

Modified theory of $f - f$ transition intensities and crystal field for systems with anomalously strong configuration interaction

Research Article

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Abstract:

A new theory explaining the intensity of $f - f$ transitions and the crystal field using an approximation of a strong configuration interaction is proposed. The theory enables the anomalous influence of excited configurations with charge transfer on some multiplets of the f shell to be taken into account. With the help of this theory, a satisfactory description of the absorption transitions and luminescence branching ratios from 1D_2 and 3P_0 multiplets for the Pr^{3+} ion in double molybdates has been achieved for the first time. For further validation the theory, was used to provide a description of Stark splitting of Pr^{3+} - multiplets in elpasolites and determine the covalence parameters; these parameters were found to be in good agreement with values obtained by the other methods.

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1. Introduction

The problem of providing a consistent description of the absorption intensity of $f - f$ transitions and luminescence branching ratios from some multiplets of Pr^{3+} ion has not received a satisfactory solution until now. It is well-known that the application of the Judd–Ofelt method [1, 2] often fails to provide a correct description for the absorption transitions. Application of the modified theories [3–5] al-

lows one to improve the description of the intensity of the absorption transitions considerably.

However for some systems, for example that of the Pr^{3+} ion in $\text{M}^+\text{Bi}(\text{XO}_4)_2$, $\text{M}^+ = \text{Li}, \text{Na}$ and $\text{X}=\text{W}, \text{Mo}$ [6], it is not possible to achieve a satisfactory description of the intensities of both the absorption and luminescent transitions simultaneously within the framework of these theories.

The reason a simultaneous description can not be achieved is due to the significant influence of excited configurations on the intensity of the absorption and luminescent transitions; then smaller the energy gap between the excited configuration and the Pr^{3+} multiplet is the greater its influence. The influence of excited configurations on intensities of the intermultiplet transitions is taken into

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account by modified theories [3–5] but not sufficiently. The development of improved laser materials to meet many practical applications is an active area of research, and this area of work has produced considerable experimental data on the intensities of the absorption and luminescent transitions [7–9] which can not be satisfactorily described within the framework of existing theories [1–5]. In this paper, a new theory describing the intensities of absorption and luminescent transitions which includes an approximation for the strong configuration interaction is offered. In this theory the anomalous strong interaction between some multiplets with ligands of the nearest environment is taken into account.

The existing theories [1–5] give poor agreement between the calculated and experimental luminescence branching ratios for Pr^{3+} ion in double molybdates. The absorption and emission transitions of Pr^{3+} ion in double molybdates was chosen as the first application of the new theory and has provided, for the first time, a satisfactory description of the experimental data [6] for this system.

To further test the new theory, it has been used to provide a description of Stark splitting of Pr^{3+} multiplets in elpasolites and to obtain the covalence parameters.

2. Theoretical background

The Judd-Ofelt method [1, 2] assumes that the energy levels of excited configurations lie much higher than those of the multiplets of f^N configuration. Therefore the excited configurations have an identical influence on all multiplets, and the set of intensity parameters, Ω_k , is common for all $f-f$ transitions of the given system. Such an assumption is approximates a weak configuration interaction. In the approximation of a weak configuration interaction, the line strength of the electric dipole transition between $\gamma J, \gamma' J'$ multiplets is given by

$$S_{JJ'}^{ed} = e^2 \sum_{k=2,4,6} \Omega_k \langle \gamma J \| U^k \| \gamma' J' \rangle^2, \quad (1)$$

where e is the charge of electron, and $\langle \gamma J \| U^k \| \gamma' J' \rangle$ are the reduced matrix elements of the unit tensor U^k .

Calculating the intensity parameters, Ω_k , using a microscopic model gives poor results, therefore they are usually considered as variable parameters. This approximation is not valid for rare-earth ions making a successful de-

scription of experimental data using the Judd-Ofelt method seems unlikely.

The influence of excited configurations is taken into account more consistently by approximating an intermediate configuration interaction [3, 10]. In this case we get a more complicated expression for line strength:

$$S_{JJ'}^{ed} = e^2 \sum_{k=2,4,6} \underbrace{\Omega_k [1 + 2R_k (E_J + E_{J'} - 2E_f^0)]}_{\tilde{\Omega}_k} \times \langle \gamma J \| U^k \| \gamma' J' \rangle^2 + \text{terms of odd ranks}, \quad (2)$$

where the intensity parameters, $\tilde{\Omega}_k$, linearly depend on the multiplet energy, E_J , and $E_{J'}$, included in the transition. Here, R_k represents additional parameters and E_f^0 is the energy of the centroid of a $4f^N$ configuration. Approximate formulas for estimating the of order of magnitude of Ω_k and R_k are given in [11, 12].

In some cases (see [8, 9]) the description of the system using the modified theory (2) is better than in using Judd-Ofelt method. However, for systems with strong configuration interactions, such as Am^{3+} ions in fluorozirconate glass [13] or $\text{BrCl}_6:\text{U}^{4+}$ [14], expression (2) can not provide a satisfactory description of the intensity of absorption transitions, and an approximation of a strong configuration interaction [4, 5] is more adequate.

$$S_{JJ'}^{ed} = e^2 \sum_{k=2,4,6} \underbrace{\Omega_k \left(\frac{\Delta}{\Delta - E_J} + \frac{\Delta}{\Delta - E_{J'}} \right)^2}_{\Omega_k} \langle \gamma J \| U^k \| \gamma' J' \rangle^2, \quad (3)$$

where Δ is energy of excited configuration.

Single crystals of $\text{M}^+\text{Bi}(\text{XO}_4)_2$, $\text{M}^+=\text{Li, Na}$ and $\text{X}=\text{W, Mo}$ [6] are described as systems with a strong configuration interaction. However, it was found that it was not possible to provide satisfactory, simultaneous, descriptions of the intensities of the absorption and luminescent transitions by applying expression (3). The reason behind this failure is that expression (3) can be derived if the determinant contribution to the line strength of the transition is given either by only one excited configuration, or by several excited configurations with similar energy, Δ . To take the influence of several excited configurations with different energies, Δ_l , into account, we shall use expression (12) of [4] for the effective operator of electric dipole moment, D_{eff} :

$$(D_{\text{eff}})_{\pi}^1 = \sum_{k=2,4,6} \sum_{p,t,q} (2p+1)^{1/2} (-1)^{k+\pi} \begin{pmatrix} 1 & k & p \\ \pi & q & -t \end{pmatrix} U_{-q}^k \sum_l S_t^{(1k)p}(l) \left(\frac{\Delta_l}{\Delta_l - E_j} + \frac{\Delta_l}{\Delta_l - E_{j'}} \right) \\ + \sum_{\lambda=3,5} \sum_{p,t,q} (2p+1)^{1/2} (-1)^{\lambda+\pi} \begin{pmatrix} 1 & \lambda & p \\ \pi & q & -t \end{pmatrix} U_{-q}^{\lambda} \sum_l S_t^{(1\lambda)p}(l) \left(\frac{\Delta_l}{\Delta_l - E_j} - \frac{\Delta_l}{\Delta_l - E_{j'}} \right), \quad (4)$$

where l is summation over the excited configurations, $\begin{pmatrix} \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \end{pmatrix}$ is the 3-j symbol.

Substituting (4) in the definition of line strength for inter-multiplet electric-dipole transitions gives:

$$S_{JJ'} = \sum_{M,M'} |\langle \gamma JM | \mathbf{D} | \gamma' J' M' \rangle|^2. \quad (5)$$

Neglecting the terms of odd ranks λ we shall obtain a more complicated expression for the intensity of transitions than (3):

$$S_{JJ'} = \sum_{k=2,4,6} \frac{1}{4(2k+1)} \sum_{p,t} \left| \sum_l S_t^{(1k)p}(l) \left(\frac{\Delta_l}{\Delta_l - E_j} + \frac{\Delta_l}{\Delta_l - E_{j'}} \right) \right|^2 \langle \gamma J \| U^k \| \gamma' J' \rangle^2, \quad (6)$$

The most significant contribution to the parameter $S_t^{(1k)p}$ is made by an excited configuration of the opposite parity. The order of his magnitude can be estimated using the following formula:

$$S_t^{(1k)p}(d) = 2 |e| \frac{B_t^{p*}(d)}{\Delta_{df}} \frac{2k+1}{\sqrt{2p+1}} \begin{Bmatrix} 1 & k & p \\ f & d & f \end{Bmatrix} \langle f \| c^p \| d \rangle \langle d \| c^1 \| f \rangle r_{df}, \quad (7)$$

where $B_t^p(d)$ are parameters of the odd-parity crystal field; $\begin{Bmatrix} \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \end{Bmatrix}$ is the 6-j symbol, $\langle f \| c^p \| d \rangle$ is the reduced matrix element of the spherical tensor and $r_{df} = \langle 4f | r | 5d \rangle$.

Excited configurations with charge transfers (the covalent effects) also contribute to $S_t^{(1k)p}$. The order of magnitude for this contribution can be estimated with the help of formula [3]:

$$S_t^{(1k)p}(c) = |e| \sum_b S^{(1k)p}(b) C_t^p(\Theta_{ab}, \Phi_{ab}), \quad (8)$$

where b denotes summation over the ligands of the nearest environment, Θ_{ab} and Φ_{ab} are the spherical angles specifying the direction to the b th ligand.

Applying the above expressions for the parameters $S^{(1k)p}(b)$ to the examples of one-electronic 4f-functions of ion Pr^{3+} [15] and 2s-, 2p-functions of O^{2-} [16], yields the following:

$$\begin{pmatrix} S^{(12)^1}(b) \\ S^{(12)^3}(b) \\ S^{(14)^3}(b) \\ S^{(14)^5}(b) \\ S^{(16)^5}(b) \\ S^{(16)^5}(b) \end{pmatrix} = \left(\frac{R_{ab}}{R_0} \right)^{3.5} \begin{pmatrix} 0.000581 & 0.000638 & 0.004514 \\ -0.089072 & 0.035778 & -0.016678 \\ 0.030419 & -0.019705 & -0.001367 \\ 0.057944 & -0.072080 & 0.030231 \\ 0.025743 & 0.064018 & -0.007230 \\ 0.253610 & 0.149733 & -0.058948 \end{pmatrix} \begin{pmatrix} \gamma_{fp1} \\ \gamma_{fp0} \\ \gamma_{fs0} \end{pmatrix}. \quad (9)$$

Here γ_{fp1} , γ_{fp0} , γ_{fs0} are the covalence parameters and $R_0 = 4.35$ a.u.

In a phenomenological approximation, it is difficult to describe the intensities of intermultiplet $f-f$ transitions using expressions (4-7) because of a large number of variable parameters Δ_l , $B_t^p(d)$ ($p = 1, 3, 5$; $t = -p..p$) and γ_{fp1} , γ_{fp0} , γ_{fs0} .

Therefore it is reasonable to use a simpler expression for line strength with a smaller number of variables O_{dk}, O_{ck} ($k = 2, 4, 6$) and $\Delta_d, \Delta_{c1}, \Delta_{c2}$:

$$S_{JJ'}^{ed} = \frac{e^2}{4} \sum_{k=2,4,6} \langle \gamma J \| U^k \| \gamma' J' \rangle^2 \times \left| O_{dk} \left(\frac{\Delta_d}{\Delta_d - E_J} + \frac{\Delta_d}{\Delta_d - E_{J'}} \right) + O_{ck} \left[\left(\frac{\Delta_{c1}}{\Delta_{c1} - E_J} + \frac{\Delta_{c1}}{\Delta_{c1} - E_{J'}} \right) + \left(\frac{\Delta_{c2}}{\Delta_{c2} - E_J} + \frac{\Delta_{c2}}{\Delta_{c2} - E_{J'}} \right) + \dots \right] \right|^2 \quad (10)$$

Here the parameters O_{dk} and energy Δ_d correspond to the excited configuration of opposite parity $4f^{N-1}5d$, and parameters O_{ck} and energies Δ_{c1}, Δ_{c2} are due to the covalent effects of excited configurations with charge transfer. According to equation (6), contributions from each excited configuration, l , in the expression for line strength (10), should be represented only by one component of type $\left(\frac{\Delta_l}{\Delta_l - E_J} + \frac{\Delta_l}{\Delta_l - E_{J'}} \right)$. However, in describing the Stark splitting of multiplets for Pr^{3+} ion in $\text{Y}_3\text{Al}_5\text{O}_{12}$ [17] including configurations with charge transfer, we have noted that this does not apply. However, a satisfactory description of 1G_4 and 3F_4 multiplets can be obtained if the covalent effects in the crystal field Hamiltonian are represented by several components with different energies Δ_{c1}, Δ_{c2} and a common set of parameters O_{ck} ($k = 2, 4, 6$). This explains why the covalent effects have a more complex representation than the excited configurations of opposite parity in equation (10).

It is known that intensity parameters Ω_k must be positive. Comparing (10) and (1) it can be shown that $\Omega_{\alpha k} = \frac{1}{4} \left(\frac{\Delta_{\alpha}}{\Delta_{\alpha} - E_J} + \frac{\Delta_{\alpha}}{\Delta_{\alpha} - E_{J'}} \right)^2 |O_{\alpha k}|^2$ ($\alpha = d, c$) and restriction on a sing of parameters $O_{\alpha k}$ is not present.

It has previously been established [11] that the same excited configurations contribute greatly to both the intensity of intermultiplet transitions, and Stark splitting of the multiplets. For a more complete analysis of the role of excited configurations we shall extend the crystal field Hamiltonian obtained in [18] to an approximation similar to Eq. (10). Using methods, developed in [18], we come to:

$$H_{CF} = \sum_{\gamma LS} E_J |\gamma[LS]JM\rangle \langle \gamma[LS]JM| + \sum_{k=2,4,6} \sum_q \left\{ B_q^k + \Delta_d \left(\frac{\Delta_d}{\Delta_d - E_J} + \frac{\Delta_d}{\Delta_d - E_{J'}} \right) \tilde{C}_q^k(d) \right. \\ \left. + \left[\Delta_{c1} \left(\frac{\Delta_{c1}}{\Delta_{c1} - E_J} + \frac{\Delta_{c1}}{\Delta_{c1} - E_{J'}} \right) + \Delta_{c2} \left(\frac{\Delta_{c2}}{\Delta_{c2} - E_J} + \frac{\Delta_{c2}}{\Delta_{c2} - E_{J'}} \right) + \dots \right] \tilde{C}_q^k(c) \right\} C_q^k. \quad (11)$$

Here, $|\gamma[LS]JM\rangle$ is the function of the multiplet, B_q^k are the crystal field parameters, $\tilde{C}_q^k(d)$ and $\tilde{C}_q^k(c)$ are additional parameters due to the excited configuration $4f^{N-1}5d$ and the covalent effects, respectively and C_q^k is the spherical tensor of rank k , which acts on the angular variables of $4f$ - electrons. The other designations are the same as in Eq. (10).

The order of magnitude of the additional parameters, $\tilde{C}_q^k(d)$, can be estimated from formula [19]:

$$\tilde{C}_q^k(d) = -\frac{2k+1}{2 \langle f \| c^k \| f \rangle} \sum_{p', p''} \sum_{t', t''} (-1)^q \begin{pmatrix} p' & p'' & k \\ t' & t'' & -q \end{pmatrix} \\ \times \left\{ \begin{matrix} p' & p'' & k \\ f & f & d \end{matrix} \right\} \langle f \| c^{p'} \| d \rangle \langle d \| c^{p''} \| f \rangle \frac{B_{t'}^{p'}(d)}{\Delta_{df}} \frac{B_{t''}^{p''}(d)}{\Delta_{df}}, \quad (12)$$

where $B_t^p(d)$ are the odd crystal field parameters.

For parameter $\tilde{C}_q^k(c)$ the following expression is valid [18]:

$$\tilde{C}_q^k(cov) = \sum_b \tilde{J}^k(b) C_q^{k*}(\Theta_{ab} \Phi_{ab}), \quad (13)$$

and for parameters $\tilde{J}^k(b)$, it is convenient to use the fol-

lowing approximate expressions [11]:

$$\tilde{J}^2(b) = \frac{5}{28} [2(\gamma_{st}^2 + \gamma_{st'}^2) + 3\gamma_{\pi t}^2], \\ \tilde{J}^4(b) = \frac{3}{14} [3(\gamma_{st}^2 + \gamma_{st'}^2) + \gamma_{\pi t}^2], \\ \tilde{J}^6(b) = \frac{13}{28} [2(\gamma_{st}^2 + \gamma_{st'}^2) - 3\gamma_{\pi t}^2]. \quad (14)$$

Here, γ_{if} ($i = \sigma, \pi, s$) is the covalence parameter corresponding to an electron jumping from the i -th shell of the ligand to the f shell of the Ln^{3+} ion.

The crystal field Hamiltonian in the approximation of weak configuration interactions can easily be obtained as a particular case of formula (11) assuming $\tilde{G}_q^k(d) = 0$ and $\tilde{G}_q^k(c) = 0$.

3. Results and discussion

Experimental and theoretical analysis of the spectroscopic characteristics of Pr^{3+} ion in $\text{M}^+\text{Bi}(\text{XO}_4)_2$, $\text{M}^+ = \text{Li, Na}$ and $\text{X} = \text{W, Mo}$ single crystals has been recently conducted [6]. The analysis of the intensity of the absorption and luminescent transitions was conducted using a Judd-Ofelt treatment, Eq. (1), of the Pr^{3+} ion in double molybdates, as this was the system for which the most detailed experimental data is available. Poor agreement between the theory and experiment was found for both the absorption (${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ transition) and for the branching ratios from ${}^3\text{P}_0$ and ${}^1\text{D}_2$ multiplets. The attempt to improve the description of branching ratios, by including the experimental β in the fit procedure, has appeared unsuccessful (see Tables 1 and 2). However, intensity parameters (see Table 3) we have obtained appreciably others than corresponding parameters given in [6]: $\Omega_2 = 9.8 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 12.8 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.3 \times 10^{-20} \text{ cm}^2$.

Further optimization of the oscillator strengths and branching ratios for models of intermediate, Eq. (2), and strong, Eq. (3), configuration interactions were carried out. The application of these models allowed an improved description of absorption transitions only. The agreement between calculated and measured branching ratios is still poor (see Tables 1 and 2) and suggests that the representation of configuration interactions by equations (2) and (3) is not complete enough. The optimum values of intensity parameters for these approaches can be found in the Table 3.

The unsatisfactory description of the luminescence branching ratios using the Judd-Ofelt approximation, Eq. (1), and using the modified theories Eqs. (2) and (3), is explained by unusually high probabilities of ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ and ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transitions occurring. Abnormal values of branching ratios for some transitions, are probably caused by an anomalous strong interaction of these multiplets, for example, the interaction of ${}^1\text{D}_2$, with the excited configurations. The anomaly in the interaction of some multiplets, with a configuration corresponding to a charge transfer, can be taken into account using the modified equation (10). Equation (10) contains denominators such as $\Delta_{c1} - E_{j'}$ and $\Delta_{c2} - E_{j'}$. The experimental data and the variation allowed

Table 1. Measured [6] and calculated using Eqs. (1) – (3), (10) the luminescence branching ratios and lifetimes for Pr^{3+} ion in double molybdate compounds.

Transition	Experiment [6]	β [%]			
		Weak (1)	Intermediate (2)	Strong (3)	Strong modif. (10)
${}^3\text{P}_0 \rightarrow {}^1\text{D}_2$	0	0.0	0.0	0.0	0.0
${}^1\text{G}_4$	0	2.0	2.4	1.5	0.8
${}^3\text{F}_4$	5	10.6	11.1	7.2	3.1
${}^3\text{F}_3$	0	0.0	0.0	0.0	0.0
${}^3\text{F}_2$	68	26.8	31.8	45.4	71.0
${}^3\text{H}_6$	9	3.0	14.7	11.3	6.2
${}^3\text{H}_5$	0	0.0	0.0	0.0	0.0
${}^3\text{H}_4$	18	57.6	40.0	34.5	18.9
${}^1\text{D}_2 \rightarrow {}^1\text{G}_4$	2	9.2	10.8	12.1	5.5
${}^3\text{F}_4$	0	37.4	40.0	46.6	5.1
${}^3\text{F}_3$	10	4.8	4.2	4.1	1.5
${}^3\text{F}_2$	0	16.8	11.2	8.7	8.7
${}^3\text{H}_6$	10	14.2	9.6	7.1	11.0
${}^3\text{H}_5$	5	0.8	0.5	0.4	0.6
${}^3\text{H}_4$	73	16.8	23.7	21.0	67.6
$\tau(\mu\text{s})$					
${}^3\text{P}_0$	0.2	3.15	2.82	2.64	1.44
${}^1\text{D}_2$	36	44.0	32.7	36.6	47.5

in the fitting parameters demonstrates that it is possible for the energy Δ_{c1} or Δ_{c2} , associated with an excited configuration with charge transfer, can turn out to be close to the energy of a multiplet. When this is the case, the contribution of this excited configuration to the line strength of a transition will be anomalously large. The equation (10) as the special case contains the equations (1), (2), and (3) and is most common equation. In the equation (10) the dependence of line strength on multiplet energy is most strong, and in the equation (1) is most weak.

Application of equation (10) to describe the absorption transitions and the luminescence branching ratios yields the following values for the variable parameters: $O_{d2} = 4.85 \times 10^{-10} \text{ cm}$, $O_{d4} = 2.12 \times 10^{-10} \text{ cm}$, $O_{d6} = 2.71 \times 10^{-10} \text{ cm}$, $\Delta_d = 35060 \text{ cm}^{-1}$, $O_{c2} = -0.133 \times 10^{-10} \text{ cm}$, $O_{c4} = -0.113 \times 10^{-10} \text{ cm}$, $O_{c6} = -0.186 \times 10^{-10} \text{ cm}$, $\Delta_{c1} = 7520 \text{ cm}^{-1}$, $\Delta_{c2} = 16640 \text{ cm}^{-1}$.

The calculated absorption oscillator strengths, luminescence branching ratios from ${}^1\text{D}_2$ and ${}^3\text{P}_0$ multiplets, and the ${}^1\text{D}_2$ lifetime, correlate well with the corresponding experimental values (see Tables 1 and 2). However, in

Table 2. Measured [6] and calculated using Eqs. (1) – (3), (10) absorption oscillator strengths of Pr^{3+} ion in crystal $\text{NaBi}(\text{MoO}_4)_2$.

$^{2S+1}L_J$	E_J [cm^{-1}]	Oscillator strength $\times 10^6$				
		\tilde{f}_{expt} [6]	f_{calc} Weak (1)	f_{calc} Inter- med. (2)	f_{calc} Strong (3)	f_{calc} Strong modif. (10)
$^3F_2 + ^3H_6$	≈ 5035	15.45	18.41	15.46	8.67	16.84
$^3F_3 + ^3F_4$	≈ 6410	12.81	22.95	12.91	17.92	12.49
1G_4	≈ 9661	0.49	0.52	0.54	0.48	0.61
1D_2	≈ 16750	5.26	2.78	5.26	4.173	10.36
3P_0	≈ 20450	11.84	17.50	13.55	12.51	12.51
$^1I_6 + ^3P_1$	≈ 21230	24.40	24.58	23.09	22.87	24.13
3P_2	≈ 22730	23.05	8.07	23.21	25.60	23.25
RMS Dev.			7.31	0.82	3.43	2.02

Table 3. Intensity parameters.

	Weak (1)	Intermediate (2)	Strong (3)
Ω_2 , [10^{-20} cm^2]	12.66	20.49	1.63
Ω_4 , [10^{-20} cm^2]	19.54	12.70	0.97
Ω_6 , [10^{-20} cm^2]	5.33	20.70	1.51
$R_2/R_4/R_6$, [10^{-4} cm]	–	–0.14/0.47/0.31	–
Δ , [cm^{-1}]	–	–	31220

comparison with the modified theories described by Eqs. (2) and (3), the description of absorption transitions has worsened a little. The energies Δ_{c1} and Δ_{c2} are shown to be close to the energies of multiplets 3F_3 , 3F_4 , 1G_4 and 1D_2 , 3P_0 respectively, therefore allowing covalent effects to contribute an anomalously major contribution to the line strength of transition in these cases.

To provide further evidence to support the theory of an abnormal interaction between some multiplets of Pr^{3+} ion and an excited configuration, the Stark splitting of multiplets of this ion in elpasolites $\text{Cs}_2\text{NaPrCl}_6$ was also analysed using the same approximation. The local symmetry of a crystal field of Pr^{3+} ion is classified as cubic. The application of two-photon spectroscopy [20] has allowed to measure energy and to identify the symmetry of 38 energy levels out of 40.

In the model of the weak configuration interaction, parameters $\tilde{C}_q^k(d) = \tilde{C}_q^k(c) = 0$, and only two of the crystal field parameters, B_0^4 and B_0^6 , in a Hamiltonian Eq. (11), are unknown. Values of $B_0^4 = 1977$ and $B_0^6 = 200.5 \text{ cm}^{-1}$ can be unambiguously determined by performing a least-

Table 4. The description of Stark splitting of multiplets of Pr^{3+} ion in elpasolite $\text{Cs}_2\text{NaPrCl}_6$ in approximation of the weak (a) and the strong (b) configuration interaction.

$^{2S+1}L_J$	Expt. [20]	$E_{\text{Expt}} - E_{\text{Calc}}$	
		Weak ^a	Strong ^b
3H_4	0	-32.7	-4.1
	242	-3.0	11.5
	422	32.3	39.0
	702	32.7	4.1
	2300	-28.6	-9.2
3H_5	2399	-29.4	-10.3
	2645	-1.6	-12.0
	2763	28.6	9.2
3H_6	4386	-30.3	-8.8
	4437	-29.1	-13.4
	4591	-49.0	-39.9
	4807	-7.5	-24.6
	4881	1.2	-20.4
3F_2	4942	30.3	8.8
	5203	-19.5	-17.1
	5297	19.5	17.1
3F_3	6616	-4.0	-3.9
	6621	-2.1	0.1
	6682	4.0	3.9
3F_4	6902	-8.8	7.9
	6965	-8.6	5.9
	7012	7.4	20.7
	7278	8.8	-7.9
	9847	96.8	-2.1
1G_4	9895	49.9	4.8
	9910	8.1	0.1
	10327	-96.8	2.1
1D_2	16666	-42.7	-0.5
	17254	42.7	0.5
3P_0	20625	0.0	0.0
1I_6	21166	-8.0	-7.8
3P_1	21218	0.0	0.0
1I_6	21255	-20.5	-21.5
	21788	-13.1	-14.2
	21967	-7.2	-8.2
3P_2	22035	8.0	7.8
	22367	-13.9	-12.7
	22494	13.9	12.7
RMS Dev.		32.0	15.0

^aHamiltonian (11), $B_0^4 = 1977 \text{ cm}^{-1}$, $B_0^6 = 200.5 \text{ cm}^{-1}$, $\tilde{C}_q^k(d) = \tilde{C}_q^k(c) = 0$.

^bHamiltonian (11), $B_0^4 = 2144 \text{ cm}^{-1}$, $B_0^6 = 205.1 \text{ cm}^{-1}$, $\Delta_{c1} = 9937 \text{ cm}^{-1}$, $\Delta_{c2} = 19172 \text{ cm}^{-1}$, $\tilde{C}_0^4(c) = 11.10 \times 10^{-4}$, $\tilde{C}_0^6(c) = 0.06 \times 10^{-4}$ (dimensionless).

squares fit between calculated and experimentally determined energies. The result of the using the approximation of a weak configuration interaction is shown in Table 4, column “Weak”. The description of Stark splitting was least satisfactory for the 1G_4 and 1D_2 multiplets. The poor description of the Stark splitting of 1D_2 multiplet was already observed for other systems [21].

Using the approximation of a strong configuration interaction, the mean-square deviation of the calculated values of the Stark level energies from the experimental values decreased by 53% (Table 4, column “Strong”). The optimum description is achieved using the following parameters: $B_0^4 = 2144 \text{ cm}^{-1}$, $B_0^6 = 205.1 \text{ cm}^{-1}$, $\Delta_{c1} = 9937 \text{ cm}^{-1}$, $\Delta_{c2} = 19172 \text{ cm}^{-1}$, and $\tilde{C}_0^4(c) = 11.10 \times 10^{-4}$, $\tilde{C}_0^6(c) = 0.06 \times 10^{-4}$ (dimensionless). In elpasolites the Pr^{3+} ion occupies the central symmetric positions, therefore no crystal field with an odd symmetry, and according to equation (12), $\tilde{C}_q^k(d) = 0$. The values for Δ_{c1} and Δ_{c2} energies are sufficiently close to the corresponding values obtained from the description of intensity characteristics for the double molybdates. By comparing Δ_{c1} and Δ_{c2} with the energies of the multiplets it is possible to draw the conclusion that terms which contain Δ_{c1} and Δ_{c2} in Eq. (11), are the most influential for considering 1G_4 and 1D_2 multiplets. In other words, the 1G_4 and 1D_2 multiplets exhibit an anomalously strong interaction with the excited configurations associated with charge transfer. The abnormal amplification of the covalent effects for multiplets 1G_4 and 1D_2 is caused by the specific spatial distribution of electronic density in singlet multiplets. The distribution of electronic density of these multiplets corresponds to those of the one-electron g - and d -orbitals and is strongly anisotropic. Amplification of the covalent effects could occur when the direction of increased electronic density coincides with the direction of a ligand. This mechanism of anomalous amplification of covalent effects for some Pr^{3+} multiplets can probably be best simulated using a Hamiltonian, Eq. (11), and operator, Eq. (10).

According to Eq. (14) the covalence parameters $\gamma_\sigma = -0.0201$ and $\gamma_\pi = 0.0162$ correspond to the parameters $\tilde{C}_0^4(c)$ and $\tilde{C}_0^6(c)$, and closely match the covalence parameters for chlorides $\gamma_\sigma = -0.0222$ and $\gamma_\pi = 0.0092$, $\gamma_s = 0.0056$, calculated in [22]; in applying Eq. (14), we have neglected the contribution from parameter γ_s . The satisfactory match between covalence parameters obtained using the model of the Stark structure of multiplets and those calculated by other methods [22] validates the use of testified the crystal field Hamiltonian, Eq. (11), and the effective line strength operator Eq. (10).

It is interesting to note that the addition of new variable parameters $\tilde{C}_0^4(c)$, $\tilde{C}_0^6(c)$, Δ_{c1} and Δ_{c2} in Eq. (11) has very

little effect on the values of B_0^4 and B_0^6 , obtained using the weak configuration interaction model.

The influence of configurations with charge transfer is not the only mechanism for improving the description of Stark splitting of multiplets in elpasolites. Reference [20] describes work that takes into account an interaction with the $4f6p$ excited configuration, and work described in [23], investigated the effect of a spin-correlated crystal field. Defining an optimum description of Stark splitting requires further examination.

4. Conclusions

The effective line strength operator, Eq. (10), and the crystal field Hamiltonian, Eq. (11), obtained by approximating a strong configuration interaction, allows the influence of the anomalous amplification of covalent effects of the Pr^{3+} ion on some multiplets (for example, 1G_4 and 1D_2) to be taken into account.

Application of the effective line strength operator, Eq. (10), has allowed a satisfactory explanation for the intensity of absorption transitions, the luminescence branching ratios, and the lifetimes of Pr^{3+} ion in the double molybdates, to be simultaneously realized for the first time.

Using the same approximation, a satisfactory description of Stark splitting of multiplets for the case of Pr^{3+} ion in elpasolites was also produced. The covalence parameters obtained using this approximation are in agreement with parameters obtained using other methods.

It is difficult to formulate general validity criterions of a particular approximation. It is possible only to note, that for ions with an odd number of f - electrons (J is a half-integer), the influence of excited configurations on the line strength of transitions and Stark splitting of multiplets are less pronounced than for ions with an integer value of J . Usually for Kramer's ions the application of Judd-Ofelt approximation and crystal field Hamiltonian approximating a weak configuration interaction provides a successful description of line strength. Probably it is explained to that in fields of a low symmetry the different components of multiplets with half-integer J are transformed on identical representations. Strong $J - J$ mixing and averaging on multiplet energies therefore is expected. Consequently the dependence of intensity parameters and crystal field parameters on multiplet energies will be negligible and the approximation of weak configuration interaction will be successful.

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