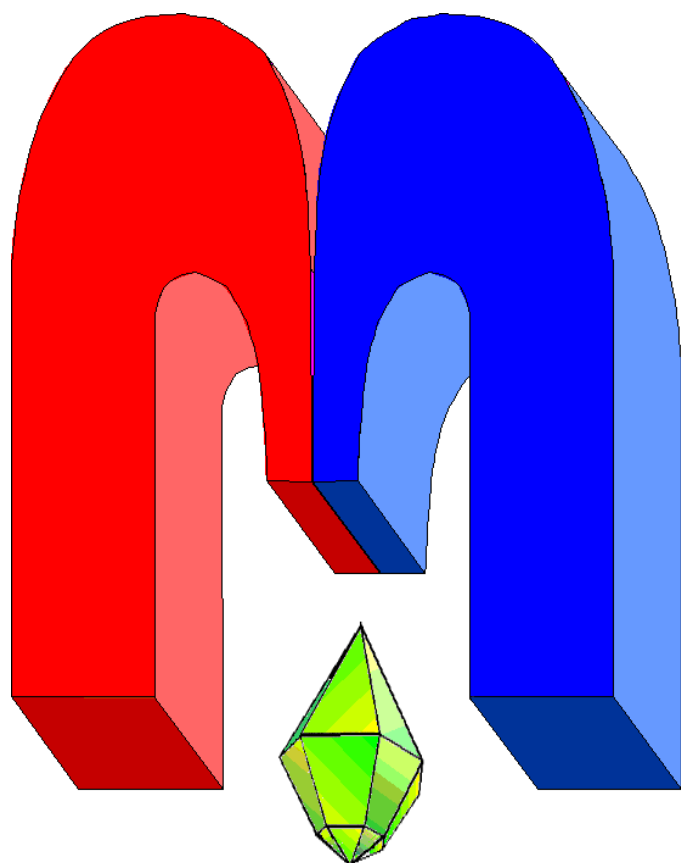


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In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Crystal field parameters and g -factors of the ground Kramers doublet of Ce^{3+} ion in LiYF_4 crystal

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Analytical expressions are obtained for g -factors of the ground Kramers doublet of the impurity Ce^{3+} ions in LiYF_4 crystal that rigorously take into account mixing of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets by crystal field. Dependence of g -factors on crystal field parameters is studied and possibilities of making conclusions about crystal field parameters values on the basis of comparison with g -factors given in literature are considered.

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1. Introduction

Impurity Ce^{3+} ions substitute for Y^{3+} ions in LiYF_4 crystal in sites with S_4 point symmetry, in the nearest surrounding of the Y-site there are eight fluorine ions which form two deformed tetrahedrons. Spectrum of the Ce^{3+} ion $4f^1$ configuration consists of 7 Kramers doublets – ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets splitted by S_4 symmetry crystal field. Safe values of crystal field parameters for the Ce^{3+} ion in LiYF_4 crystal are absent in literature due to difficulties in measuring of $4f$ crystal field energies for this compound. However, g -factors for the ground level of the Ce^{3+} ion in LiYF_4 crystal were measured in [1, 2].

The goals of the present theoretical study are: 1) to derive analytical expressions for g -factors of the ground Kramers doublet of the Ce^{3+} ion in crystal field of tetragonal symmetry S_4 , rigorously taking into account mixing of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets by crystal field (unlike earlier papers, for example [2, 3], in which such a mixing was neglected and only the ground ${}^2F_{5/2}$ multiplet was considered); 2) to investigate dependence of g -factors on crystal field parameters; 3) to consider possibility of making conclusions about $4f$ crystal field parameters values for the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal on the basis of comparison with the g -factors values for this compound measured in literature.

2. Analytical expressions for g -factors of the Ce^{3+} ion in crystal field of tetragonal symmetry S_4

We consider an effective Hamiltonian H of the impurity Ce^{3+} ion consisting of spin-orbit interaction Hamiltonian

$$H_{\text{SO}} = \xi \mathbf{S} \mathbf{L}, \quad (1)$$

where ξ is a $4f$ electron spin-orbit coupling constant, \mathbf{S} and \mathbf{L} are the spin and angular momentum of the $4f$ electron, and Hamiltonian of interaction with the S_4 symmetry crystal field [4] (in crystallographic axes)

$$H_{\text{CF}} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_4^4 C_4^{(4)} + B_{-4}^4 C_{-4}^{(4)} + B_0^6 C_0^{(6)} + B_4^6 C_4^{(6)} + B_{-4}^6 C_{-4}^{(6)}, \quad (2)$$

where B_k^p are crystal field parameters, satisfying the equation $B_k^{p*} = (-1)^k B_{-k}^p$; $C_k^{(p)}$ are components of one-electron spherical tensor operators $\mathbf{C}^{(p)}$. Note that there are only eight independent real quantities defining the effective Hamiltonian for the $4f$ electron in our model.

It is convenient to consider eigenfunctions $|J, J_z\rangle$ of the spin-orbit interaction Hamiltonian H_{SO} as a basis; here J and J_z are quantum numbers for the total momentum \mathbf{J} of the $4f$ electron. Let us express these eigenfunctions through the one-electron wavefunctions $|m, \sigma\rangle$, where m and σ are the

magnetic and spin quantum numbers of the 4f electron:

$$\begin{aligned} \left| \frac{5}{2}, \pm \frac{5}{2} \right\rangle &= \pm \sqrt{\frac{1}{7}} |\pm 2, \pm\rangle \mp \sqrt{\frac{6}{7}} |\pm 3, \mp\rangle, \quad \left| \frac{5}{2}, \pm \frac{3}{2} \right\rangle = \pm \sqrt{\frac{2}{7}} |\pm 1, \pm\rangle \mp \sqrt{\frac{5}{7}} |\pm 2, \mp\rangle, \\ \left| \frac{5}{2}, \pm \frac{1}{2} \right\rangle &= \pm \sqrt{\frac{3}{7}} |0, \pm\rangle \mp \sqrt{\frac{4}{7}} |\pm 1, \mp\rangle, \quad \left| \frac{7}{2}, \pm \frac{7}{2} \right\rangle = -|\pm 3, \pm\rangle, \quad \left| \frac{7}{2}, \pm \frac{5}{2} \right\rangle = -\sqrt{\frac{6}{7}} |\pm 2, \pm\rangle - \sqrt{\frac{1}{7}} |\pm 3, \mp\rangle, \\ \left| \frac{7}{2}, \pm \frac{3}{2} \right\rangle &= -\sqrt{\frac{5}{7}} |\pm 1, \pm\rangle - \sqrt{\frac{2}{7}} |\pm 2, \mp\rangle, \quad \left| \frac{7}{2}, \pm \frac{1}{2} \right\rangle = -\sqrt{\frac{4}{7}} |0, \pm\rangle - \sqrt{\frac{3}{7}} |\pm 1, \mp\rangle. \end{aligned} \quad (3)$$

Let us consider rigorously splitting of the multiplets $J = \frac{5}{2}$ (ground multiplet) and $J = \frac{7}{2}$ by crystal field, taking into account mixing of states of these multiplets. There is no need to fulfill numerical diagonalization of the full matrix of the Ce^{3+} ion Hamiltonian $H = H_{SO} + H_{CF}$ in the basis $|J, J_z\rangle$. Looking ahead, we may state that it follows from calculations that the largest contribution to wavefunctions of the ground 4f Kramers doublet of the Ce^{3+} ion in $LiYF_4$ comes from the $\left| \frac{5}{2}, \pm \frac{5}{2} \right\rangle$ states (let us also note that the ground doublet corresponds to irreducible representations Γ_5 and Γ_6 of the double S_4 point group in Bethe notation; the first excited and second excited 4f levels have symmetries (Γ_7, Γ_8) and (Γ_5, Γ_6) respectively). The state $\left| \frac{5}{2}, \frac{5}{2} \right\rangle$ is mixed by crystal field interaction H_{CF} (2) only with the states $\left| \frac{5}{2}, -\frac{3}{2} \right\rangle$, $\left| \frac{7}{2}, \frac{5}{2} \right\rangle$ and $\left| \frac{7}{2}, -\frac{3}{2} \right\rangle$. Thus, it is sufficient to numerically diagonalize a matrix 4×4 of the Ce^{3+} ion Hamiltonian $H = H_{SO} + H_{CF}$ (see (1) and (2)) with the following elements:

$$\begin{aligned} \left\langle \frac{5}{2}, \frac{5}{2} \right| H \left| \frac{5}{2}, \frac{5}{2} \right\rangle &= -2\xi - \frac{6}{21} B_0^2 + \frac{1}{21} B_0^4, \quad \left\langle \frac{5}{2}, -\frac{3}{2} \right| H \left| \frac{5}{2}, -\frac{3}{2} \right\rangle = -2\xi + \frac{2}{35} B_0^2 - \frac{1}{7} B_0^4, \\ \left\langle \frac{7}{2}, \frac{5}{2} \right| H \left| \frac{7}{2}, \frac{5}{2} \right\rangle &= \frac{3}{2} \xi - \frac{1}{21} B_0^2 - \frac{13}{77} B_0^4 + \frac{25}{429} B_0^6, \quad \left\langle \frac{7}{2}, -\frac{3}{2} \right| H \left| \frac{7}{2}, -\frac{3}{2} \right\rangle = \frac{3}{2} \xi + \frac{1}{7} B_0^2 - \frac{3}{77} B_0^4 - \frac{15}{143} B_0^6, \\ \left\langle \frac{5}{2}, \frac{5}{2} \right| H \left| \frac{5}{2}, -\frac{3}{2} \right\rangle &= \frac{\sqrt{14}}{21} B_0^4, \quad \left\langle \frac{5}{2}, \frac{5}{2} \right| H \left| \frac{7}{2}, \frac{5}{2} \right\rangle = -\frac{\sqrt{6}}{21} B_0^2 + \frac{10\sqrt{6}}{231} B_0^4 - \frac{5\sqrt{6}}{429} B_0^6, \\ \left\langle \frac{5}{2}, \frac{5}{2} \right| H \left| \frac{7}{2}, -\frac{3}{2} \right\rangle &= \frac{4\sqrt{35}}{231} B_0^4 - \frac{10\sqrt{7}}{143} B_0^6, \quad \left\langle \frac{5}{2}, -\frac{3}{2} \right| H \left| \frac{7}{2}, \frac{5}{2} \right\rangle = -\frac{8\sqrt{21}}{231} B_0^4 - \frac{10\sqrt{105}}{429} B_0^6, \\ \left\langle \frac{5}{2}, -\frac{3}{2} \right| H \left| \frac{7}{2}, -\frac{3}{2} \right\rangle &= \frac{\sqrt{10}}{35} B_0^2 + \frac{8\sqrt{10}}{231} B_0^4 - \frac{5\sqrt{10}}{143} B_0^6, \quad \left\langle \frac{7}{2}, \frac{5}{2} \right| H \left| \frac{7}{2}, -\frac{3}{2} \right\rangle = \frac{\sqrt{210}}{77} B_0^4 + \frac{5\sqrt{42}}{429} B_0^6. \end{aligned} \quad (4)$$

Numerically diagonalizing the matrix with the elements (4) we obtain one of the wavefunctions of the ground Kramers doublet of the Ce^{3+} ion in $LiYF_4$ in the form

$$|\psi_1\rangle = \frac{1}{N} \left(\left| \frac{5}{2}, \frac{5}{2} \right\rangle + \alpha \left| \frac{5}{2}, -\frac{3}{2} \right\rangle + \beta \left| \frac{7}{2}, \frac{5}{2} \right\rangle + \gamma \left| \frac{7}{2}, -\frac{3}{2} \right\rangle \right), \quad N = \sqrt{1 + |\alpha|^2 + |\beta|^2 + |\gamma|^2}. \quad (5)$$

In (5) $|\alpha| < 1$, $|\beta| < 1$, $|\gamma| < 1$ and, since the ${}^2F_{7/2}$ multiplet is separated by the energy $\frac{7}{2}\xi$ from the ${}^2F_{5/2}$ multiplet, it is expected that $|\beta| < |\alpha|$, $|\gamma| < |\alpha|$. The second wavefunction of the ground Kramers

doublet of the Ce^{3+} ion in $LiYF_4$ can be obtained from (5) as

$$|\psi_2\rangle = \hat{\theta}|\psi_1\rangle = \frac{1}{N} \left(\left| \frac{5}{2}, -\frac{5}{2} \right\rangle + \alpha^* \left| \frac{5}{2}, \frac{3}{2} \right\rangle - \beta^* \left| \frac{7}{2}, -\frac{5}{2} \right\rangle - \gamma^* \left| \frac{7}{2}, \frac{3}{2} \right\rangle \right), \quad (6)$$

where $\hat{\theta}$ is the time reversal operator [5]. The wavefunction $|\psi_2\rangle$ can also be obtained directly by diagonalization of the Ce^{3+} ion Hamiltonian H matrix in the basis $\left| \frac{5}{2}, -\frac{5}{2} \right\rangle, \left| \frac{5}{2}, \frac{3}{2} \right\rangle, \left| \frac{7}{2}, -\frac{5}{2} \right\rangle, \left| \frac{7}{2}, \frac{3}{2} \right\rangle$ with elements similar to (4) but with the opposite signs of crystal field parameters components and the matrix elements cross between $J = \frac{5}{2}$ and $J = \frac{7}{2}$ states taken with the opposite signs themselves.

Now let us consider the Zeeman energy

$$H_{Ze} = \mu_B (2\mathbf{S} + \mathbf{L}) \mathbf{H}, \quad (7)$$

where $\mathbf{H} = (H_x, H_y, H_z)$ is magnetic field, μ_B is the Bohr magneton. In the basis of the Ce^{3+} ion ground Kramers doublet states the Zeeman energy can be represented as

$$H_{Ze} = \mu_B g_{\parallel} S_z^{\text{eff}} H_z + \mu_B g_{\perp} (S_x^{\text{eff}} H_x + S_y^{\text{eff}} H_y), \quad (8)$$

where \mathbf{S}^{eff} is the effective spin operator with $S = 1/2$, g_{\parallel} and g_{\perp} are g -factors when the magnetic field is applied parallel and perpendicular to the tetragonal z -axis, respectively.

Successively calculating matrix elements $\langle \psi_1 | H_{Ze} | \psi_1 \rangle$ and $\langle \psi_1 | H_{Ze} | \psi_2 \rangle$ (see (5), (6)) for the Zeeman energy in the forms (7) and (8) we derived the following formulas for the g -factors of the ground Kramers doublet of the Ce^{3+} ion:

$$g_{\parallel} = \frac{2}{7N^2} (15 - 9|\alpha|^2 + 20|\beta|^2 - 12|\gamma|^2 - \sqrt{6}(\beta + \beta^*) - \sqrt{10}(\alpha\gamma^* + \alpha^*\gamma)), \quad (9)$$

$$g_{\perp} = \frac{2}{7N^2} |6\sqrt{5}\alpha + \sqrt{30}\alpha\beta + \sqrt{2}\gamma - 16\sqrt{3}\beta\gamma|. \quad (10)$$

If we put $\beta = \gamma = 0$ (9) and (10) transform into formulas obtained earlier [2, 3] for the case when mixing of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets is not considered. Such g -factors, calculated for the isolated ${}^2F_{5/2}$ multiplet, depend only on $|\alpha|$ and satisfy the equation

$$\frac{1}{16} (g_{\parallel} - g_L)^2 + \frac{1}{5} g_{\perp}^2 = g_L^2, \quad (11)$$

where $g_L = 6/7$ is the Lande g -factor for the ${}^2F_{5/2}$ multiplet. In a plane with axes $(g_{\parallel}, g_{\perp})$ (11) is an equation of an ellipse which will further be referred to as the « ${}^2F_{5/2}$ multiplet ellipse».

3. Investigation of dependence of g -factors of the Ce^{3+} ion in $LiYF_4$ on crystal field parameters

In [1] the following values of g -factors for the ground Kramers doublet of the Ce^{3+} ion in $LiYF_4$ crystal have been measured:

$$g_{\parallel}^{\text{exp}} = 2.737, \quad g_{\perp}^{\text{exp}} = 1.475. \quad (12)$$

Paper [2] gives close values $g_{\parallel}^{\text{exp}} = 2.765$, $g_{\perp}^{\text{exp}} = 1.473$. We will further rely on the [1] values (12). In the plane with axes $(g_{\parallel}, g_{\perp})$ the experimental point $(g_{\parallel}^{\text{exp}}, g_{\perp}^{\text{exp}})$ lies inside the ${}^2F_{5/2}$ multiplet ellipse (11) with the closest point of the ellipse $(g_{\parallel} = 2.779, g_{\perp} = 1.587)$ achieved for $|\alpha| = 0.5306$.

Distance between the experimental point (12) and the closest point of the ${}^2F_{5/2}$ multiplet ellipse amounts nearly 0.12, thus implying necessity of rigorous considering of mixing of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets and hence using the derived exact formulas (9), (10) for g -factors.

In [4] we used the following crystal field parameters in modeling of the interconfiguration $4f-5d$ absorption spectrum of the Ce³⁺ ion in LiYF₄ (in cm⁻¹):

$$B_0^2 = 360, \quad B_0^4 = -1400, \quad B_4^4 = -1240 + i \cdot 751, \quad B_0^6 = -67.2, \quad B_4^6 = -1095 + i \cdot 458. \quad (13)$$

Signs and orders of magnitude of the parameters (13) are in agreement with parameters common in literature for trivalent rare earth ions doped in the LiYF₄ crystal, obtained either from fitting experimental data (for example, [6]) or from microscopic calculations [7]. We will follow these crystal field parameters signs in our investigation, they are determined by geometry of the system in the first place. In [4] the value $\xi = 625 \text{ cm}^{-1}$ was used for the spin-orbit coupling constant, this value also being in agreement with the common in literature (for example, 615 cm⁻¹ in [6] and 628 cm⁻¹ in [8]). Diagonalization of the matrix (4) with the Ce³⁺ ion Hamiltonian parameters used in [4] gives the following coefficients in the expansions (5), (6) of the ground Kramers doublet wavefunctions:

$$\alpha = 0.4646 + i \cdot 0.2787, \quad \beta = -0.0304 - i \cdot 0.0081, \quad \gamma = -0.0128 + i \cdot 0.0061, \quad (14)$$

and the following g -factors values, calculated according to (9), (10):

$$g_{\parallel} = 2.846, \quad g_{\perp} = 1.552. \quad (15)$$

In accordance with small values of $|\beta|$ and $|\gamma|$ in (14), these g -factors lie very close to the ${}^2F_{5/2}$ multiplet ellipse (11) – incidentally, as this was not the aim in [4] – with the closest point of the ellipse $g_{\parallel} = 2.849$, $g_{\perp} = 1.560$ achieved for $|\alpha| = 0.5148$ being at distance of 0.009.

Note that signs of the real and imaginary parts of the α coefficient in wavefunctions (5), (6) of the ground Kramers doublet of the Ce³⁺ ion in LiYF₄ should always be positive. Indeed, since the ${}^2F_{7/2}$ multiplet is separated by the energy gap of $7\xi/2 \approx 2200 \text{ cm}^{-1}$ from the ${}^2F_{5/2}$ multiplet, admixture of the $\left| \frac{5}{2}, -\frac{3}{2} \right\rangle$ state in wavefunction (5) is determined mainly by the matrix element $\left\langle \frac{5}{2}, \frac{5}{2} \left| H \right| \frac{5}{2}, -\frac{3}{2} \right\rangle$ (see (4)). Considering diagonalization procedure of the Hamiltonian matrix 2×2 on basis states $\left| \frac{5}{2}, \frac{5}{2} \right\rangle$ and $\left| \frac{5}{2}, -\frac{3}{2} \right\rangle$, it is easy to see that the real and imaginary parts of the coefficient α that defines this admixture have the same signs as $-\left\langle \frac{5}{2}, \frac{5}{2} \left| H \right| \frac{5}{2}, -\frac{3}{2} \right\rangle^* = -\frac{\sqrt{14}}{21} B_4^{4*}$ and, in accordance with (13), are both positive.

Let us investigate dependence of g -factors calculated as (9), (10) on coefficients α , β , γ in wavefunctions (5), (6). The following question interests us: which coefficients values give g -factors that lie inside the ${}^2F_{5/2}$ multiplet ellipse (11) at a distance of nearly 0.12, similarly to the experimental g -factors (12).

We use the realistic set of coefficients (14) established in [4] as a starting point and successively vary the real and imaginary parts of the coefficients; it is very convenient that corresponding g -factors (15) lie very close to the ${}^2F_{5/2}$ multiplet ellipse and close to experimental values (12). Varying of $\text{Re } \alpha$ and $\text{Im } \alpha$ would give different points on the ${}^2F_{5/2}$ multiplet ellipse (11), but not the shifts inside the ellipse that we are interested in, therefore we fix the α coefficient value at the level of (14).

In Fig. 1 g -factors calculated with the use of expressions (9), (10) are shown by triangles for $\text{Re } \beta$ ranging from -0.1804 to 0.4696 (66 values with the increment 0.01), as well as the experimental point (12) [1] and the ${}^2F_{5/2}$ multiplet ellipse (11), which are also be shown in all figures below. The

starting point (15) of the variation procedure is highlighted by a round frame. As seen in Fig. 1, g -factors calculated for different $\text{Re}\beta$ values form a distorted parabola in the plane $(g_{\parallel}, g_{\perp})$ with the axis directed along the ${}^2F_{5/2}$ multiplet ellipse; the lower branch of the parabola corresponds to negative $\text{Re}\beta$ values; shift by only ≈ 0.05 inside the ellipse is reached at best. A very similar situation is found in Fig. 1 for g -factors shown by squares which correspond to $\text{Im}\beta$ ranging from -0.3081 to 0.2919 (61 values with the increment 0.01). The calculated g -factors again form a distorted parabola in the plane $(g_{\parallel}, g_{\perp})$ with the axis directed along the ${}^2F_{5/2}$ multiplet ellipse; the lower branch of the parabola corresponds to negative $\text{Im}\beta$ values; shift by only ≈ 0.04 inside the ellipse is reached at best.

A different situation is found in Fig. 2, where g -factors calculated as (9), (10) are shown by triangles for $\text{Re}\gamma$ ranging from -0.2128 to 0.1872 (41 values with the increment 0.01); the center point (15) of the variation procedure is highlighted by a round frame. As seen in Fig. 2, g -factors corresponding to different $\text{Re}\gamma$ values form a distorted parabola in the plane $(g_{\parallel}, g_{\perp})$ with the axis directed across the ${}^2F_{5/2}$ multiplet ellipse. Calculations show that the demanded shift by 0.12 inside the ellipse is reached at $\text{Re}\gamma \approx -0.17$ (the lower branch of the parabola) or $\text{Re}\gamma \approx 0.25$ (the upper branch of the parabola). A very similar situation is found in Fig. 2 for g -factors shown by squares which correspond to $\text{Im}\gamma$ ranging from -0.1939 to 0.2061 (41 values with the increment 0.01). The calculated g -factors again form a distorted parabola in the plane $(g_{\parallel}, g_{\perp})$ with the axis directed across the ${}^2F_{5/2}$ multiplet ellipse. The demanded shift by 0.12 inside the ellipse is reached at $\text{Im}\gamma \approx -0.19$ (the lower branch of the parabola) or $\text{Im}\gamma \approx 0.21$ (the upper branch of the parabola).

The behavior of the g -factors in Fig. 1, Fig. 2 can be qualitatively understood from analysis of the expressions (9), (10). If we neglect the dependence of the normalization factor $1/N$ (see (5)) on α, β, γ coefficients, then g_{\parallel} is defined by a quadratic form of the β coefficient for the fixed γ coefficient (and visa versa), while g_{\perp} is a linear form of the β coefficient for the fixed γ coefficient (and visa versa). Therefore we obtain a roughly quadratic dependence of g_{\parallel} on g_{\perp} in Fig. 1, Fig. 2. The differences in the corresponding parabolas axes directions, which are nearly perpendicular for varying the β and γ coefficients separately, origin from different signs of $|\beta|^2$ and $|\gamma|^2$ in g_{\parallel} – see (9).

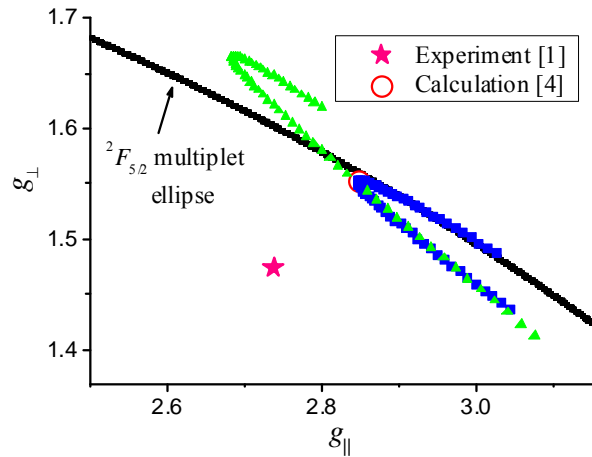


Figure 1. Diagram of g -factors of the ground Kramer's doublet of Ce^{3+} ion in LiYF_4 : triangles – calculated for various $\text{Re}\beta$, squares – calculated for various $\text{Im}\beta$. In this Figure and below: line – g -factors for the isolated ${}^2F_{5/2}$ multiplet, asterisk – experiment [1], round frame – calculation [4].

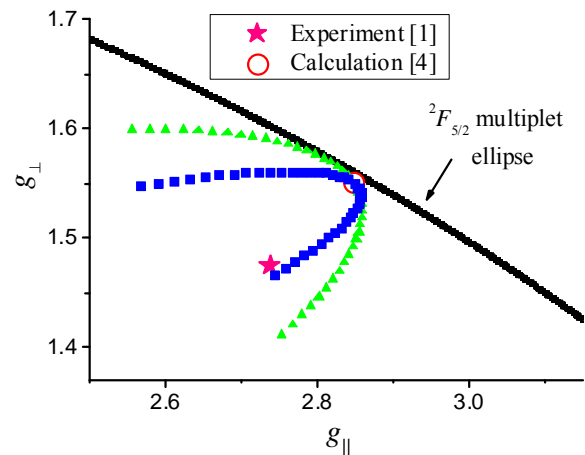


Figure 2. Diagram of g -factors of the ground Kramer's doublet of Ce^{3+} ion in LiYF_4 : triangles – calculated for various $\text{Re}\gamma$, squares – calculated for various $\text{Im}\gamma$.

Comparison of Fig. 1 and Fig. 2 shows that it is the coefficient γ in wavefunctions (5), (6) of the ground Kramers doublet of the Ce^{3+} ion in $LiYF_4$ crystal that is foremost responsible for shifts inside the ${}^2F_{5/2}$ multiplet ellipse towards the experimental g-factors (12). A simple suggestion can be made on the basis of the Ce^{3+} ion Hamiltonian matrix (4) analysis that large γ values are achieved at large values of the $\left\langle \frac{5}{2}, \frac{5}{2} \left| H \left| \frac{7}{2}, -\frac{3}{2} \right. \right. \right\rangle$ matrix element in the first place, i.e. at large values of crystal field parameters $B_{\pm 4}^4$, $B_{\pm 4}^6$. Of course, if both coefficients β and γ are sufficiently different from zero, non-linear effects that are more difficult to analyze occur, for example for $Re\beta \approx -0.1$ smaller absolute values of negative $Re\gamma$ or $Im\gamma$ coefficients are demanded (also ≈ -0.1) to obtain the shift by 0.12 inside the ${}^2F_{5/2}$ multiplet ellipse.

Let us investigate numerically dependence of g-factors (9), (10) on crystal field parameters B_k^p (calculations show that dependence on the spin-orbit coupling constant ξ is weak, besides the value of the latter is considered to be well established in literature – see for example [6, 8]). We use the set of crystal field parameters (13) given in [4] as a starting point (highlighted by a round frame in all figures) and successively vary all parameters yet keeping their signs, as has already been stressed above; the real and imaginary parts are varied independently for complex parameters with $k \neq 0$.

In Fig. 3 g-factors calculated for $Re B_4^6$ ranging from -1995 cm^{-1} to -95 cm^{-1} (20 values with the increment 100 cm^{-1}) are shown by triangles, larger absolute values of $Re B_4^6$ correspond to smaller g_{\parallel} values, and g-factors calculated for $Im B_4^6$ ranging from 8 cm^{-1} to 1958 cm^{-1} (20 values with the increment 100 cm^{-1}) are shown by squares, larger values of $Im B_4^6$ also correspond to smaller g_{\parallel} values.

As seen in Fig. 3 the conclusion made above is confirmed that large absolute values of $Re B_4^6$ and $Im B_4^6$ lead to significant absolute values of the γ coefficient and, consequently, significant shifts inside the ${}^2F_{5/2}$ multiplet ellipse on the g-factors diagram, towards the experimental g-factors (12) – compare with Fig. 2. As follows from Fig. 3 the necessary shift is obtained for $Re B_4^6 \approx -2000 \text{ cm}^{-1}$ or $Im B_4^6 \approx 2000 \text{ cm}^{-1}$.

A different situation is found for the $B_{\pm 4}^4$ crystal field parameters. In Fig. 4 g-factors calculated for $Re B_4^4$ ranging from -3640 cm^{-1} to -240 cm^{-1} (18 values with the increment 200 cm^{-1}) are shown by triangles, larger absolute

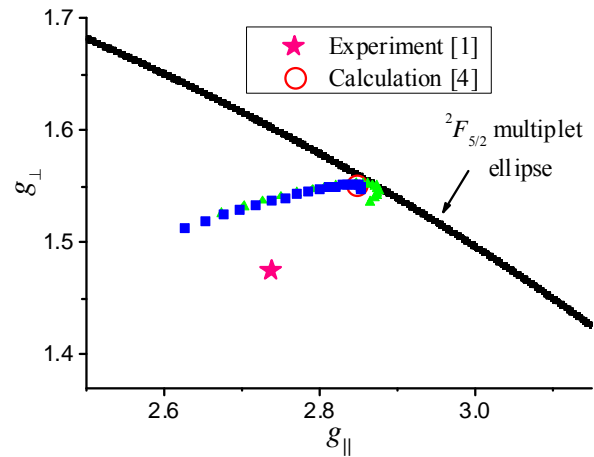


Figure 3. Diagram of g-factors of the ground Kramers doublet of Ce^{3+} ion in $LiYF_4$: triangles – calculated for various $Re B_4^6$, squares – calculated for various $Im B_4^6$.

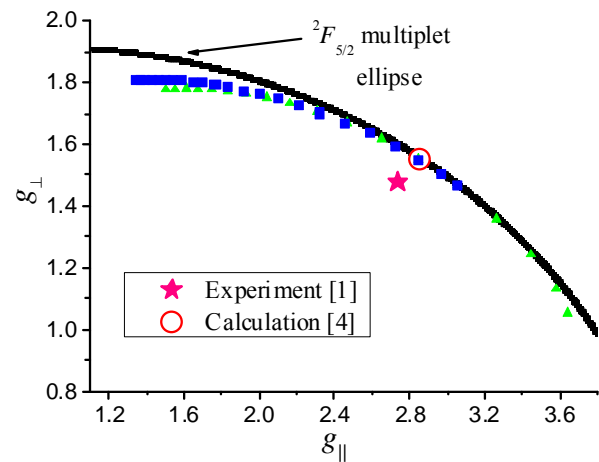


Figure 4. Diagram of g-factors of the ground Kramers doublet of Ce^{3+} ion in $LiYF_4$: triangles – calculated for various $Re B_4^4$, squares – calculated for various $Im B_4^4$.

values of $\text{Re}B_4^6$ correspond to smaller g_{\parallel} values, and g -factors calculated for $\text{Im}B_4^4$ ranging from 351 cm^{-1} to 4751 cm^{-1} (23 values with the increment 200 cm^{-1}) are shown by squares, larger values of $\text{Im}B_4^6$ also correspond to smaller g_{\parallel} values. As seen in Fig. 4, unlike the case of $B_{\pm 4}^6$ parameters and in contradiction with theoretical predictions given above, varying of $B_{\pm 4}^4$ parameters do not lead to expressed change of the γ coefficient and g -factors do not demonstrate such behavior as in Fig. 2. For very large absolute values of $\text{Re}B_4^4$ and $\text{Im}B_4^4$ significant shifts inside the ${}^2F_{5/2}$ multiplet ellipse on the g -factors diagram can, in principle, be obtained – see the left edge of the g -factors diagram in Fig. 4 – but such crystal field parameters values are impossible. The reason for discrepancy with our theoretical conclusions made above may lie in the fact that the $B_{\pm 4}^4$ crystal field parameters mix the states $\left| \frac{5}{2}, \pm \frac{5}{2} \right\rangle$ not only with the states $\left| \frac{7}{2}, \mp \frac{3}{2} \right\rangle$, giving rise to the γ coefficient in wavefunctions (5), (6), but also with the states $\left| \frac{5}{2}, \mp \frac{3}{2} \right\rangle$, and also mix the latter with the states $\left| \frac{7}{2}, \pm \frac{5}{2} \right\rangle$, thus complicating the overall picture of mixing of the Ce^{3+} ion states by crystal field.

As follows from calculation, varying of crystal field parameters B_0^2 , B_0^4 , B_0^6 within reasonable limits either leads to behavior of g -factors similar to that obtained in Fig. 1, with shifts along the ${}^2F_{5/2}$ multiplet ellipse on the g -factors diagram, or simply does not affect significantly the calculated g -factors (this is the case for the B_0^6 parameter).

Results obtained in this section for successive varying of different crystal field parameters were confirmed in a series of calculations with all crystal fields parameters being varied simultaneously (over 1 million sets of crystal field parameters values have been tested).

4. Conclusions

Analytical expressions have been derived for g -factors of the ground Kramers doublet of the Ce^{3+} ion in crystal field of tetragonal (S_4) symmetry, rigorously taking into account mixing of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets by crystal field: g -factors were expressed through coefficients of the ground doublet wavefunctions expansion in the eigenfunctions of the total momentum \mathbf{J} of the $4f$ electron. Dependence of g -factors on the wavefunction coefficients values was investigated. These results can be applied to the entire class of compounds with Ce^{3+} (or Yb^{3+}) centers in tetragonal crystal field.

Dependence of g -factors of the ground Kramers doublet of the Ce^{3+} ion in LiYF_4 on crystal field parameters was studied, comparison with experimental data [1] was fulfilled. It was revealed that large values of the $B_{\pm 4}^6$ parameters are demanded to achieve agreement with the measurements results. However, such large values ($\text{Re}B_4^6 \approx -2000 \text{ cm}^{-1}$, $\text{Im}B_4^6 \approx 2000 \text{ cm}^{-1}$) do not seem reasonable. We suggest that to achieve agreement with experiment it is necessary to consider covalency effects for the impurity Ce^{3+} ion and introduce a reduction factor k for the orbital momentum of the $4f$ electron in the Zeeman energy [5] (compare with (7))

$$H_{ze} = \mu_B (2\mathbf{S} + k\mathbf{L})\mathbf{H}. \quad (16)$$

Let us note, as an argument in favor of considering covalency effects in this compound, that the effective ionic radius of the Ce^{3+} ion is the largest for trivalent lanthanide ions, it amounts 1.143 \AA and is bigger than the ionic radius of the Y^{3+} ion (1.019 \AA) [9].

Another aspect of the problem of crystal field parameters determination for $\text{LiYF}_4:\text{Ce}^{3+}$ is that correct $4f$ energy levels for this compound should be provided. Experimental determination of the latter is a challenging task itself. Recently in [8] an attempt was made to determine several of the Ce^{3+} $4f$ crystal field levels from the measured with high spectral resolution $5d$ - $4f$ luminescence spectrum in

the LiYF₄:Ce³⁺ crystal at low temperatures: peaks observed in the luminescence spectrum were interpreted as zero-phonon lines corresponding to transitions from the lowest 5*d* state to different 4*f* levels of the Ce³⁺ ion. However, no modeling of vibrational structure of the luminescence spectrum was performed in [8], that could allow distinguishing zero-phonon and electron-vibrational transitions.

We are planning to fulfill a further investigation of 4*f* crystal field parameters in LiYF₄:Ce³⁺ in the context of both *g*-factors values, which will be calculated taking into account covalency effects according to (16), and 4*f* crystal field levels, which will be improved over [8] by modeling the vibrational structure of the 5*d*-4*f* luminescence spectrum of this compound, in future.

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