

Description of Stark Structure of the Elpasolites $\text{Cs}_2\text{NaPrCl}_6$, $\text{Cs}_2\text{NaYCl}_6$ and $\text{Cs}_2\text{NaYBr}_6$

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Abstract The analysis of the Stark structure of multiplets of the ion Pr^{3+} in the $\text{Cs}_2\text{NaPrCl}_6$, $\text{Cs}_2\text{NaYCl}_6$, $\text{Cs}_2\text{NaYBr}_6$ crystal systems is performed in the approximation of the weak and anomalous strong configuration interaction. The calculations in the approximation of the anomalous strong configuration interaction let considerably improve the description of the Stark structure of multiplets and thus provide an opportunity to estimate covalence parameters on the basis of experimental data on the Stark structure. Covalence parameters (the parameters of distribution of electronic density) obtained this way are well conformed to the parameters calculated by means of microscopic models.

Keywords Configuration Interaction, Crystal Field, Stark Structure, Pr^{3+} , Covalence Parameters

1. Introduction

Cubic elpasolite crystals are appropriate for investigating the optical spectra and the lanthanide $4f^N$ electronic state structure.

The concept of a crystal field is the key in the description of the experimental data of Stark splitting of multiples of ions with the empty f-shell.

Fundamental spectroscopical properties of lanthanoids were considered in extensive monographs [1-3] in which various approaches in the description of the crystal systems activated by 4f-elements are described.

The results of researches of optical properties of trivalent lanthanoids are given in work [4]. It is reported in [5, 6] about the results of studying of properties of lanthanoids in crystal systems LaCl_3 and LaF_3 .

Further the theoretical models received for 4f-elements, were applied to interpretation of spectroscopical properties of 5f-elements. The works W.T. Carnall and coauthors [7-11] should be noted because the basic principles of studying of lanthanoids [12, 13], were generalized on actinoids there.

The comparative analysis of optical properties of actinoids and lanthanoids is provided in works [14, 15].

The description of Stark structure by means of a spin-correlated crystal field is given in the following works: B.R. Judd et al. [16-20], D.J. Newman et al. [21-23], J.R.G. Thorn et al. [24-26] and J.B. Grubber et al. [27]. The crystal field is described by taking into account the effect of the excited configuration $4f^N np$ in the works [28-32]. Eremin's works [33, 34], Anikeenak's works [35] and Kaminskii's works [36] are devoted to studying the crystal field and methods of its description. But there is no general opinion concerning theoretical models of a crystal field.

Theoretical study of cubic elpasolite and prediction of their optical properties has a great importance. The theory of the crystal field currently remains an actual problem in the theoretical research of the crystal systems activated by f-elements. It becomes especially obvious at attempt to apply a one-electron crystal field Hamiltonian in one-configuration approximation to high symmetric systems by such elpasolites. For such systems the Hamiltonian contains only two independent crystal field parameters. The accidental coincidences are almost excluded, the disadvantages of the theory are also more obvious. In connection with this in the articles [24-26] it is offered to use the spin-correlated crystal field Hamiltonian for the improvement of the description of Stark structure and the authors of the articles [30-32] suggest to perform calculations taking into account the influence of an excited $4f^N np$ -configuration. Both methods have allowed to improve considerably the description of experimental results. However it is impossible to use any of methods without alternative. For example, the application of the spin-correlated crystal field Hamiltonian to low symmetric systems does not ensure that improvement between experiment and theory has been achieved [37]. The account of influence of excited $4f^N np$ -configuration is accompanied by considerable change in crystal field parameters of a one-electronic Hamiltonian. It confirms the nonorthogonality of new added effects. Many practical and theoretical difficulties were also revealed during the application of the correlation-crystal-field Hamiltonian

[38,39].

The electric dipole f-f transitions become possible due to the covalence effects and admixing of opposite parity configurations. We assume that the same effects essentially influence the Stark splitting of multiplets. The modified crystal field theory [40,41] allows to take these effects into account. The modified theory was applied for the description of the Stark levels of multiplets of the ion Tm^{3+} in elpasolites Cs_2NaYCl_6 , Cs_2NaTmF_6 , Rb_2NaTmF_6 and the ion Pr^{3+} in elpasolite $Cs_2NaPrCl_6$ [40,41].

The articles [42-44] give the results of the description of the Stark levels of multiplets of Pr^{3+} ion on the basis of the standard theories for systems $Cs_2NaPrCl_6$, Cs_2NaYCl_6 and Cs_2NaYBr_6 . The description of the Stark levels of multiplets of Pr^{3+} ion in $Cs_2NaPrCl_6$, Cs_2NaYCl_6 and Cs_2NaYBr_6 performed in this paper is made using a modified crystal field theory.

The modified theory in this work is tested on the basis of the experimental data [42] on the Stark splitting of multiplets of the ion Pr^{3+} in the cubic elpasolites $Cs_2NaPrCl_6$, Cs_2NaYCl_6 and Cs_2NaYBr_6 . The application of the modified theory [40,41] allows to take into account the influence of covalence effects and also to reduce a root-mean-square deviation of the theoretical data from the experimental. Besides, the considered theory allows to receive the parameters of distribution of electronic density (covalence parameters) on the basis of the description of Stark levels.

2. Theoretical Bases

The one-electron crystal field Hamiltonian [3]

$$H_{cf} = \sum_{k,q} B_q^k C_q^k \tag{1}$$

is usually used for the description of the Stark structure of multiplets in the approximation of the weak configuration interaction. Here, B_q^k are the crystal field parameters and

$C_q^k = \sum_{i=1}^N c_q^k(\vartheta_i, \varphi_i)$ is the spherical tensor of rank k, which acts on the angular variables of 4f-electrons.

Parameters of a crystal field are treated as fitting, or are calculated on a microscopic model. Root mean square deviation of the theoretical values received on (1) considerably exceeds the experimental errors [45-48]. Moreover, the Hamiltonian (1) sometimes does not allow to receive even a qualitative consent with experiment [49-51].

It is convenient to carry out the analysis of the experimental data by means of an effective Hamiltonian for polyatomic systems. An effective Hamiltonian acting in a basis of considerably lower dimensionality has the same eigenvalues as the actual Hamiltonian.

We will use the expression for matrix elements of the effective Hamiltonian, offered in [52]:

$$\begin{aligned} \langle n | H_{eff} | n' \rangle &\approx \langle n | H | n' \rangle + \\ &+ \sum_b \frac{\langle n | H_n | b \rangle \langle b | H_n | n' \rangle}{\Delta_{nb}} - \\ &- \sum_{b,n''} \frac{1}{2\Delta_{nb}\Delta_{nb}} (\langle n | H_n | b \rangle \langle b | H_n | n'' \rangle \langle n'' | W | n' \rangle + \\ &+ \langle n | W | n'' \rangle \langle n'' | H_n | b \rangle \langle b | H_n | n' \rangle) - \\ &- \sum_{b,n''} \frac{\langle n | H_n | b \rangle S_{bn''} \langle n'' | W | n' \rangle + \langle n | W | n'' \rangle S_{n''b} \langle b | H_n | n' \rangle}{\Delta_{nb}} \end{aligned} \tag{2}$$

Here $\langle n | H_n | b \rangle = \langle n | H | b \rangle - \langle n | H^0 | n \rangle \langle n | b \rangle$, W is a perturbation operator, H^0 is a nonperturbed Hamiltonian, n , n' , n'' and b represent the eigenstates of the ground and excited configuration, respectively.

In [52] the expression for an effective Hamiltonian of a crystal field in an approximation of the intermediate configuration interaction on the basis of an efficient Hamiltonian (2) in the third order of a perturbation theory is received:

$$H_{cf} = \sum_{k,q} \underbrace{B_q^k + (E_J + E_{J'} - 2E_f^0) G_q^k}_{\tilde{B}_q^k} C_q^k \tag{3}$$

where E_J and $E_{J'}$ are the multiplet energies, E_f^0 is the centroid of the $4f^N$ configuration, and G_q^k are the parameters related to the interconfiguration interaction.

The crystal field parameters B_q^k and the interconfiguration interaction parameters \tilde{G}_q^k specify the amplitude of terms with different functional dependences on the energy E_J . So they belong to different orthogonal operators, and can be unambiguously determined from the description of the Stark structure of the multiplets.

Note that if we set the interconfiguration interaction parameters \tilde{G}_q^k as equal to zero, then the expression (3) matches the crystal field Hamiltonian in the weak configuration interaction approximation (1).

Sometimes Hamiltonian in approximation of strong configuration interaction [53]

$$H_{cf} = \sum_{k,q} \underbrace{B_q^k + \left(\frac{\Delta^2}{\Delta - E_J} + \frac{\Delta^2}{\Delta - E_{J'}} \right) \tilde{G}_q^k}_{\tilde{B}_q^k} C_q^k \tag{4}$$

will be more adequate. Here Δ is the average energy of an excited configuration.

Formula (4) is valid if the interconfiguration-interaction parameters \tilde{G}_q^k are determined mainly by one excited configuration or several configurations with similar values of Δ .

The calculations carried out in approximation of the intermediate (3) and strong configuration interaction (4)

take into account the influence of excited configurations on the Stark structure of the crystal systems activated by f-elements. But for some systems the influence of excited configurations can be so strong (as for example for the elpasolites [40, 41]) that it is necessary to use the Hamiltonian received in the approximation of the anomalous strong configuration interaction [40,41] for its account :

$$H_{cf} = \sum_{k,q} \left\{ B_q^k + \left(\frac{\Delta_d^2}{\Delta_d - E_J} + \frac{\Delta_d^2}{\Delta_d - E_{J'}} \right) \tilde{G}_q^k(d) + \sum_i \left(\frac{\Delta_{ci}^2}{\Delta_{ci} - E_J} + \frac{\Delta_{ci}^2}{\Delta_{ci} - E_{J'}} \right) \tilde{G}_q^k(c) \right\} C_q^k \quad (5)$$

Here, $\tilde{G}_q^k(d)$ and $\tilde{G}_q^k(c)$ are additional parameters due to the excited configuration $4f^{N-1}5d$ and the covalent effects, respectively.

The parameters \tilde{G}_q^k are normally determined by configurations of the opposite parity $4f^{N-1}5d$ and configurations with charge transfer. But as the ion Pr³⁺ takes central-symmetrical positions in cubic elpasolites Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆, the addend $\left(\frac{\Delta_d^2}{\Delta_d - E_J} + \frac{\Delta_d^2}{\Delta_d - E_{J'}} \right) \tilde{G}_q^k(d)$ which corresponds to the configuration of the opposite parity, is equal to zero and in this case the Hamiltonian (5) can be presented as follows:

$$H_{cf} = \sum_{k,q} \left\{ B_q^k + \sum_i \left(\frac{\Delta_{ci}^2}{\Delta_{ci} - E_J} + \frac{\Delta_{ci}^2}{\Delta_{ci} - E_{J'}} \right) \tilde{G}_q^k(c) \right\} C_q^k \quad (6)$$

For parameter $\tilde{G}_q^k(c)$ the following expression is [53]:

$$\tilde{G}_q^k(c) = \sum_b \tilde{J}^k(b) C_q^{k*}(\Theta_b, \Phi_b) \quad (7)$$

and for parameters $\tilde{J}^k(b)$, it is convenient to use the following approximate expressions [54]:

$$\begin{aligned} \tilde{J}^2(b) &\approx \frac{5}{28} [2\gamma_{cf}^2 + 3\gamma_{\pi f}^2] \\ \tilde{J}^4(b) &\approx \frac{3}{14} [3\gamma_{cf}^2 + \gamma_{\pi f}^2] \\ \tilde{J}^6(b) &\approx \frac{13}{28} [2\gamma_{cf}^2 - 3\gamma_{\pi f}^2] \end{aligned} \quad (8)$$

Here, γ_{cf} and $\gamma_{\pi f}$ are the covalence parameters corresponding to an electron jumping from the shell of the

ligand to the f-shell of the Ln³⁺ ion.

In the Hamiltonian (6) only the contribution from the processes with charge transfer is taken into account.

3. Results and Discussion

In the elpasolites Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆ the ion Pr³⁺ takes positions with the local symmetry O_h. The Hamiltonian (1) has two parameters of the crystal field B_0^4 and B_0^6 . In addition, there are parameters Δ_{ci} corresponding to the energy of the configuration with a charge transfer, and also parameters of the covalence γ_{cf} and $\gamma_{\pi f}$ (8) appear in the approximation of the anomalous strong configuration interaction (6). For these systems calculations have been accomplished in the approximation of the weak (1) and anomalous strong configuration interaction (6). It is shown in all cases that the accuracy of the description in the approximation of the weak configuration interaction is not satisfactory as the deviation of the theoretical data from the experimental is rather substantial.

Thirty seven experimental levels out of forty [42] are known for the elpasolite Cs₂NaPrCl₆, but in the article [42] nine levels are excluded from calculations. In our calculations using the offered Hamiltonian (6) it is possible to reduce a root-mean-square deviation by 49% in comparison with the approximation of the weak configuration interaction and thus to include four more values of energy in the calculations (table 1).

Thirty two experimental levels are given for the system Cs₂NaYCl₆, seven values are excluded from calculations [42]. The offered theory improves the description by 61% and thus only four levels of energy are excluded from the minimization procedure (table 1).

In the article [42] twenty six experimental values of energy are given for the elpasolite Cs₂NaYBr₆; two levels are excluded from calculations. The calculations implemented by means of the Hamiltonian (6) allow to reduce a root-mean-square deviation of the theoretical data from experimental by 67% and thus allow to use all the experimental values of energy given in the article [42] (table 1).

The values of parameters of the crystal field B_0^4 and B_0^6 for all systems, obtained from the procedure of minimization in the approximation of the weak configuration interaction slightly differ from the corresponding parameters obtained in the approximation of anomalous strong configuration interaction (table 2 and table 3). It means that new operational forms of the Hamiltonian (6) describe effects which are not represented in the Hamiltonian (1).

Table 1. The comparison of the experimental [42] and calculated levels of energy in the approximation of the weak (1) and anomalous strong configuration interaction (6) for the crystal systems Cs₂NaPrCl₆:Pr³⁺, Cs₂NaYCl₆:Pr³⁺ and Cs₂NaYBr₆:Pr³⁺. All quantities are given in cm⁻¹

Cs ₂ NaPrCl ₆ :Pr ³⁺				Cs ₂ NaYCl ₆ :Pr ³⁺				Cs ₂ NaYBr ₆ :Pr ³⁺			
^s L _J	E _{expt} , [42]	E _{calc1} (1)	E _{calc2} (6)	^s L _J	E _{expt} , [42]	E _{calc1} (1)	E _{calc2} (6)	^s L _J	E _{expt} , [42]	E _{calc1} (1)	E _{calc2} (6)
³ H ₄	0	58.9	12.7	³ H ₄	0	19.2	0.6	³ H ₄	0	48.1	-0.9
	236	262.4	251.3		245	247.0	248.6		224	236.7	217.1
	422	404.4	419.5		428	402.2	422.8		378	370.3	371.3
	701	642.1	688.3		721	701.8	720.4		618	569.9	618.9
³ H ₅	2300	2335.9	2307.6	³ H ₅	2300	2307.7	2297.1	³ H ₅	2281	2313.3	2280.4
	2400	2435.9	2417.0		2404	2410.5	2411.8		2367	2410.8	2388.7
	2643	2620.3	2625.8		2648	2641.5	2641.7		2589	2566.3	2586.1
	2740	2704.1	2732.4		2748	2740.3	2750.9		2674	2641.7	2674.6
³ H ₆	4392	4409.6	4370.6	³ H ₆	4385	4368.2	4389.4	³ H ₆	4374	4394.6	4386.6
	4437	4453.6	4423.4		4438	4422.9	4437.1		4439	4431.9	4424.7
	4567*	4633.0	4640.6		4574*	4610.8	4621.4		-	4606.7	4595.2
	4682*	4754.9	4758.7		4687*	4771.9	4735.5		-	4703.7	4689.3
	4807	4828.3	4854.2		4811	4853.0	4819.9		4747	4771.2	4766.5
	4878	4860.4	4899.4		4866	4882.8	4861.6		4824	4803.4	4811.4
³ F ₂	5203	5217.4	5210.7	³ F ₂	5204	5217.2	5219.4	³ F ₂	5127	5141.5	5139.6
	5294	5279.6	5286.3		5303	5289.8	5287.6		5212	5197.5	5199.4
³ F ₃	6613	6618.7	6615.4	³ F ₃	-	6621.7	6614.7	³ F ₃	-	6534.9	6537.0
	6618	6626.9	6628.7		6619	6625.7	6624.2		6546	6546.0	6546.0
	6679	6673.3	6676.6		6682	6675.3	6676.8		-	6589.8	6598.9
³ F ₄	6964	6965.3	6969.8	³ F ₄	6966	6940.1	6968.6	³ F ₄	6908	6899.4	6910.9
	7011	7010.9	7002.3		7010	6995.3	7015.7		6952	6938.2	6948.2
	7055	7035.2	7018.3		7050	7024.9	7039.0		-	6958.7	6965.9
	7279	7277.7	7273.2		7281	7306.9	7278.4		7168	7176.6	7165.1
¹ G ₄	9853	9792.3	9847.6	¹ G ₄	-	9815.4	9817.8	¹ G ₄	9824	9759.5	9823.9
	-	9858.4	9891.7		-	9915.7	9905.2		-	9803.8	9851.0
	9899	9895.4	9912.8		-	9974.6	9952.4		9861	9826.9	9862.3
	10325	10385.7	10330.4		-	10538.6	10559.7		10208	10272.5	10208.1
¹ D ₂	16671	16736.4	16665.5	¹ D ₂	16647	16680.5	16645.2	¹ D ₂	16608	16608.0	16608.0
	17257	17191.6	17262.5		17255	17221.5	17256.8		-	17010.3	17075.3
³ P ₀	20624	20624.0	20624.0	³ P ₀	20600	20600.0	20600.0	³ P ₀	20486	20486.0	20486.0
³ P ₁	21221	21263.6	21236.0	³ P ₁	21197	21183.3	21197.9	³ P ₁	21091	21091.0	21091.0
¹ I ₆	21164	21164.0	21164.0	¹ I ₆	21139	21139.0	21139.0	¹ I ₆	21131	21131.0	21131.0
	21529*	21357.1	21358.8		21470*	21344.1	21342.5		-	21173.5	21201.6
	21863*	21462.8	21454.3		-	21411.3	21421.9		-	21271.5	21304.6
	21962*	21828.9	21841.3		21972*	21854.8	21838.3		-	21589.6	21681.9
	22036	21993.4	22021.0		22028	22041.7	22027.1		-	21740.3	21852.3
	-	22043.0	22073.9		-	22098.4	22083.7		-	21785.2	21902.3
³ P ₂	22368	22386.5	22382.0	³ P ₂	22347	22354.9	22356.1	³ P ₂	22229	22229.0	22229.0
	22494	22475.5	22480.0		22471	22463.1	22461.9		-	22306.5	22320.6
¹ S ₀	-	46912.8	46913.5	¹ S ₀	-	46917.7	46918.3	¹ S ₀	-	46910.2	46910.2
σ		34.1	17.3	σ		19.2	7.4	σ		29.7	9.8

Note: * Hereinafter – the levels which are not included into the procedure of quadratic adjustment.

Table 2. The parameters of the Hamiltonian of the crystal field (1), calculated in the approximation of the weak configuration interaction.

	B_0^4, cm^{-1}	B_0^6, cm^{-1}
Cs ₂ NaPrCl ₆	1787	216
Cs ₂ NaYCl ₆	2128	220
Cs ₂ NaYBr ₆	1578	216

Table 3. The parameters of the Hamiltonian of the crystal field (6), calculated in the approximation of the anomalous strong configuration interaction.

	Cs ₂ NaPrCl ₆	Cs ₂ NaYCl ₆	Cs ₂ NaYBr ₆
B_0^4, cm^{-1}	2043	2199	1869
B_0^6, cm^{-1}	264	263	237
γ_{of}	-0.0219	-0.0213	-0.0241
$\gamma_{\pi f}$	0.0136	0.0136	0.0163
$\Delta_{c1}, \text{cm}^{-1}$	6871	4753	4722
$\Delta_{c2}, \text{cm}^{-1}$	9926	6964	6967
$\Delta_{c3}, \text{cm}^{-1}$	18129	18849	9900

It has been revealed earlier that a considerable improvement of the Stark structure of some multiplets is achieved, if the values of parameters Δ_{ci} are close to energies of these multiplets [41]. As the results of quadratic adjustment for systems Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆, such values of parameters Δ_{ci} (table 3) have been gained that correspond to low located multiplets (table 1), which does not contradict the deductions made earlier [41].

An important feature of the offered theory is that the covalence parameters act as varied parameters in calculations. The covalence parameters for Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆ received this way (table 3), perfectly comply with the parameters given for chlorides [55]: $\gamma_{of} = -0.0222$ and $\gamma_{\pi f} = 0.0092$. Besides in the article [41] there are given the covalence parameters, calculated for the crystal system Cs₂NaYCl₆:Tm³⁺ with the help of the viewed theory, they have the values close to those obtained for Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆ (table 3). Thus, it is possible to determine parameters of covalence which are usually obtained in experiments on double electron-nuclear resonance or counted by means of microscopic models basing on experimental data of optical spectroscopy.

4. Conclusions

The executed calculations allow to assert that the proposed theory of the crystal field [40,41] can be successfully applied for the description of Stark structure of the cubic elpasolites Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆, activated by ions Pr³⁺ as substantial reduction

of a root-mean-square deviation of the theoretical data from the experimental is observed for all systems.

An important feature of the proposed theory includes the fact that covalence parameters that describe the degree of electron-density shift from one ion to another appeared to be variable in the calculations. Covalence parameters are usually calculated using wave functions. However, a set of the corresponding functions for the examined system is necessary for this. Furthermore, such calculations are very unwieldy and laborintensive and present a separate problem.

The covalence parameters obtained by describing the Stark structure using the examined theory for Cs₂NaPrCl₆, Cs₂NaYCl₆ and Cs₂NaYBr₆ agreed satisfactorily with the parameters of covalence received by means of microscopic models [55]. Thus, the covalence parameters, which are usually obtained in double electron-nuclear resonance experiments or are calculated using microscopic models, can be determined from experimental optical spectroscopic data.

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