped with  $\text{Pr}^{3+}$  ions exhibits its own features of optical properties. In particular, such features are revealed as influence of the inner  $5d$  electron shell on optical transitions inside the  $4f^2$  electron shell. In  $\text{Pr}^{3+}$  ion, the lower level of the  $5d$  shell, which is split by the crystal field, turned out to be located below the  ${}^1S_0$  level of the  $4f^2$  shell. Such a fact allows a cascade-like radiative decay of  $\text{Pr}^{3+}$  to be realized with an emission more than one photon at the quantum yield exceeding 1.

The unique properties of  $\text{Pr}^{3+}$  make it a prospective object to test theories describing experiments and to establish the right way in searching the adequate explanation

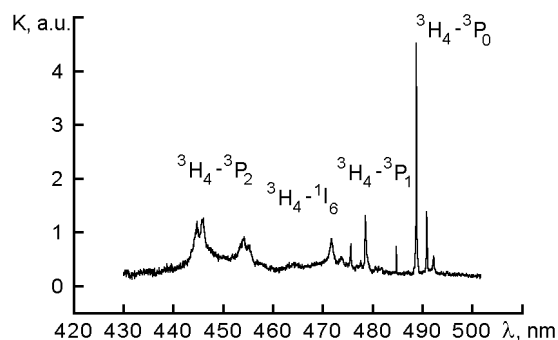


Fig. 1. Absorption spectrum of  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystal at the  ${}^3H_4-{}^3P_{0,1,2}$  transitions.

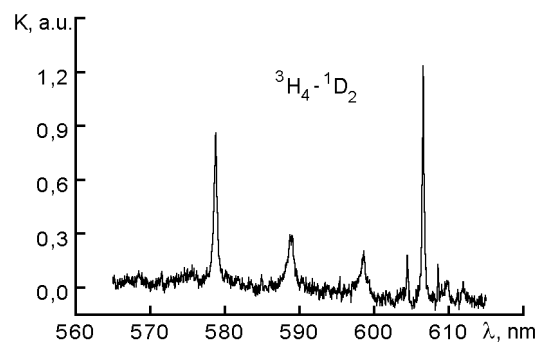


Fig. 2. Absorption spectrum of  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystal at the  ${}^3H_4-{}^1D_2$  transition.

of phenomena observed. In this connection, the Judd-Ofelt theory (J-O) [4, 5] is a very effective tool to determine radiative characteristics of doped RE ions. In this work, using the J-O theory, we have obtained the experimental parameters  $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$  for  $\text{Pr}^{3+}$  doped in  $\text{Y}_2\text{SiO}_5$  and estimated the rate of nonradiative transitions from metastable states in relation to the rate of radiative transitions in this crystal matrix.

$\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystals were grown by Czochralski technique at the Institute for Single Crystals, National Academy of Sciences of Ukraine.  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystal structure belongs to the monoclinic syngony and has B2/b space group. Entering the crystal lattice,  $\text{Pr}^{3+}$  ions substitute isomorphically yttrium ions and form two optical centers [6]. These crystal sites are characterized by a low symmetry and lack of central symmetry, so that the J-O theory can be applied to this crystal. In this work, only the first type optical center [6] has been considered. Absorption spectra of the  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystals were recorded at nitrogen temperature in the 400 nm–1.2  $\mu\text{m}$  spectral range. Most lines of  $\text{Pr}^{3+}$  multiplet transitions are located within the 430–490 nm spectral range (Fig. 1). The absorption spectrum of  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystal is difficult to interpret due to the fact that  $\text{Pr}^{3+}$  ions form two optical centers in the crystal matrix. However, the lines observed in the absorption spectrum were ascribed to multiplet transitions of each optical center [6]. Another group of the spectral lines is located within 570–610 nm and associated with the transitions from the lower Stark components of the  ${}^3H_4$  multiplet to sublevels of the  ${}^1D_2$  multiplet (Fig. 2). The most available group of lines in the IR range is located near 1  $\mu\text{m}$  and associated with transitions between the levels of  ${}^3H_4-{}^1G_4$  multiplets (Fig. 3).

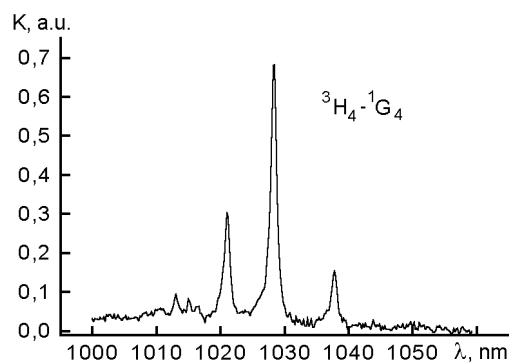


Fig. 3. Absorption spectrum of  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystal at the  ${}^3H_4-{}^1G_4$  transition.

The observed radiative transitions of RE ions in solids are mainly of electro-dipole character and become allowed due to admixing of the  $4f^{n-1}5d$  electronic shell quantum states to wave functions of  $4f^2$  electron shell. Such a possibility appears due to existence of the external crystal field. There are two main approaches in the J-O theory to consider such systems:

1. All  $4f^{n-1}5d$  states are degenerate (i.e. have the same energy).
2. The energy difference between the  $4f^n$  configuration levels is much less than the difference between these energies and the  $4f^{n-1}5d$  state energy.

The use of such statements simplifies considerably the theoretical problem and leads to the "simple" expression describing the intensity of electro-dipole transitions between initial  $J$  and final  $J'$  multiplet states in the following form:

$$S_{JJ'} = \sum_{k=2,4,6} \Omega_k |\langle 4f^2[J] || U^{(k)} || 4f^2[J'] \rangle|^2. \quad (1)$$

However, to use this expression for praseodymium ions, it is necessary to deter-

mine how the states with the same  $J$  are mixed in the crystal matrix. This is connected to the fact that the wave functions obtained at the same  $J$  but from different  $LS$  terms do not diagonalize the spin-orbit interaction matrix that has the following form for  $4f^2$  electrons [7]:

$$\begin{aligned} & \langle 4f^2 LSJ | H_{SO} | 4f^2 L'S'J \rangle = \quad (2) \\ & = 2\eta(-1)^{S'+L+J+1} \sqrt{\frac{252}{2}(2L+1)(2L'+1)(2S+1)(2S'+1)} \times \\ & \quad \times \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L' & 3 & 1 \end{Bmatrix} \begin{Bmatrix} 1/2 & L & 1/2 \\ S' & 1/2 & 1 \end{Bmatrix}. \end{aligned}$$

Using Slater parameters obtained for  $\text{Pr}^{3+}$  ions in  $\text{Y}_2\text{SiO}_5$ , we have written and diagonalized the energetic matrix taking into account the spin-orbit interaction [8]. The diagonalizing basis obtained is presented in Table.

The known weight coefficients provide the value  $U(k) = |\langle 4f^2[J] || U^{(k)} || 4f^2[J'] \rangle|^2$  to be determined after the calculation of reduced matrix elements of one-electron operators [9]:

$$\begin{aligned} & \langle 4f^2[LSJ] || U^{(k)} || 4f^2[L'S']J' \rangle = \\ & = \delta(S, S') \cdot (-1)^{S+L'+J+L} \times \\ & \quad \times \frac{2\sqrt{(2J+1)(2J'+1)(2L+1)(2L'+1)}}{2\sqrt{(2J+1)(2J'+1)(2L+1)(2L'+1)}} \times \\ & \quad \times \begin{Bmatrix} L & k & L' \\ J' & S & J \end{Bmatrix} \begin{Bmatrix} l & L & l \\ L' & l & k \end{Bmatrix}. \quad (3) \end{aligned}$$

Such calculations are to be carried out for  $\text{Pr}^{3+}$  in each specific crystal matrix. The weight coefficients obtained for  $\text{Pr}^{3+}$  in other crystal matrix cannot be used.

Using  $U(k)$  values and absorption coefficients within the multiplets, we can determine  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  parameters (Eq. 1) [10]:

$$\int_{\text{absorption line}} k(\lambda) d\lambda = \frac{8\pi^3 e^2}{3hc} \frac{N_0 \bar{\lambda}}{2J+1} \frac{(n^2+2)^2}{9n} S_{JJ'}, \quad (4)$$

where  $k(\lambda)$  is the absorption coefficient at  $\lambda$  wavelength;  $\bar{\lambda}$ , the mean wavelength that corresponds to the multiplet transition;  $n$ , the refractive index of the crystal at the absorption wavelength;  $N_0$ , the multiplet population.

For the  $\text{Y}_2\text{SiO}_5$  crystal the mean refractive index is  $-1.795$ . The conducted calculations and least-squares fitting of calculated and measured in the experiment absorption coefficients provide the Judd-Ofelt intensity parameters for  $\text{Pr}^{3+}$  ions in  $\text{Y}_2\text{SiO}_5$  crystals:

$$\Omega_2 = 5.83 \cdot 10^{-20} \text{cm}^2,$$

Table. Weight coefficient values

[J]	Linear combination of wave functions
$[^3H_4]$	$0.984 ^3H_4\rangle + 0.169 ^1G_4\rangle - 0.035 ^3F_4\rangle$
$[^3H_5]$	$ ^3H_5\rangle$
$[^3H_6]$	$0.997 ^3H_6\rangle - 0.069 ^1I_6\rangle [^3F_2]$
$[^3F_3]$	$ ^3F\rangle$
$[^3F_4]$	$0.861 ^3F_4\rangle - 0.49 ^1G_4\rangle + 0.115 ^3H_4\rangle$
$[^1G_4]$	$0.82 ^1G_4\rangle + 0.507 ^3F_4\rangle - 0.128 ^3H_4\rangle$
$[^1D_2]$	$0.922 ^1D_2\rangle - 0.345 ^3P_2\rangle - 0.173 ^3F_2\rangle$
$[^1I_6]$	$ ^1I_6\rangle$
$[^3P_0]$	$0.99 ^3P_0\rangle + 0.103 ^1S_0\rangle$
$[^3P_1]$	$ ^3P_1\rangle$
$[^3P_2]$	$0.938 ^3P_2\rangle + 0.343 ^1D_2\rangle - 0.043 ^3F_2\rangle$
$[^1S_0]$	$0.994 ^1S_0\rangle - 0.103 ^3P_0\rangle$

$$\Omega_4 = 0.73 \cdot 10^{-20} \text{cm}^2,$$

$$\Omega_6 = 1.48 \cdot 10^{-20} \text{cm}^2.$$

The values obtained exhibit a spread within 15 % that is a characteristic feature of praseodymium ion and is associated with the influence of  $5d$  electron shell states. The crystal field causes a splitting of this electron shell states so that the lower state energy becomes comparable with  $^3P_1$  and higher-lying multiplet state energies [11]. Such a distribution of the energy states is not considered within the J-O theory. Moreover, the obtained values of intensity parameters exceed those obtained for praseodymium ion in  $\text{LaF}_3$  matrix [12], but are smaller than those obtained in silicate glasses [13]. That indicates the intermediate covalence degree of the  $\text{Y}_2\text{SiO}_5$  matrix.

Using J-O parameters, the spontaneous radiative emission rates can be calculated using the following expression [10]:

$$A_{JJ'} = \frac{64\pi^3 e^2}{3hc(2J+1)\bar{\lambda}^3} \frac{n(n^2+2)^2}{9} S_{JJ'}. \quad (5)$$

The total radiative rate is calculated as

$$A_j = \sum_{J'} A_{JJ'}. \quad (6)$$

The calculations provide radiative lifetimes for  $^3P_0$  and  $^1D_2$  multiplet states that are  $23 \mu\text{s}$  and  $134 \mu\text{s}$ , respectively. The calculated radiative lifetime of the  $^3P_0$  multiplet state is much longer than that observed in experiment. For the  $\text{Y}_2\text{SiO}_5$  crystal, the

experimental radiative lifetime is 5  $\mu\text{s}$  at nitrogen temperature and is temperature-dependent. At the same time, the experimental radiative lifetime of the  $^1D_2$  multiplet state is 110  $\mu\text{s}$ . It slightly differs from the calculated value and is almost temperature-independent.

Thus, it has been shown that the radiative lifetimes calculated using the Judd-Ofelt intensity parameters reveal a good correlation with the lifetimes observed in experiments and allow channels of non-radiative relaxation to be estimated with a high probability. However, the calculation of absorption coefficients for higher-lying multiplet states gives a significant spread of  $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$  parameters that evidences a strong influence of the  $4f^25d$  electron states. The obtained experimental parameters provide any spectroscopic characteristics of a specified optical center in  $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$  crystal to be determined after the calculation of the transition intensity by Eq. 1 using Eq. 3 and data presented in Table. The experimental parameters are of great importance for foreign ions doped in nano-scale crystals, because their determi-

nation in such matrices presents some difficulties.

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## Застосування теорії Джадда-Офелта до іона празеодиму у кристалі оксіортосилікату ітрію

**П.Н.Жмурін**

Представлено результати застосування теорії Джадда-Офелта до іона празеодиму, допованого у кристал оксіортосилікату ітрію. Вперше визначено параметри для такої кристалічної структури і на їх основі проведено розрахунки радіаційного часу життя мультиплетних станів  $^3P_0$  та  $^1D_2$ . Отримані часи дозволили встановити істотний вплив каналів безвипромінювального гасіння для стану  $^3P_0$ . Точніший збіг розрахункових спектроскопічних характеристик із спостережуваними значеннями можливий тільки при врахуванні впливу електронних станів  $4f^25d$  на властивості електронної оболонки  $4f^2$ , яке в рамках теорії Джадда-Офелта не розглядається.