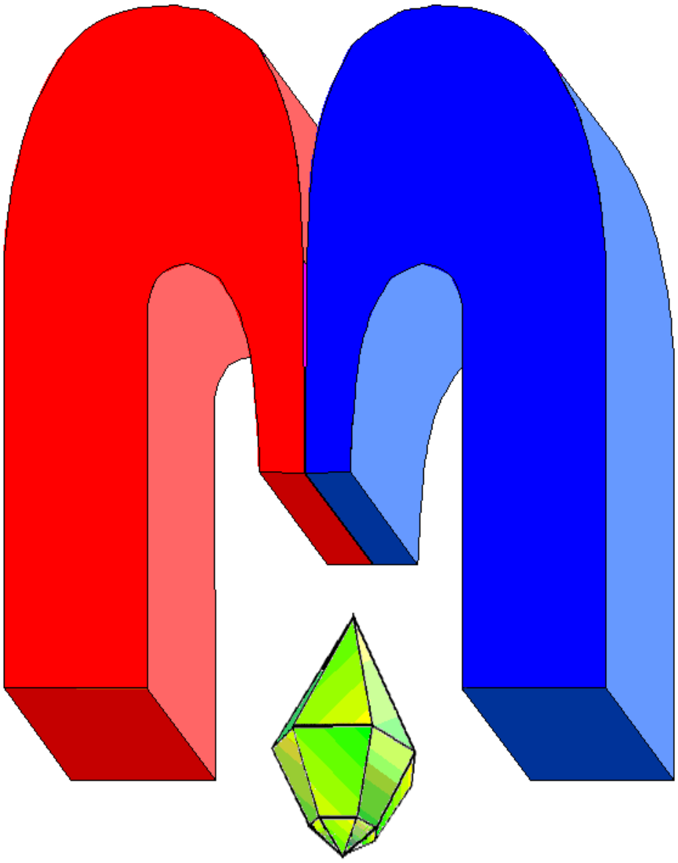
ISSN 2072-5981



Magnetic Resonance in Solids

Electronic Journal

Volume ***17*,**
Issue ***1***
Paper No ***15103*,**
1-8 pages
2015

http://mrsej.kpfu.ru
http://mrsej.ksu.ru

Established and published by Kazan University
Sponsored by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press, August 2, 1996
First Issue was appeared at July 25, 1997

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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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(Received December 11, 2015; accepted December 19, 2015)

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 filed parameters values on the basis of comparison with *g*-factors given in literature are considered.

PACS: 75.10.Dg, 76.30.-v

Keywords: crystal field parameters, *g*-factors, $LiYF_4$:Ce^{3+}

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 4*f* 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 4*f* crystal filed parameters values for the $LiYF_4$: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

$$H_{\mathrm{SO}} = \xi \mathbf{SL}, \tag{1}$$

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

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

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 $\boldsymbol{C}^{(p)}$. Note that there are only eight independent real quantities defining the effective Hamiltonian for the 4*f* 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 4*f* 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:

$$\left|\frac{5}{2},\pm\frac{5}{2}\right\rangle=\pm\sqrt{\frac{1}{7}}\left|\pm2,\pm\right\rangle\mp\sqrt{\frac{6}{7}}\left|\pm3,\mp\right\rangle,\ \left|\frac{5}{2},\pm\frac{3}{2}\right\rangle=\pm\sqrt{\frac{2}{7}}\left|\pm1,\pm\right\rangle\mp\sqrt{\frac{5}{7}}\left|\pm2,\mp\right\rangle,$$

$$\left|\frac{5}{2},\pm\frac{1}{2}\right\rangle=\pm\sqrt{\frac{3}{7}}\left|0,\pm\right\rangle\mp\sqrt{\frac{4}{7}}\left|\pm1,\mp\right\rangle,\ \left|\frac{7}{2},\pm\frac{7}{2}\right\rangle=-\left|\pm3,\pm\right\rangle,\ \left|\frac{7}{2},\pm\frac{5}{2}\right\rangle=-\sqrt{\frac{6}{7}}\left|\pm2,\pm\right\rangle-\sqrt{\frac{1}{7}}\left|\pm3,\mp\right\rangle,$$

$$\left|\frac{7}{2},\pm\frac{3}{2}\right\rangle=-\sqrt{\frac{5}{7}}\left|\pm1,\pm\right\rangle-\sqrt{\frac{2}{7}}\left|\pm2,\mp\right\rangle,\ \left|\frac{7}{2},\pm\frac{1}{2}\right\rangle=-\sqrt{\frac{4}{7}}\left|0,\pm\right\rangle-\sqrt{\frac{3}{7}}\left|\pm1,\mp\right\rangle. \tag{3}$$

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 $H=H_{\mathrm{SO}}+H_{\mathrm{CF}}$ in the basis $\left|J,J_z\right\rangle$. 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 $H=H_{\mathrm{SO}}+H_{\mathrm{CF}}$ (see (1) and (2)) with the following elements:

$$\left\langle\frac{5}{2},\frac{5}{2}\right|H\left|\frac{5}{2},\frac{5}{2}\right\rangle=-2\xi-\frac{6}{21}B_0^2+\frac{1}{21}B_0^4,\ \left\langle\frac{5}{2},-\frac{3}{2}\right|H\left|\frac{5}{2},-\frac{3}{2}\right\rangle=-2\xi+\frac{2}{35}B_0^2-\frac{1}{7}B_0^4,$$

$$\left\langle\frac{7}{2},\frac{5}{2}\right|H\left|\frac{7}{2},\frac{5}{2}\right\rangle=\frac{3}{2}\xi-\frac{1}{21}B_0^2-\frac{13}{77}B_0^4+\frac{25}{429}B_0^6,\ \left\langle\frac{7}{2},-\frac{3}{2}\right|H\left|\frac{7}{2},-\frac{3}{2}\right\rangle=\frac{3}{2}\xi+\frac{1}{7}B_0^2-\frac{3}{77}B_0^4-\frac{15}{143}B_0^6,$$

$$\left\langle\frac{5}{2},\frac{5}{2}\right|H\left|\frac{5}{2},-\frac{3}{2}\right\rangle=\frac{\sqrt{14}}{21}B_4^4,\ \left\langle\frac{5}{2},\frac{5}{2}\right|H\left|\frac{7}{2},\frac{5}{2}\right\rangle=-\frac{\sqrt{6}}{21}B_0^2+\frac{10\sqrt{6}}{231}B_0^4-\frac{5\sqrt{6}}{429}B_0^6,$$

$$\left\langle\frac{5}{2},\frac{5}{2}\right|H\left|\frac{7}{2},-\frac{3}{2}\right\rangle=\frac{4\sqrt{35}}{231}B_4^4-\frac{10\sqrt{7}}{143}B_4^6,\ \left\langle\frac{5}{2},-\frac{3}{2}\right|H\left|\frac{7}{2},\frac{5}{2}\right\rangle=-\frac{8\sqrt{21}}{231}B_{-4}^4-\frac{10\sqrt{105}}{429}B_{-4}^6,$$

$$\left\langle\frac{5}{2},-\frac{3}{2}\right|H\left|\frac{7}{2},-\frac{3}{2}\right\rangle=\frac{\sqrt{10}}{35}B_0^2+\frac{8\sqrt{10}}{231}B_0^4-\frac{5\sqrt{10}}{143}B_0^6,\ \left\langle\frac{7}{2},\frac{5}{2}\right|H\left|\frac{7}{2},-\frac{3}{2}\right\rangle=\frac{\sqrt{210}}{77}B_4^4+\frac{5\sqrt{42}}{429}B_4^6. \tag{4}$$

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

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

In (5) $\left|\alpha\right|<1$, $\left|\beta\right|<1$, $\left|\gamma\right|<1$ 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 $\left|\beta\right|<\left|\alpha\right|$, $\left|\gamma\right|<\left|\alpha\right|$. The second wavefunction of the ground Kramers doublet of the Ce^{3+} ion in LiYF_4 can be obtained from (5) as

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

where $\hat{\theta}$ is the time reversal operator [5]. The wavefunction $\left|\psi_2\right\rangle$ 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

$$H_{\mathrm{Ze}} = \mu_{\mathrm{B}}\left(2\mathbf{S}+\mathbf{L}\right)\mathbf{H}, \tag{7}$$

where $\mathbf{H}=\left(H_x,H_y,H_z\right)$ 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

$$H_{\mathrm{Ze}} = \mu_{\mathrm{B}} g_{\parallel} S_z^{\mathrm{eff}} H_z + \mu_{\mathrm{B}} g_{\perp}\left(S_x^{\mathrm{eff}} H_x + S_y^{\mathrm{eff}} H_y\right), \tag{8}$$

where $\mathbf{S}^{\mathrm{eff}}$ 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 $\left\langle\psi_1\right|H_{\mathrm{Ze}}\left|\psi_1\right\rangle$ and $\left\langle\psi_1\right|H_{\mathrm{Ze}}\left|\psi_2\right\rangle$ (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:

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

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

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 $\left|\alpha\right|$ and satisfy the equation

$$\frac{1}{16}\left(g_{\parallel}-g_{\mathrm{L}}\right)^2+\frac{1}{5}g_{\perp}^2=g_{\mathrm{L}}^2, \tag{11}$$

where $g_{\mathrm{L}}=6/7$ is the Lande g-factor for the ${}^2F_{5/2}$ multiplet. In a plane with axes $\left(g_{\parallel},g_{\perp}\right)$ (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:

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

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

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 Ce^{3+} ion in LiYF$_4$ (in cm^{-1}):

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

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 LiYF$_4$ 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 $\xi = 625\,\mathrm{cm}^{-1}$ 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 Ce^{3+} ion Hamiltonian parameters used in [4] gives the following coefficients in the expansions (5), (6) of the ground Kramers doublet wavefunctions:

$$\alpha = 0.4646 + i \cdot 0.2787, \quad \beta = -0.0304 - i \cdot 0.0081, \quad \gamma = -0.0128 + i \cdot 0.0061, \tag{14}$$

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

$$g_{\|} = 2.846, \quad g_{\perp} = 1.552. \tag{15}$$

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 $g_{\|} = 2.849,\ g_{\perp} = 1.560$ 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 Ce^{3+} ion in LiYF$_4$ should always be positive. Indeed, since the $^2F_{7/2}$ multiplet is separated by the energy gap of $7\xi/2 \approx 2200\,\mathrm{cm}^{-1}$ 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 $\left\langle\frac{5}{2},\frac{5}{2}\middle|H\middle|\frac{5}{2},-\frac{3}{2}\right\rangle$ (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 $-\left\langle\frac{5}{2},\frac{5}{2}\middle|H\middle|\frac{5}{2},-\frac{3}{2}\right\rangle^* = -\frac{\sqrt{14}}{21}B_4^{4*}$ 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 $\mathrm{Re}\,\alpha$ and $\mathrm{Im}\,\alpha$ 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 $\mathrm{Re}\,\beta$ 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 $\mathrm{Re}\,\beta$ values form a distorted parabola in the plane $\left(g_{\parallel}, g_{\perp}\right)$ with the axis directed along the $^2F_{5/2}$ multiplet ellipse; the lower branch of the parabola corresponds to negative $\mathrm{Re}\,\beta$ 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 $\mathrm{Im}\,\beta$ 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 $\left(g_{\parallel}, g_{\perp}\right)$ with the axis directed along the $^2F_{5/2}$ multiplet ellipse; the lower branch of the parabola corresponds to negative $\mathrm{Im}\,\beta$ values; shift by only ≈ 0.04 inside the ellipse is reached at best.

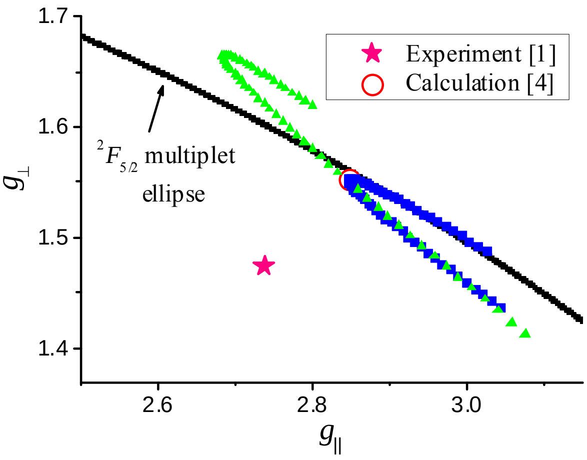

Figure 1. Diagram of g-factors of the ground Kramers doublet of Ce^{3+} ion in LiYF$_4$: triangles – calculated for various $\mathrm{Re}\,\beta$, squares – calculated for various $\mathrm{Im}\,\beta$. In this Figure and below: line – g-factors for the isolated $^2F_{5/2}$ multiplet, asterisk – experiment [1], round frame – calculation [4].

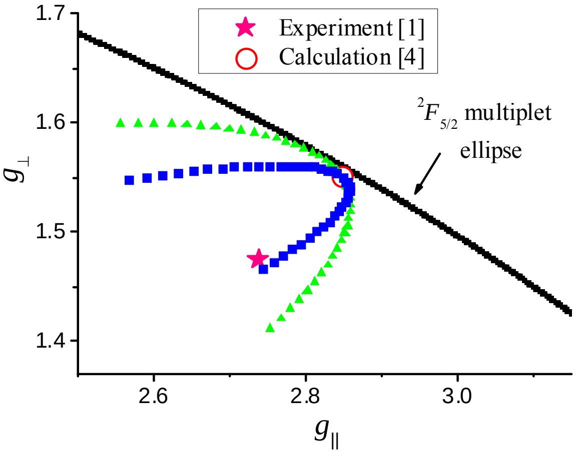

Figure 2. Diagram of g-factors of the ground Kramers doublet of Ce^{3+} ion in LiYF$_4$: triangles – calculated for various $\mathrm{Re}\,\gamma$, squares – calculated for various $\mathrm{Im}\,\gamma$.

A different situation is found in Fig. 2, where g-factors calculated as (9), (10) are shown by triangles for $\mathrm{Re}\,\gamma$ 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 $\mathrm{Re}\,\gamma$ values form a distorted parabola in the plane $\left(g_{\parallel}, g_{\perp}\right)$ 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 $\mathrm{Re}\,\gamma \approx -0.17$ (the lower branch of the parabola) or $\mathrm{Re}\,\gamma \approx 0.25$ (the upper branch of the parabola). A very similar situation is found in Fig. 2 for g-factors shown by squares which correspond to $\mathrm{Im}\,\gamma$ 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 $\left(g_{\parallel}, g_{\perp}\right)$ with the axis directed across the $^2F_{5/2}$ multiplet ellipse. The demanded shift by 0.12 inside the ellipse is reached at $\mathrm{Im}\,\gamma \approx -0.19$ (the lower branch of the parabola) or $\mathrm{Im}\,\gamma \approx 0.21$ (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).

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 $\left\langle \frac{5}{2},\frac{5}{2}\middle| H \middle| \frac{7}{2},-\frac{3}{2}\right\rangle$ matrix element in the first place, i.e. at large values of crystal field parameters $B^4_{\pm4}$, $B^6_{\pm4}$. 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 $\mathrm{Re}\,\beta \approx -0.1$ smaller absolute values of negative $\mathrm{Re}\,\gamma$ or $\mathrm{Im}\,\gamma$ 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^p_k (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 $\mathrm{Re}\,B^6_4$ 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 $\mathrm{Re}\,B^6_4$ correspond to smaller $g_{\parallel}$ values, and g-factors calculated for $\mathrm{Im}\,B^6_4$ ranging from 8 cm^{-1} to 1958 cm^{-1} (20 values with the increment 100 cm^{-1}) are shown by squares, larger values of $\mathrm{Im}\,B^6_4$ also correspond to smaller $g_{\parallel}$ values.

As seen in Fig. 3 the conclusion made above is confirmed that large absolute values of $\mathrm{Re}\,B^6_4$ and $\mathrm{Im}\,B^6_4$ 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 $\mathrm{Re}\,B^6_4 \approx -2000$ cm^{-1} or $\mathrm{Im}\,B^6_4 \approx 2000$ cm^{-1}.

A different situation is found for the $B^4_{\pm4}$ crystal field parameters. In Fig. 4 g-factors calculated for $\mathrm{Re}\,B^4_4$ ranging from -3640 cm^{-1} to -240 cm^{-1} (18 values with the increment 200 cm^{-1}) are shown by triangles, larger absolute

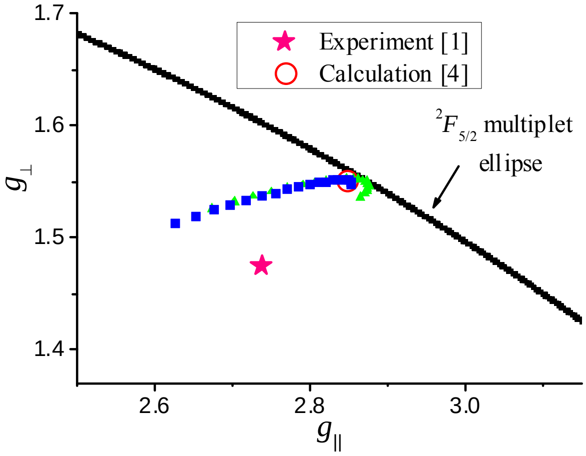

Figure 3. Diagram of g-factors of the ground Kramers doublet of Ce^{3+} ion in LiYF$_4$: triangles – calculated for various $\mathrm{Re}\,B^6_4$, squares – calculated for various $\mathrm{Im}\,B^6_4$.

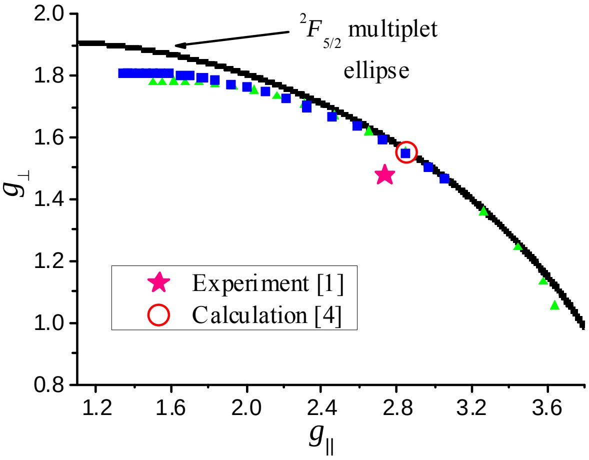

Figure 4. Diagram of g-factors of the ground Kramers doublet of Ce^{3+} ion in LiYF$_4$: triangles – calculated for various $\mathrm{Re}\,B^4_4$, squares – calculated for various $\mathrm{Im}\,B^4_4$.

values of $\mathrm{Re}\,B_4^6$ correspond to smaller $g_{\|}$ values, and g-factors calculated for $\mathrm{Im}\,B_4^4$ ranging from 351 cm^{-1} to 4751 cm^{-1} (23 values with the increment 200 cm^{-1}) are shown by squares, larger values of $\mathrm{Im}\,B_4^6$ also correspond to smaller $g_{\|}$ values. As seen in Fig. 4, unlike the case of $B_{\pm4}^6$ parameters and in contradiction with theoretical predictions given above, varying of $B_{\pm4}^4$ 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 $\mathrm{Re}\,B_4^4$ and $\mathrm{Im}\,B_4^4$ 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 $B_{\pm4}^4$ 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 **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 $\mathrm{LiYF_4}$ on crystal field parameters was studied, comparison with experimental data [1] was fulfilled. It was revealed that large values of the $B_{\pm4}^6$ parameters are demanded to achieve agreement with the measurements results. However, such large values ($\mathrm{Re}\,B_4^6 \approx -2000\,\mathrm{cm}^{-1}$, $\mathrm{Im}\,B_4^6 \approx 2000\,\mathrm{cm}^{-1}$) 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))

$$H_{\mathrm{Ze}} = \mu_{\mathrm{B}}\left(2\mathbf{S} + k\mathbf{L}\right)\mathbf{H}. \tag{16}$$

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 Å and is bigger than the ionic radius of the Y^{3+} ion (1.019 Å) [9].

Another aspect of the problem of crystal field parameters determination for $\mathrm{LiYF_4{:}Ce^{3+}}$ 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 $LiYF_4$:Ce^{3+} 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 Ce^{3+} 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 $LiYF_4$:Ce^{3+} 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.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University and the RFBR Grant 14-02-00826.

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