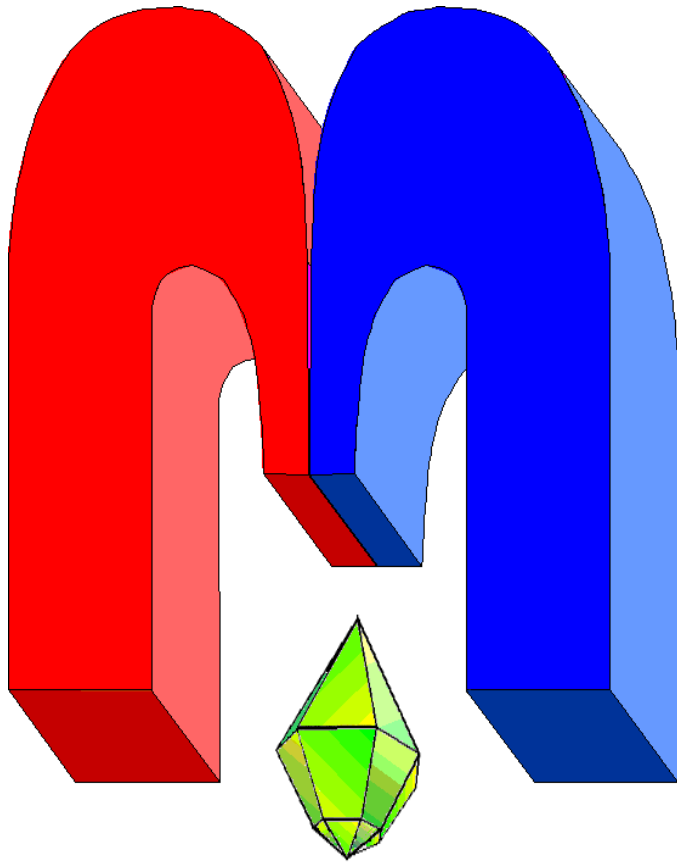


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In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Study of the crystal field in CeF_3 and $\text{CeF}_3:\text{Pr}^{3+}$

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The crystal field analysis based on calculations in the framework of the semi phenomenological exchange charge model was carried out. The set of crystal field parameters for Ce^{3+} and Pr^{3+} ions in the matrix CeF_3 related to the crystallographic system of coordinates has been obtained and used to reproduce satisfactory the crystal field energies of Ce^{3+} and Pr^{3+} ions.

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1. Introduction

The rare-earth trifluorides CeF_3 in the tysonite structure have been studied in the past as a model system for testing theories of rare-earth magnetism in insulators [1-3] and due to their prospects for applications. In recent years interest in the study of rare-earth trifluorides RF_3 (R is rare-earth ion Ce, Pr,...) has returned thanks to advances in the fabrication of nanoparticles of pure rare-earth fluorides RF_3 and rare-earth ions doped nanoparticles as well (see, for example, [4-8]). The great interest appeared due to potential applications of the nanosized materials in high resolution displaying, electroluminescent devices and markers for biomolecules. Knowledge of the crystal field parameters is important in describing magnetic and optical properties of trifluorides, as well as for the investigation of trifluorides by resonance methods (¹⁹F NMR, rare-earth NMR, EPR).

In the present work data about Ce^{3+} and Pr^{3+} optical energy spectra in CeF_3 host [9, 10] taken from literature have been analyzed in the framework of the crystal field theory. We have found sets of the crystal field parameters (CFP) for the Ce^{3+} and Pr^{3+} ions which describe satisfactory Stark energies of the rare-earth ions in CeF_3 matrix.

2. Discussion

The space group of the tysonite lattice RF_3 (R = Ce, Pr) has been the subject of controversial discussions over decades. Only recently this question has been settled in favor of the microtweened trigonal D_{3d}^4 ($P\bar{3}c1$) structure [11-13]. Assuming microtweened trigonal D_{3d}^4 structure, the R^{3+} ion has C_2 site symmetry and there are six formula units per one cell. The parameters of the CeF_3 crystal cell are $a = 0.7112$ nm, $c = 0.7279$ nm, $p = 0.6602$ [11, 14]. The rare-earth ion with the crystallographic coordinates ($ap0\ c/4$). The same parameters describe the crystal fields acting on the $\text{Ce}^{3+}/\text{Pr}^{3+}$ ions at the sites ($-ap\ -ap\ c/4$), ($0\ -ap\ -c/4$) with the local coordinate systems rotated by $2\pi/3$ and $4\pi/3$, respectively, around the c -axis; at the three other sites with the local coordinate systems rotated by $\pi/3$, π and $5\pi/3$, the crystal fields are described by the same complex conjugated parameters. Atomic parameters of CeF_3 (D_{3d}^4 structure) are presented in Table 1 [11].

The parameters of the electrostatic interaction of the open 4f-shell electron belonging to the rare-earth ion in CeF_3 , with the charges of the ions of the CeF_3 crystal lattice, in the first approximation can be represented as a sum of terms, corresponding to the interaction of the point charges with the electric fields:

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Table 1. Experimental values of atomic positions in the CeF₃ in the D_{3d}^4 phase.

| Atom | x | y | z |
|------|--------|--------|--------|
| Ce | 0.6602 | 0 | 0.25 |
| F1 | 0.3659 | 0.0537 | 0.0814 |
| F2 | 0.3333 | 0.6667 | 0.1867 |
| F3 | 0 | 0 | 0.25 |

$$B_q^{(pc)k} = -\sum_L \frac{e^2 q_L (1 - \sigma_k^{nl}) \langle r^k \rangle (-1)^q C_{-q}^{(k)}(\theta_L, \varphi_L)}{R_L^{k+1}}, \quad (1)$$

where eq_L is the charge of the ligand, L ; θ_L and φ_L are angles in a spherical coordinate system with the origin at the nucleus of the rare-earth ion; R is the distance from the rare-earth ion to the ligand L . The values of the moments of the spatial density of the Ce³⁺ 4f-electrons are $\langle r^2 \rangle = 1.120$, $\langle r^4 \rangle = 3.455$, $\langle r^6 \rangle = 21.226$ a.u. [15] and of the Pr³⁺ 4f-electrons are $\langle r^2 \rangle = 1.086$, $\langle r^4 \rangle = 2.822$, $\langle r^6 \rangle = 15.726$ a.u. [15]; σ_k^{nl} are the shielding factors.

In order to correct the Coulomb interaction for the spatial distribution of the ligand charges, we used the semi phenomenological exchange charge model [16]:

$$B_q^{(ec)k} = \sum_L \frac{2(2k+1)}{2l+1} \cdot \frac{e^2}{R_L} \cdot S_k^{nl}(R_L) (-1)^q C_{-q}^{(k)}(\theta_L, \varphi_L), \quad (2)$$

Where S_k^{nl} represents the bilinear forms of overlap integrals for the wave functions of the Ce³⁺/Pr³⁺ ion's 4f-valence electrons, and the wave functions of the 2s, 2p-electrons of the ligand ions (F):

$$S_k^{nl} = G_s |S_s^{nl}|^2 + G_\sigma |S_\sigma^{nl}|^2 + G_\pi \gamma_k |S_\pi^{nl}|^2 \quad (3)$$

Here $S_s^{nl}(R_L) = \langle nl0 | n''00 \rangle$, $S_\sigma^{nl}(R_L) = \langle nl0 | n''10 \rangle$, $S_\pi^{nl}(R_L) = \langle nl1 | n''11 \rangle$, the coefficients $\gamma_2 = 3/2$, $\gamma_4 = 1/3$, $\gamma_6 = -3/2$ for 4f-электронов (n and l are quantum numbers). G_s , G_σ и G_π are the parameters of the model with initial values $G_s = 1.0$, $G_\sigma = 5.0$, $G_\pi = 1.5$ for Pr³⁺ [1] and $G_s = 1.0$, $G_\sigma = 4.0$, $G_\pi = 1.0$ for Ce³⁺ ion.

Then the crystal field parameters were calculated as the sum of the inputs determined by expressions (1) and (2):

$$B_q^k = B_q^{(pc)k} + B_q^{(ec)k}. \quad (4)$$

The calculated values for the crystal field parameters for Ce³⁺ ion in CeF₃ are shown in Table 2 (column "CeF₃ calc."), the CFP for Pr³⁺ ions in CeF₃ host are shown in Table 2 (column "CeF₃:Pr calc."). Finally, the sets of CF parameters are obtained by varying the calculated values to minimize the squared deviation of the theoretically obtained energy values of the experimentally defined energy sublevels of multiplets for Ce³⁺ ions in CeF₃ [9] and for Pr³⁺ ions in CeF₃:Pr³⁺ [10]. The experimentally defined and calculated energy levels for CeF₃ and CeF₃:Pr³⁺ are represented in Table 3 and Table 4, correspondingly. The final sets of CF parameters for Ce³⁺ and Pr³⁺ ions are represented in the Table 2 in columns "CeF₃ fit." and "CeF₃:Pr fit.". Also the CP parameters fitted for Pr³⁺ ion in PrF₃ and adjusted to CeF₃ by Gerlinger and Schaack [9] are represented in column "CeF₃ ref."

Calculations of the Ce³⁺ in and Pr³⁺ electron energies in CeF₃ were performed over a complete basis of electron states of the rare-earth ions (14 states for Ce³⁺ and 91 states for Pr³⁺), using the Hamiltonian:

$$H = H_{fi} + \sum_{k,q} B_q^{(k)} C_q^{(k)}. \quad (5)$$

Here, the first term represents the energy of the free ion. The constants of the electrostatic and spin-orbital interaction for Pr³⁺ ion were accepted as being relatively equal F2 = 69360 cm⁻¹, F4 = 50626 cm⁻¹, F6 = 32633 cm⁻¹, $\xi = 726$ cm⁻¹ (initial values in Ref. [17]), the parameters of configuration interactions were taken from [17]. Spin-orbital constant for Ce³⁺ was taken as $\xi = 628.5$ cm⁻¹ [9].

Table 2. The CP parameters (in cm⁻¹) used to calculate the Ce³⁺ and Pr³⁺ energy levels.

| <i>k, q</i> | CeF ₃ ref. | CeF ₃ calc. | CeF ₃ fit. | CeF ₃ :Pr calc. | CeF ₃ :Pr fit. |
|-------------|-----------------------|------------------------|-----------------------|----------------------------|---------------------------|
| 2 0 | -285 | -104 | -193 | -103 | -215 |
| 2 2 Re | -121 | 23 | -67 | 22 | 38 |
| 2 2 Im | 0 | 5.7 | 0 | 5.2 | 15 |
| 4 0 | 755 | 699 | 637 | 614 | 855 |
| 4 2 Re | 379 | 485 | 413 | 429 | 356 |
| 4 2 Im | 230 | 131 | 160 | 115 | 128 |
| 4 4 Re | 537 | 508 | 500 | 451 | 300 |
| 4 4 Im | 410 | 263 | 660 | 231 | 182 |
| 6 0 | 634 | 721 | 974 | 620 | 560 |
| 6 2 Re | -1316 | -1103 | -1581 | -944 | -1315 |
| 6 2 Im | -70 | -81 | -55 | -68 | -75 |
| 6 4 Re | -26 | -156 | -78 | -133 | -150 |
| 6 4 Im | -609 | -508 | -922 | -436 | -634 |
| 6 6 Re | -596 | -604 | -675 | -517 | -559 |
| 6 6 Im | -827 | -638 | -754 | -589 | -500 |

Table 3. Experimentally defined energy levels of the Ce³⁺ in CeF₃ [9] (“CeF₃ exp.”) and calculated (“CeF₃ calc.”) with parameter set from column “CeF₃ fit.” of Table 2.

| ^{2S+1} L _J | CeF ₃ exp. | CeF ₃ calc. |
|--------------------------------|-----------------------|------------------------|
| ² F _{5/2} | 0 | 0 |
| | ≈160 | 154 |
| | ≈280 | 277 |
| ² F _{7/2} | 2161 | 2277 |
| | 2239 | 2374 |
| | 2640 | 2667 |
| | 2860 | 2787 |

Table 4. Experimentally defined energy levels of the Pr³⁺ in CeF₃ [10] (“CeF₃:Pr exp.”) and calculated (“CeF₃:Pr calc.”) with parameter set from column “CeF₃:Pr fit.” of Table 2.

| $^{2S+1}L_J$ | CeF ₃ :Pr exp. | CeF ₃ :Pr calc. | $^{2S+1}L_J$ | CeF ₃ :Pr exp. | CeF ₃ :Pr calc. |
|-----------------------------|---------------------------|----------------------------|-----------------------------|---------------------------|----------------------------|
| ³ H ₄ | 0 | 0 | ¹ I ₆ | 21482 | 21527 |
| | 49 | 59 | | 21542 | 21553 |
| | 110 | 112 | | 21580 | 21580 |
| | 184 | 172 | | | 21596 |
| | 244 | 240 | | | 21611 |
| | 261 | 269 | | 21626 | 21614 |
| | | 324 | | | 21650 |
| | | 489 | | | 21693 |
| | | 525 | | | 21748 |
| | | | | | |
| ¹ D ₂ | 16818 | 16816 | | | 21809 |
| | 16841 | 16841 | | | 21999 |
| | 16906 | 16909 | | | 22031 |
| | | 16930 | | | |
| | | 17100 | | | |
| ³ P ₀ | 20991 | 20961 | ³ P ₂ | 22701 | 22692 |
| | | | | 22743 | 22735 |
| | | | | | 22754 |
| | | | | | 22770 |
| ³ P ₁ | 21413 | 21400 | | 22838 | 22843 |
| | 21432 | 21428 | | | |
| | 21450 | 21459 | | | |

3. Conclusion

This paper presents a calculation of CF parameters for the Ce³⁺ and Pr³⁺ ions in CeF₃ crystal, using the semi phenomenological model of exchange charges. The calculated CF parameters were in good agreement with the previously determined CF parameters for CeF₃ trifluoride. Obtained parameters allow for a satisfactory description of the Ce³⁺ and Pr³⁺ energy levels in CeF₃ host determined earlier. The standard deviation of the calculated energies of the Pr³⁺ ion from the experimental values is less than ~15 cm⁻¹, however the standard deviation for Ce³⁺ ion is about 66 cm⁻¹. As it is seen, results of our calculations based on the set of the crystal field parameters which has been obtained in this study are in qualitative agreement with the experimental data.

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