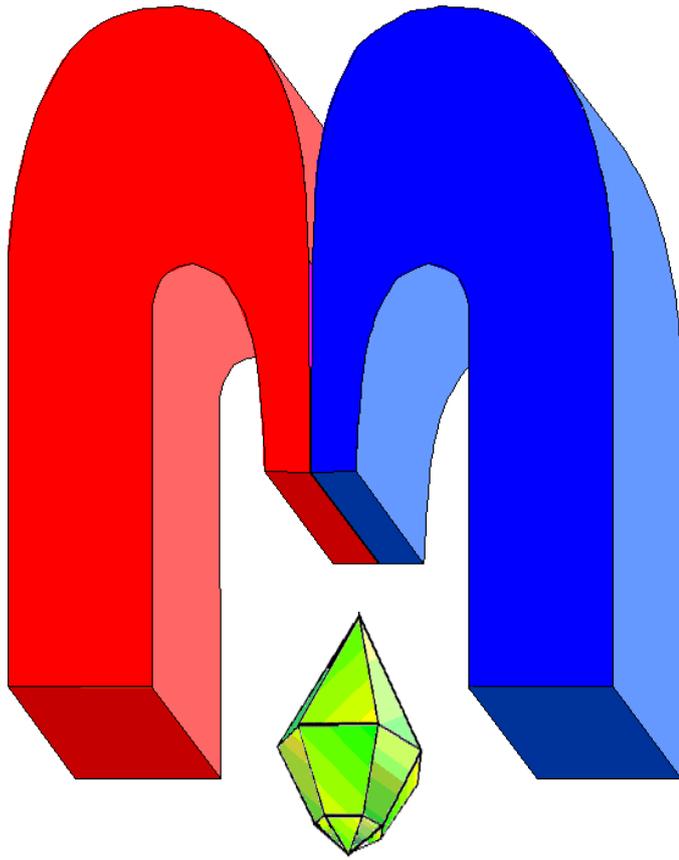


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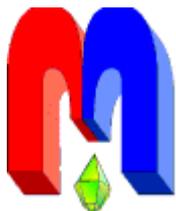


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In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# Determination of tetragonal crystalline electric field parameters for Yb<sup>3+</sup> and Ce<sup>3+</sup> ions from experimental g-factors values and energy levels of Kramers doublets

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The tetragonal crystalline electric field parameters for Yb<sup>3+</sup> and Ce<sup>3+</sup> ions are expressed via ground multiplet exited doublets energies and parameters defining doublets' wave functions. The crystalline electric field parameters for Yb<sup>3+</sup> ion in YbRh<sub>2</sub>Si<sub>2</sub>, YbIr<sub>2</sub>Si<sub>2</sub> and KMgF<sub>3</sub> crystals extracted from excited state doublets energies and g-factors of ground state doublet are compared with parameters determined in other works.

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**Keywords:** crystalline electric field parameters, g-factors, Yb-based intermetallides, heavy-fermion systems

## 1. Introduction

Our work was initially stimulated by investigation of heavy-fermion Kondo lattice compounds. Very peculiar magnetic, thermal and transport properties of 4*f*-electron based heavy-fermion systems are determined by the interplay of the strong repulsion of 4*f*-electrons on the rare-earth ion sites, their hybridization with wide-band conduction electrons and an influence of the crystalline electric field. The main features of the electron paramagnetic resonance (EPR) signal observed in YbRh<sub>2</sub>Si<sub>2</sub> and YbIr<sub>2</sub>Si<sub>2</sub> [1, 2] (anisotropy of the *g*-factor and the EPR linewidth) and static magnetic susceptibility [3] of these compounds reflect local properties of the Yb<sup>3+</sup> ion in the crystalline electric field (CEF).

In this paper we present the detailed calculation of CEF parameters from energies of ground multiplet exited Kramers doublets and *g*-factors of ground state Kramers doublet. Our results could be applied to the entire classes of compounds with Yb<sup>3+</sup> and Ce<sup>3+</sup> tetragonal centers.

## 2. Diagram of Yb<sup>3+</sup> g-factors

A free Yb<sup>3+</sup> ion has a 4*f*<sup>13</sup> configuration with one term <sup>2</sup>*F*. The spin-orbit interaction splits the <sup>2</sup>*F* term into two multiplets: <sup>2</sup>*F*<sub>7/2</sub> with *J* = 7/2 and <sup>2</sup>*F*<sub>5/2</sub> with *J* = 5/2, where *J* is value of the total momentum **J** = (*J*<sub>x</sub>, *J*<sub>y</sub>, *J*<sub>z</sub>). Multiplets are separated by about 1 eV [4]. As the spin-orbit coupling is much stronger than the CEF in the case of rare earth, we will consider only the ground multiplet <sup>2</sup>*F*<sub>7/2</sub> with states |*J* = 7/2, *M<sub>J</sub>*⟩ ≡ |*M<sub>J</sub>*⟩, where *M<sub>J</sub>* is the eigenvalue of *J<sub>z</sub>*, *z* is the tetragonal axis. The Hamiltonian of the Yb<sup>3+</sup> ion interaction with the tetragonal CEF could be written via equivalent operators *O<sub>k</sub><sup>q</sup>*(**J**) [4]:

$$H = \alpha B_2^0 O_2^0 + \beta (B_4^0 O_4^0 + B_4^4 O_4^4) + \gamma (B_6^0 O_6^0 + B_6^4 O_6^4), \quad (1)$$

where *B<sub>k</sub><sup>q</sup>* are the CEF parameters,  $\alpha = 2/63$ ,  $\beta = -2/1155$ ,  $\gamma = 4/27027$  [4].

As follows from the group theory, the two-valued irreducible representation *D*<sup>7/2</sup> of rotation group contains two two-dimensional irreducible representations  $\Gamma_7^t$  and  $\Gamma_6^t$  of the double tetragonal group:  $D^{7/2} = 2\Gamma_7^t + 2\Gamma_6^t$  [4]. Therefore the states of Yb<sup>3+</sup> in the tetragonal CEF are four Kramers doublets. As the decomposition of *D*<sup>7/2</sup> includes twice each of representations  $\Gamma_7^t$  and  $\Gamma_6^t$ , the matrix of operator (1) could be expressed via two two-dimensional matrices

$$\begin{pmatrix} 2C_1 & C_3 \\ C_3 & 2C_2 \end{pmatrix} \text{ and } \begin{pmatrix} 2A_1 & A_3 \\ A_3 & 2A_2 \end{pmatrix}, \quad (2)$$

the former corresponding to bases |5/2⟩, |-3/2⟩ and |-5/2⟩, |3/2⟩, the latter corresponding to bases |7/2⟩, |-1/2⟩ and |-7/2⟩, |1/2⟩. It is convenient to introduce parameters *C*, *A* and *D*:

$$\begin{aligned} C = C_1 - C_2 = 4B_2^0/21 + 40B_4^0/77 - 560B_6^0/429, & \quad A = A_1 - A_2 = 4B_2^0/7 + 8B_4^0/77 + 80B_6^0/143, \\ D = -C_1 - C_2 = A_1 + A_2 = 2B_2^0/21 - 64B_4^0/77 - 160B_6^0/429, & \end{aligned} \quad (3)$$

where  $C_1 + C_2 + A_1 + A_2 = 0$  as traces of *O<sub>k</sub><sup>q</sup>* are equal to zero. *C*<sub>3</sub> and *A*<sub>3</sub> are

$$C_3 = -8\sqrt{3}B_4^4/77 - 80\sqrt{3}B_6^4/1287, \quad A_3 = -8\sqrt{35}B_4^4/385 + 80\sqrt{35}B_6^4/3003. \quad (4)$$

**Table 1.** Energies, wave functions and  $g$ -factors of  $\text{Yb}^{3+}$  ion in tetragonal crystalline electric field.

$E_{1,2} = -D \pm C / \cos \varphi_7$	$E_{3,4} = D \pm A / \cos \varphi_6$
$ ^1\Gamma_7^t \uparrow, \downarrow\rangle = \pm c_1  \pm 5/2\rangle \pm c_2  \mp 3/2\rangle$	$ ^3\Gamma_6^t \uparrow, \downarrow\rangle = \pm a_1  \mp 7/2\rangle \pm a_2  \pm 1/2\rangle$
$ ^2\Gamma_7^t \uparrow, \downarrow\rangle = \mp c_2  \pm 5/2\rangle \pm c_1  \mp 3/2\rangle$	$ ^4\Gamma_6^t \uparrow, \downarrow\rangle = \mp a_2  \mp 7/2\rangle \pm a_1  \pm 1/2\rangle$
$g_{\parallel} (^{1,2}\Gamma_7^t) = g_J (5c_{1,2}^2 - 3c_{2,1}^2) = g_J (1 \pm 4 \cos \varphi_7)$	$g_{\parallel} (^{3,4}\Gamma_6^t) = g_J (a_{2,1}^2 - 7a_{1,2}^2) = -g_J (3 \pm 4 \cos \varphi_6)$
$g_{\perp} (^{1,2}\Gamma_7^t) = \mp 4\sqrt{3}g_J c_1 c_2 = \mp 2\sqrt{3}g_J \sin \varphi_7$	$g_{\perp} (^{3,4}\Gamma_6^t) = -4g_J a_{2,1}^2 = -2g_J (1 \mp \cos \varphi_6)$

Let us define eigenvectors of matrices (2) ( $c_{1,2}, \pm c_{2,1}$ ) and ( $a_{1,2}, \pm a_{2,1}$ ) via angular parameters  $\varphi_7$  and  $\varphi_6$  which correspond to  $\Gamma_7^t$  and  $\Gamma_6^t$  symmetries:  $c_1 = \cos(\varphi_7/2)$ ,  $c_2 = \sin(\varphi_7/2)$  and  $a_1 = \cos(\varphi_6/2)$ ,  $a_2 = \sin(\varphi_6/2)$ . Since matrices (2) are diagonal in the bases of their eigenvectors we can find the relations between our angular parameters and CEF parameters:  $\tan \varphi_7 = C_3/C$ ,  $\tan \varphi_6 = A_3/A$ , it is enough to take  $-\pi/2 \leq \varphi_7, \varphi_6 \leq \pi/2$ . The eigenenergies  $E_k$ , wave functions and  $g$ -factors of Kramers doublets are given in table 1. In this table  $^k\Gamma_7^t$  and  $^k\Gamma_6^t$  are symmetry symbols, where  $k = 1..4$  is the number of Kramers doublet. The arrow  $\uparrow$  or  $\downarrow$  in wave functions corresponds to the upper or lower sign and denotes up and down effective spin projection. They have been chosen such that  $\langle \uparrow | J_+ | \downarrow \rangle \neq 0$ , where  $J_+ = J_x + iJ_y$ . Moreover, the phases of the wave function have been chosen as  $\theta |\uparrow\rangle = |\downarrow\rangle$ , where  $\theta$  is a time reversing operator [4]. In  $g$ -factors left and right indexes correspond to the upper and lower signs;  $g_J = 8/7$  is the Lande  $g$ -factor.

The Zeeman energy  $g_J \mu_B \mathbf{H} \mathbf{J}$  in the basis  $|\uparrow\rangle, |\downarrow\rangle$  of each doublet could be represented by matrix

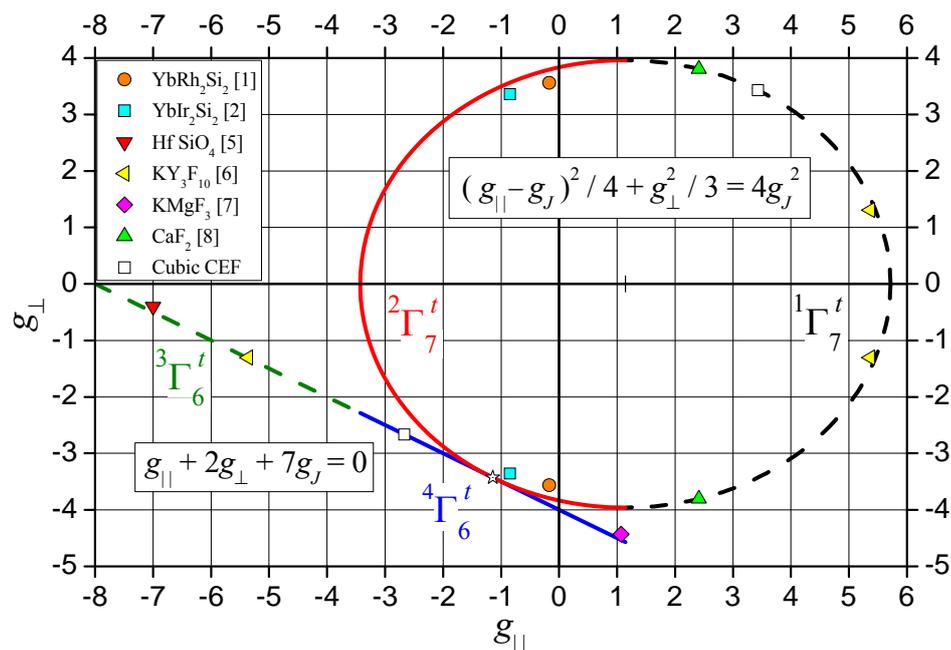
$$H_{Zeeman} = g_{\parallel} \mu_B H_z S_z + g_{\perp} \mu_B (H_x S_x + H_y S_y), \quad (5)$$

where

$$g_{\parallel} = 2g_J \langle \uparrow | J_z | \uparrow \rangle, \quad g_{\perp} = g_J \langle \uparrow | J_+ | \downarrow \rangle, \quad (6)$$

and  $\mathbf{H}$  is the magnetic field,  $\mathbf{S}$  is the effective spin operator with  $S = 1/2$ ,  $\mu_B$  is the Bohr magneton,  $g_{\parallel}$  and  $g_{\perp}$  are  $g$ -factors when the field is applied parallel and perpendicular to the tetragonal  $z$ -axis, respectively (tab. 1).

In the case of cubic symmetry  $B_2^0 = 0$ ,  $B_4^4 = 5B_4^0$  and  $B_6^4 = -21B_6^0$ , so that  $\tan \varphi_7 = -\sqrt{3}$ ,  $\tan \varphi_6 = -\sqrt{35}$ ,  $c_1 = \sqrt{3}/2$ ,  $c_2 = -1/2$ ,  $a_1 = \sqrt{7/12}$ ,  $a_2 = -\sqrt{5/12}$ . In accordance with expansion  $\Gamma_8 = \Gamma_7^t + \Gamma_6^t$  [4] the doublets  $^2\Gamma_7^t$  and  $^3\Gamma_6^t$  merge into a cubic quartet  $\Gamma_8$  with energy  $E(\Gamma_8) = -16B_4^0/77 + 1280B_6^0/429$ . The doublets  $^1\Gamma_7^t$  and  $^4\Gamma_6^t$  turn into cubic doublets  $\Gamma_7$  and  $\Gamma_6$  with energies  $E(\Gamma_7) = 144B_4^0/77 - 320B_6^0/143$  and  $E(\Gamma_6) = -16B_4^0/11 - 1600B_6^0/429$  and with isotropic  $g$ -factors  $g(\Gamma_7) = 3g_J = 3.429$  and  $g(\Gamma_6) = -7/3g_J = -2.667$ , respectively. Here  $\Gamma_{6,7,8}$  are irreducible representations of double cubic group [4].


**Figure 1.** The diagram of  $g$ -factors of  $\text{Yb}^{3+}$  ion in tetragonal crystalline electric field and experimental  $g$ -points taken from literature (tab. 2).

As  $g$ -factors of each doublet depend only on one parameter  $\varphi_6$  or  $\varphi_7$  (tab. 1) we can find the equation relating  $g_{\parallel}$  and  $g_{\perp}$ . Figure 1 represents the diagram of  $g$ -factors. The solid and dashed parts of the line  $g_{\parallel} + 2g_{\perp} + 7g_J = 0$  correspond to the doublets  $^4\Gamma_6^t$  and  $^3\Gamma_6^t$ , the solid and dashed parts of the ellipse  $(g_{\parallel} - g_J)^2 / 4 + g_{\perp}^2 / 3 = 4g_J^2$  correspond to the doublets  $^2\Gamma_7^t$  and  $^1\Gamma_7^t$ . The line and the ellipse meet in the point  $(-g_J, -3g_J)$  marked by a star.

On the diagram (fig. 1) we marked experimental values of  $\text{Yb}^{3+}$   $g$ -factors in several crystals (see also

**Table 2.** Experimental  $g$ -factors of  $\text{Yb}^{3+}$  ion in tetragonal crystalline electric field given in figure 1.

	YbRh <sub>2</sub> Si <sub>2</sub> [1]	YbIr <sub>2</sub> Si <sub>2</sub> [2]	HfSiO <sub>4</sub> [5]	KY <sub>3</sub> F <sub>10</sub> [6]	KMgF <sub>3</sub> [7]	CaF <sub>2</sub> [8]
$ g_{\parallel} $	0.17(7)	0.85(1)	6.998(6)	5.363(5)	1.070(1)	2.412(3)
$ g_{\perp} $	3.561(6)	3.357(5)	0.4(3)	1.306(2)	4.430(3)	3.802(5)

tab. 2). This allows us to estimate the signs of  $g$ -factors and to make assumptions about the ground state Kramers doublet on the basis of measured absolute values of  $g$ -factors.

For example, it is evident that the ground state doublet of  $\text{Yb}^{3+}$  ion in HfSiO<sub>4</sub> is  $^3\Gamma'_6$  and both parallel and perpendicular  $g$ -factors have a negative sign (if we choose the positive sign in Zeeman energy as in (5)). The ground state doublet of  $\text{Yb}^{3+}$  ion in KMgF<sub>3</sub> is  $^4\Gamma'_6$ , the sign of  $g_{\parallel}$  is positive, the sign of  $g_{\perp}$  is negative. In CaF<sub>2</sub> crystal the tetragonal center of  $\text{Yb}^{3+}$  is in state  $^1\Gamma'_7$  and the sign of  $g_{\parallel}$  is positive but the sign of  $g_{\perp}$  can be both positive and negative (two points on fig. 1). In KY<sub>3</sub>F<sub>10</sub> the absolute values of  $g$ -factors have such values that do not allow to select the ground state between  $^3\Gamma'_6$  and  $^1\Gamma'_7$ . In YbRh<sub>2</sub>Si<sub>2</sub> and YbIr<sub>2</sub>Si<sub>2</sub> crystals  $g_{\perp}$  can also be both positive and negative if ground state doublet is  $^2\Gamma'_7$ . But  $^4\Gamma'_6$  could be considered as candidates for the ground state. A slight difference between experimental and theoretical values can be explained mainly by taking into account the Kondo interaction, i.e. an exchange coupling between the  $4f$ -electrons of the  $\text{Yb}^{3+}$  ion and conduction electrons [3].

### 3. Calculation of CEF parameters for $\text{Yb}^{3+}$ ion. Comparison with another papers.

Let us calculate the CEF parameters for the given excited state doublets energies  $\Delta_1 < \Delta_2 < \Delta_3$ . It follows from (3) that

$$B_2^0 = 3A/2 + C/2 + D/2, \quad B_4^0 = A/16 + 5C/16 - D, \quad B_6^0 = 39A/160 - 91C/160 - 13D/40 \quad (7)$$

and from (4) that

$$B_4^4 = -7\sqrt{35}A_3/16 - 35\sqrt{3}C_3/16, \quad B_6^4 = 117\sqrt{35}A_3/160 - 273\sqrt{3}C_3/160. \quad (8)$$

Taking one of the doublets with energy  $E_k$  (tab. 1) as the ground, defining the differences of doublets energies as  $E_{mk} = E_m - E_k$  and solving this system of linear equations we can express  $C$ ,  $A$  and  $D$  through  $E_{mk}$ . Substituting relations  $A_3 = A \tan \varphi_6$  and  $C_3 = C \tan \varphi_7$  into (8) and then  $C$ ,  $A$  and  $D$  into (7) and (8) we find:

$$\begin{aligned} B_2^0 &= \frac{1}{8}b + \frac{3}{4}b_6 \cos \varphi_6 + \frac{1}{4}b_7 \cos \varphi_7, \\ B_4^0 &= -\frac{1}{4}b + \frac{1}{32}b_6 \cos \varphi_6 + \frac{5}{32}b_7 \cos \varphi_7, & B_4^4 &= -\frac{7\sqrt{35}}{32}b_6 \sin \varphi_6 - \frac{35\sqrt{3}}{32}b_7 \sin \varphi_7, \\ B_6^0 &= -\frac{13}{160}b + \frac{39}{320}b_6 \cos \varphi_6 - \frac{91}{320}b_7 \cos \varphi_7, & B_6^4 &= \frac{117\sqrt{35}}{320}b_6 \sin \varphi_6 - \frac{273\sqrt{3}}{320}b_7 \sin \varphi_7, \end{aligned} \quad (9)$$

where  $b$ ,  $b_6$  and  $b_7$  are determined in table 3. To use (9) we have to choose the ground state doublet and the excited state doublets sequence to express energy differences  $E_{mk}$  in table 3 through experimental values  $\Delta_1 < \Delta_2 < \Delta_3$ .

**Table 3.**  $b$ ,  $b_6$  and  $b_7$  in (9).

Ground state	$b$	$b_6$	$b_7$
$^1\Gamma'_7$	$E_{31} - E_{21} + E_{41}$	$E_{31} - E_{41}$	$-E_{21}$
$^2\Gamma'_7$	$E_{32} - E_{12} + E_{42}$	$E_{32} - E_{42}$	$E_{12}$
$^3\Gamma'_6$	$E_{43} - E_{13} - E_{23}$	$-E_{43}$	$E_{13} - E_{23}$
$^4\Gamma'_6$	$E_{34} - E_{14} - E_{24}$	$E_{34}$	$E_{14} - E_{24}$

Angular parameters  $\varphi_6$  and  $\varphi_7$  can take the values  $-\pi/2 \leq \varphi_6, \varphi_7 \leq \pi/2$  independently, the energy scheme does not depend on them. To determine the values of  $\varphi_6$  and  $\varphi_7$  we have to use additional experimental results. Thus the experimental values of ground state Kramers doublet  $g$ -factors can help us to define the ground state using figure 1 and one of the angular parameters:  $\varphi_6$  in the case of  $\Gamma'_6$  ground state doublet symmetry or  $\varphi_7$  in

the case of  $\Gamma'_7$  ground state doublet symmetry. But the sign of this angular parameter remain undefined. For doublets with  $\Gamma'_6$  symmetry it happens because  $g_{\parallel}$  and  $g_{\perp}$  depend only on  $\cos \varphi_6$  (tab. 1), and for doublets with  $\Gamma'_7$  symmetry the reason is that in usual EPR experiments we are able to define only the absolute values of  $g$ -factors, therefore we have to consider two points on  $g$ -diagram (fig. 1) with opposite signs of  $g_{\perp} \sim \sin \varphi_7$  (tab. 1). Notice that only  $B_4^4$  and  $B_6^4$  in (9) depend on the signs of  $\varphi_6$  and  $\varphi_7$ .

**Table 4.**  $g$ -factors values from figure 2 and corresponding values of parameters  $\varphi_6$  or  $\varphi_7$  (see tab. 1).

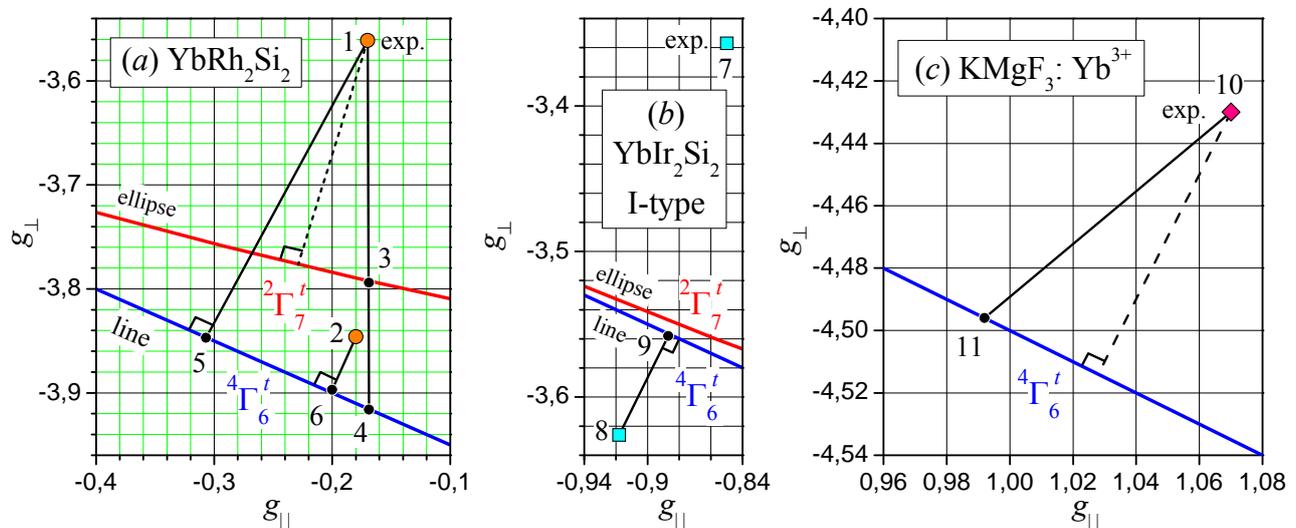
Compound	$g$ -point	$g_{\parallel}$	$g_{\perp}$	Ref.	$\varphi_6$ or $\varphi_7$
$\text{YbRh}_2\text{Si}_2$	1	- 0.17	- 3.561	[1]*	$\varphi_7 = - 1.2798$ $\varphi_6 = \pm 0.7769$ $\varphi_6 = \pm 0.8191$ $\varphi_6 = \pm 0.787$
	2	- 0.18	- 3.846	[10]	
	3	- 0.169	- 3.794	[9]	
	4	- 0.169	- 3.916	[9]	
	5	- 0.307	- 3.847	[9]	
	6	- 0.20	- 3.897	[10]	
$\text{YbIr}_2\text{Si}_2$	7	- 0.85	- 3.357	[2]*	$\varphi_6 = \pm 0.9811$
	8	- 0.918	- 3.626	[10]	
	9	- 0.887	- 3.558	[10]	
$\text{KMgF}_3$	10	1.070	- 4.430	[7]	$\varphi_6 = \pm 0.2576$
	11	0.992	- 4.496	[7]	

\*  $g$ -factors absolute values measured at 5 K

We have compared our results with [9], [10] and [7]. In these papers the CEF parameters for  $\text{Yb}^{3+}$  ion in  $\text{YbRh}_2\text{Si}_2$  [9,10],  $\text{YbIr}_2\text{Si}_2$  [10] and  $\text{KMgF}_3$  [7] crystals were calculated with the use of least squares method, i.e. authors tried to find CEF parameters which give best coincidence between numerically calculated and experimental values of ground state doublet  $g$ -factors and energy levels. Figure 2 and table 4 represent experimentally measured and theoretically calculated  $g$ -factors from [9], [10] and [7]. CEF parameters obtained in these papers are given in table 5.

In [9]  $\text{YbRh}_2\text{Si}_2$  compound has been investigated (fig. 2a). Using the least squares method the absolute values of  $g$ -factors (tab. 2) and energies of three excited levels (17, 25 and 43 meV [11]) have been taken into account. All obtained sets of CEF parameters (tab. 5) satisfy exactly the experimental energy scheme of  ${}^2F_{7/2}$  multiplet and give negative signs of  $g_{\parallel}$  and  $g_{\perp}$  (points 3, 4 and 5 on fig. 2a), i.e. correspond to the lowest point from two points for given crystal on figure 1.

In the case of  $\Gamma_7'$  symmetry of ground state doublet CEF parameters calculated by authors of [9] (tab. 5) correspond to point 3 on figure 2a, but it is not the closest point to the experimental one. CEF parameters from [9] could be obtained from our expressions (9) for  $\Delta_i$ ,  $\varphi_6$ ,  $\varphi_7$  and doublets sequence given in table 5. Considering the case of  $\Gamma_6'$  ground state doublet symmetry the authors of [9] note that the mean values of experimental  $g$ -factors  $\langle |g| \rangle = (|g_{\parallel}| + 2|g_{\perp}|)/3 = 2.43$  are closer to the absolute value of cubic  $\Gamma_6$  doublet  $g$ -factor ( $g = 2.67$ ) than to the absolute value of cubic  $\Gamma_7$  doublet  $g$ -factor ( $g = 3.43$ ). However, we have to notice that taking into consideration the signs of  $g$ -factors, the point  $g_{\parallel} = g_{\perp} = \langle g \rangle = -2.43$  lies almost on the ellipse corresponding to doublet  ${}^2\Gamma_7'$  on figure 1. This doublet  ${}^2\Gamma_7'$  is not originated from the cubic doublet  $\Gamma_7$  but appears to be a result of the cubic quartet  $\Gamma_8$  splitting (see above). Moreover, the  $g$ -curve of doublet  ${}^2\Gamma_7'$  is closer to the experimental  $g$ -point than  $g$ -line of doublet  ${}^4\Gamma_6'$ . The CEF parameters calculated by authors of [9] for the case of  $\Gamma_6'$  ground state doublet symmetry correspond to the optimal point 5 on the figure 2a (the values of parameters are not given in [9]).


**Figure 2.** Experimentally measured (tab. 2) and theoretically calculated  $g$ -factors of  $\text{Yb}^{3+}$  ion in (a)  $\text{YbRh}_2\text{Si}_2$ , (b)  $\text{YbIr}_2\text{Si}_2$  and (c)  $\text{KMgF}_3$  from [9], [10] and [7]. Numerical values of numbered  $g$ -points are given in table 4.

**Table 5.** Comparison of  $\text{Yb}^{3+}$  ion CEF parameters in  $\text{YbRh}_2\text{Si}_2$ ,  $\text{YbIr}_2\text{Si}_2$  and  $\text{KMgF}_3$  crystals from [9], [10] and [7] with parameters calculated from (9). CEF parameters  $B_k^q$ , parameter of the spin-orbit interaction  $\zeta$  and excited state doublets energies  $\Delta_i$  are given in meV.

Compound	YbRh <sub>2</sub> Si <sub>2</sub>						YbIr <sub>2</sub> Si <sub>2</sub>		KMgF <sub>3</sub>	
	[9]	Eq. (9)	[9]	Eq. (9)	[10]	Eq. (9)	[10]	Eq. (9)	[7]	Eq. (9)
$B_2^0$	11.7	11.73	25.0	24.92	21.70	21.74	2.75	2.78	105.38	105.56
$B_4^0$	-7.4	-7.4	1.9	1.83	-0.02	-0.02	5.18	5.17	4.84	4.58
$B_4^4$	77.6	77.62	46.0	45.64	51.88	51.79	42.10	42.13	157.95	152.6
$B_6^0$	-4.0	-3.98	1.7	1.61	4.92	4.93	8.64	8.63	-0.124	-0.125
$B_6^4$	-18.5	-18.52	-60.5	-60.04	-56.33	-56.22	-33.01	-33.05	16.98	17.52
$\zeta$			359.8						360.03	
$\varphi_6$		-1.2818		-0.7769		-0.787		-0.9811		-0.2576
$\varphi_7$		-1.2798		-0.4525		0.9557		0.4634		-0.9135
Doublets sequence	2, 4, 1, 3		4, 2, 1, 3		4, 1, 2, 3		4, 1, 3, 2		4, 2, 1, 3	
g-point	3		4		6		9		11	
$\Delta_1, \Delta_2, \Delta_3$	17, 25, 43						18, 25, 36		13.14, 87.28, 125.59	

Besides, the authors of [9] have calculated CEF parameters for  $\Gamma_6^t$  ground state doublet symmetry case taking into account all states of  $^2F$  term and therefore considering both crystal field and spin-orbit interaction with spin-orbit interaction constant as an additional fitting parameter. The  $g$ -factors values calculated in [9] correspond to the point 4 on the figure 2a which still lies on the line we have plotted considering only ground  $^2F_{7/2}$  multiplet. CEF parameters (tab. 5) are also well reproduced by expressions (9).

In [10]  $\text{YbRh}_2\text{Si}_2$  and  $\text{YbIr}_2\text{Si}_2$  crystals have been considered. In the frame of the least squares method authors took into account only states of ground multiplet  $^2F_{7/2}$ , the experimental values of energies (17, 25 and 43 meV for  $\text{YbRh}_2\text{Si}_2$  [11] and 18, 25 and 36 meV for  $\text{YbIr}_2\text{Si}_2$  [12]) and  $g$ -factors (see point 1 on fig. 2a and point 7 on fig. 2b) increased at 8 % (see point 2 on fig. 2a and point 8 on fig. 2b). The authors argue that this increase of the absolute values of  $g$ -factors is caused by the interaction with conduction electrons.  $\Gamma_6^t$  symmetry doublet was considered as ground state. The theoretical  $g$ -points found in [10] are the optimal points 6 and 9 (fig. 2a,b). The corresponding CEF parameters coincide with those calculated from expressions (9) (tab. 5).

In paper [7] CEF parameters of  $\text{Yb}^{3+}$  ion in  $\text{KMgF}_3$  crystal have been found (tab. 5). Using the least squares method the experimental values of  $g$ -factors (tab. 2) and experimental energy of whole  $^2F$  term levels have been taken into account. Obtained CEF parameters satisfy the experimental energy scheme of  $^2F$  term very well, but are reproduced by our expressions (9) only approximately (tab. 5), because we have found these expressions taking into account only ground multiplet  $^2F_{7/2}$ . Experimental  $g$ -points 10 and theoretical  $g$ -points 11 corresponding to CEF parameters from [7] are given on fig. 2c. It is remarkable that point 11 lies on the line  $g_{\parallel} + 2g_{\perp} + 8 = 0$  which we have plotted considering only the ground multiplet  $^2F_{7/2}$ . This can be explained as follows. Expressing wave functions of ground state doublet  $\Gamma_6^t$  in term of ionic states  $|J, M_J\rangle$  of  $^2F$  term as  $|\uparrow, \downarrow\rangle = \pm p_1 |7/2, \mp 7/2\rangle \pm p_2 |7/2, \pm 1/2\rangle + p_3 |5/2, \pm 1/2\rangle$  where  $p_1^2 + p_2^2 + p_3^2 = 1$  we find that

$$g_{\parallel} = -8 + \frac{64}{7} p_2^2 - \frac{8\sqrt{3}}{7} p_2 p_3 + \frac{62}{7} p_3^2, \quad g_{\perp} = -\frac{32}{7} p_2^2 + \frac{4\sqrt{3}}{7} p_2 p_3 + \frac{18}{7} p_3^2. \quad (10)$$

In this case  $g_{\parallel}$  and  $g_{\perp}$  are related by the equation  $g_{\parallel} + 2g_{\perp} + 8 = 14p_3^2$ , but as the admixture of excited  $^2F_{5/2}$  multiplet is small ( $p_3 = 0.00551$  [7]) we obtain previous relation  $g_{\parallel} + 2g_{\perp} + 8 = 0$ .

Note that consideration of experimental energy levels of whole  $^2F$  term for  $\text{YbRh}_2\text{Si}_2$  and  $\text{YbIr}_2\text{Si}_2$  crystals could eliminate the uncertainty in CEF parameters determination (9).

#### 4. CEF parameters for $\text{Ce}^{3+}$ ion.

The ground multiplet of free  $\text{Ce}^{3+}$  ion is  $^2F_{5/2}$  and the excited multiplet  $^2F_{7/2}$  has energy greater for 273 meV [4]. Let us consider ground multiplet  $^2F_{5/2}$  with states  $|J = 5/2, M_J\rangle \equiv |M_J\rangle$ , where  $M_J$  is the eigenvalue of  $J_z$ . The Hamiltonian of the  $\text{Ce}^{3+}$  ion interaction with the tetragonal CEF could be written via equivalent operators  $O_k^q(\mathbf{J})$  [4]:

**Table 6.** The energies, states and  $g$ -factors of  $Ce^{3+}$  ion in tetragonal crystalline electric field.

$E_{1,2} = D \pm A / \cos \varphi$	$E_3 = -2D$
$ ^1\Gamma_7' \uparrow, \downarrow\rangle = a_1  \pm 5/2\rangle + a_2  \mp 3/2\rangle$	$ ^3\Gamma_6' \uparrow, \downarrow\rangle =  \pm 1/2\rangle$
$ ^2\Gamma_7' \uparrow, \downarrow\rangle = a_2  \pm 5/2\rangle - a_1  \mp 3/2\rangle$	
$g_{\parallel} (^{1,2}\Gamma_7') = g_J (5a_{1,2}^2 - 3a_{2,1}^2) = g_J (1 \pm 4 \cos \varphi)$	$g_{\parallel} (^3\Gamma_6') = g_J$
$g_{\perp} (^{1,2}\Gamma_7') = \pm 2\sqrt{5}g_J a_1 a_2 = \pm \sqrt{5}g_J \sin \varphi$	$g_{\perp} (^3\Gamma_6') = 3g_J$

$$H = \alpha B_2^0 O_2^0 + \beta (B_4^0 O_4^0 + B_4^4 O_4^4), \quad (11)$$

where  $B_k^q$  are the CEF parameters,  $\alpha = -2/35$ ,  $\beta = 2/315$  [4].

The two-valued irreducible representation  $D^{5/2}$  of rotation group contains two two-dimensional irreducible representations  $\Gamma_7'$  and  $\Gamma_6'$  of the double tetragonal group:  $D^{5/2} = 2\Gamma_7' + \Gamma_6'$  [4]. Therefore the states of  $Ce^{3+}$  in the tetragonal CEF are three Kramers doublets. The decomposition of  $D^{5/2}$  includes once  $\Gamma_6'$  and twice  $\Gamma_7'$  representations. The doublet with  $|\pm 1/2\rangle$  states and energy  $\langle \pm 1/2 | H | \pm 1/2 \rangle$  corresponds to  $\Gamma_6'$  representation. To find energies and states corresponding to  $\Gamma_7'$  representation we have to diagonalize two-dimensional matrices

$$\begin{pmatrix} 2A_1 & A_3 \\ A_3 & 2A_2 \end{pmatrix} \quad (12)$$

of operator (11) on bases  $|5/2\rangle$ ,  $|-3/2\rangle$  and  $|-5/2\rangle$ ,  $|3/2\rangle$ . It is convenient to use parameters  $A$ ,  $D$  and  $A_3$ :

$$A = A_1 - A_2 = -12B_2^0/35 + 16B_4^0/21, \quad D = A_1 + A_2 = -8B_2^0/35 - 8B_4^0/21, \quad A_3 = 8\sqrt{5}B_4^4/105. \quad (13)$$

The eigenvectors of matrix (12) ( $a_{1,2}$ ,  $\pm a_{2,1}$ ) could also be written via angular parameter:  $a_1 = \cos(\varphi/2)$ ,  $a_2 = \sin(\varphi/2)$ . Diagonalizing the matrix (12) we find that  $\tan \varphi = A_3/A$ ,  $-\pi/2 \leq \varphi \leq \pi/2$ . The energies  $E_k$  ( $k = 1..3$ ), states  $|\uparrow\rangle$ ,  $|\downarrow\rangle$  and  $g$ -factors of Kramers doublets are given in table 6. In this table the arrow  $\uparrow$  ( $\downarrow$ ) and the left (right) index correspond to the upper (lower) sign;  $g_J = 6/7$  is the Lande  $g$ -factor.

For the  $\Gamma_7'$  doublets the  $g_{\parallel}$  and  $g_{\perp}$  are related by expression  $(g_{\parallel} - g_J)^2/16 + g_{\perp}^2/5 = g_J^2$ . The left and right parts of ellipse constructed in  $(g_{\parallel}, g_{\perp})$  axis would correspond to  $^2\Gamma_7'$  and  $^1\Gamma_7'$  doublets, respectively.

Let us define the CEF parameters for given energies of excited state doublets  $\Delta_1 < \Delta_2$ . It follows from (13) that

$$B_2^0 = -5A/4 - 5D/2, \quad B_4^0 = 3A/4 - 9D/8, \quad B_4^4 = 105A_3/8\sqrt{5}. \quad (14)$$

Choosing one of the doublets with energy  $E_k$  (tab. 6) as a ground state, solving system of linear equations  $E_{mk} = E_m - E_k$  we can express  $A$  and  $D$  through  $E_{mk}$ . Substituting relation  $A_3 = A \tan \varphi$  and then  $A$  and  $D$  into (14) we can find:

$$B_2^0 = \frac{5}{12}b + \frac{5}{8}\tilde{b} \cos \varphi, \quad B_4^0 = \frac{3}{16}b - \frac{3}{8}\tilde{b} \cos \varphi, \quad B_4^4 = -\frac{105}{16\sqrt{5}}\tilde{b} \sin \varphi, \quad (15)$$

**Table 7.**  $b$  and  $\tilde{b}$  in (15).

Ground state	$b$	$\tilde{b}$
$^1\Gamma_7'$	$2E_{31} - E_{21}$	$E_{21}$
$^2\Gamma_7'$	$2E_{32} - E_{12}$	$-E_{12}$
$^3\Gamma_6'$	$-E_{23} - E_{13}$	$E_{23} - E_{13}$

where  $b$  and  $\tilde{b}$  are determined in table 7. To use (15) we have to choose the ground state doublet and the excited state doublets sequence to express energy differences  $E_{mk}$  in table 7 through experimental values  $\Delta_1 < \Delta_2$ . The value of angular parameter  $\varphi$  in (15) lies within interval  $-\pi/2 \leq \varphi \leq \pi/2$ , the energy scheme does not depend on it. To define the value of  $\varphi$  it is necessary to use other experimental data. In the case of  $\Gamma_7'$  ground state doublet symmetry the experimental values of  $g$ -factors could help to define  $\varphi$ . However, as the sign of  $g$ -factor cannot be defined from usual EPR experiment and  $g_{\perp} \sim \sin \varphi$  (tab. 6), so the sign of  $\varphi$  and therefore the sign of  $B_4^4$  in (15) stay undefined.

In the case of cubic symmetry  $B_2^0 = 0$ ,  $B_4^4 = 5B_4^0$ , so  $\tan \varphi = \sqrt{5}/2$ ,  $a_1 = \sqrt{5}/6$ ,  $a_2 = \sqrt{1}/6$ . The doublets  $^1\Gamma_7'$  and  $^3\Gamma_6'$  merge into a cubic quartet  $\Gamma_8$  with energy  $E(\Gamma_8) = 16B_4^0/21$  in accordance with expansion  $\Gamma_8 = \Gamma_7' + \Gamma_6'$  [4]. The doublet  $^2\Gamma_7'$  turns into a cubic doublet  $\Gamma_7$  with energy  $E(\Gamma_7) = -32B_4^0/21$  and with isotropic  $g$ -factor  $g(\Gamma_7) = -5/3g_J = -1.429$ . Here  $\Gamma_{7,8}$  are irreducible representations of the double cubic group.

## 5. Summary

For  $\text{Yb}^{3+}$  and  $\text{Ce}^{3+}$  ions all possible sets of tetragonal crystalline electric field parameters that satisfy the given experimental energy scheme of ground multiplet are defined.

For  $\text{Yb}^{3+}$  ion the CEF parameters (9) beside the energies of Kramers doublets depend also on angular parameters  $\varphi_6$  and  $\varphi_7$ , defining wave functions of  $\Gamma'_6$  and  $\Gamma'_7$  symmetry doublets correspondingly. Their values are undefined and lie within the interval  $-\pi/2 \leq \varphi_6, \varphi_7 \leq \pi/2$  independently. To define these parameters exactly it is necessary to use another experimental set of data. For example, experimental absolute values of ground state doublet  $g$ -factors allow to define the absolute value for one of angular parameters.

The earlier published CEF parameters for  $\text{Yb}^{3+}$  ion in  $\text{YbRh}_2\text{Si}_2$ ,  $\text{YbIr}_2\text{Si}_2$  and  $\text{KMgF}_3$  crystals calculated with the use of least squares method could be obtained from our formulas (see tab. 5).

For  $\text{Ce}^{3+}$  ion the CEF parameters (15) beside the energies of Kramers doublets depend also on angular parameter  $-\pi/2 \leq \varphi \leq \pi/2$ , defining wave functions of  $\Gamma'_7$  symmetry doublets. In case of  $\Gamma'_7$  ground state doublet symmetry the experimental absolute values of  $g$ -factors could help to define the absolute value of this parameter.

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