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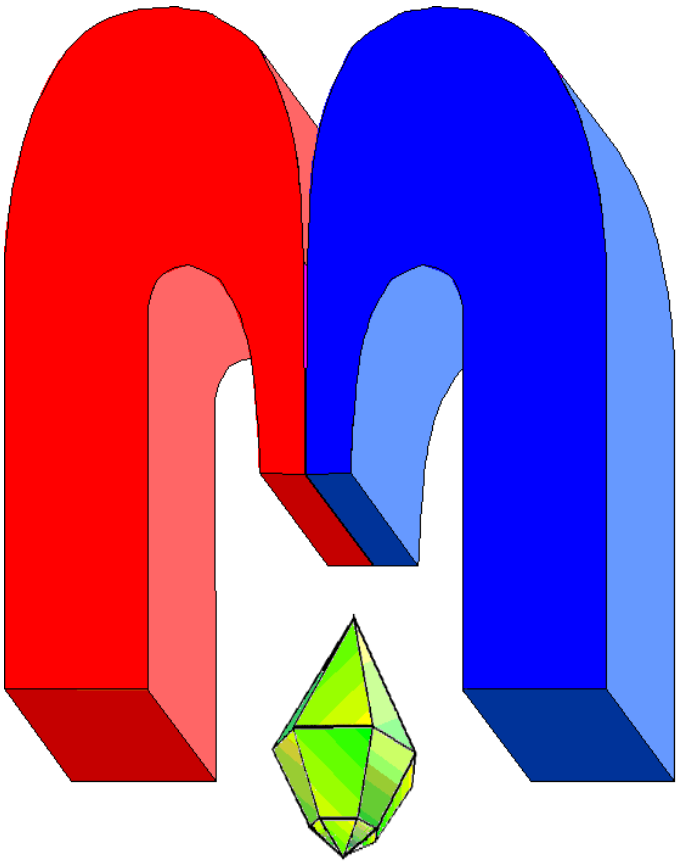

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* In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Determination of tetragonal crystalline electric field parameters for Yb^{3+} and Ce^{3+} ions from experimental *g*-factors values and energy levels of Kramers doublets

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The tetragonal crystalline electric field parameters for Yb^{3+} and Ce^{3+} ions are expressed via ground multiplet exited doublets energies and parameters defining doublets' wave functions. The crystalline electric field parameters for Yb^{3+} ion in $YbRh_2Si_2$, $YbIr_2Si_2$ and $KMgF_3$ 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 $YbRh_2Si_2$ and $YbIr_2Si_2$ [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^{3+} 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^{3+} and Ce^{3+} tetragonal centers.

2. Diagram of Yb^{3+} g-factors

A free Yb^{3+} ion has a $4f^{13}$ configuration with one term ^2F. The spin-orbit interaction splits the ^2F term into two multiplets: $^2F_{7/2}$ with $J = 7/2$ and $^2F_{5/2}$ with $J = 5/2$, where J is value of the total momentum $\mathbf{J} = (J_x, J_y, J_z)$. 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 $^2F_{7/2}$ with states $|J = 7/2, M_J\rangle \equiv |M_J\rangle$, where M_J is the eigenvalue of J_z, z is the tetragonal axis. The Hamiltonian of the Yb^{3+} ion interaction with the tetragonal CEF could be written via equivalent operators $O_k^q(\mathbf{J})$ [4]:

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

where B_k^q 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 $D^{7/2}$ of rotation group contains two two-dimensional irreducible representations Γ_7^t and Γ_6^t of the double tetragonal group: $D^{7/2} = 2\Gamma_7^t + 2\Gamma_6^t$ [4]. Therefore the states of Yb^{3+} in the tetragonal CEF are four Kramers doublets. As the decomposition of $D^{7/2}$ includes twice each of representations Γ_7^t and Γ_6^t, the matrix of operator (1) could be expressed via two two-dimensional matrices

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

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

$$C = C_1 - C_2 = 4B_2^0/21 + 40B_4^0/77 - 560B_6^0/429\,, \qquad A = A_1 - A_2 = 4B_2^0/7 + 8B_4^0/77 + 80B_6^0/143\,, \tag{3}$$
$$D = -C_1 - C_2 = A_1 + A_2 = 2B_2^0/21 - 64B_4^0/77 - 160B_6^0/429\,,$$

where $C_1 + C_2 + A_1 + A_2 = 0$ as traces of O_k^q are equal to zero. C_3 and A_3 are

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

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

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

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 φ_7 and φ_6 which correspond to Γ_7^t and Γ_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 $-\pi/2 \le \varphi_7, \varphi_6 \le \pi/2$. 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 ↑ or ↓ 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 θ 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 $g_J \mu_B \mathbf{HJ}$ in the basis $|\uparrow\rangle$, $|\downarrow\rangle$ of each doublet could be represented by matrix

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

where

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

and **H** is the magnetic field, **S** is the effective spin operator with $S = 1/2$, μ_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 Γ_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 Γ_7 and Γ_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].

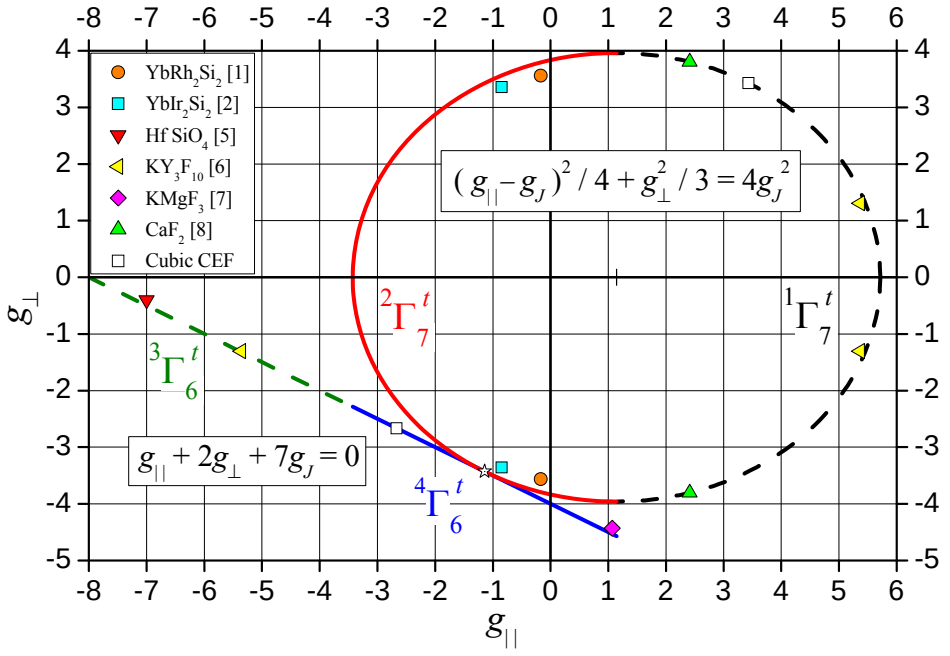

Figure 1. The diagram of *g*-factors of Yb^{3+} ion in tetragonal crystalline electric field and experimental *g*-points taken from literature (tab. 2).

As *g*-factors of each doublet depend only on one parameter φ_6 or φ_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 Yb^{3+} *g*-factors in several crystals (see also

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

	$YbRh_2Si_2$ [1]	$YbIr_2Si_2$ [2]	$HfSiO_4$ [5]	KY_3F_{10} [6]	$KMgF_3$ [7]	CaF_2 [8]
$\lvert g_\parallel \rvert$	0.17(7)	0.85(1)	6.998(6)	5.363(5)	1.070(1)	2.412(3)
$\lvert g_\perp \rvert$	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 Yb^{3+} ion in $HfSiO_4$ is ${}^3\Gamma_6^t$ 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 Yb^{3+} ion in $KMgF_3$ is ${}^4\Gamma_6^t$, the sign of $g_\parallel$ is positive, the sign of $g_\perp$ is negative. In CaF_2 crystal the tetragonal center of Yb^{3+} is in state ${}^1\Gamma_7^t$ 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_3F_{10} the absolute values of *g*-factors have such values that do not allow to select the ground state between ${}^3\Gamma_6^t$ and ${}^1\Gamma_7^t$. In $YbRh_2Si_2$ and $YbIr_2Si_2$ crystals $g_\perp$ can also be both positive and negative if ground state doublet is ${}^2\Gamma_7^t$. But ${}^4\Gamma_6^t$ 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 4*f*-electrons of the Yb^{3+} ion and conduction electrons [3].

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

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

$$B_2^0 = 3A/2 + C/2 + D/2, \qquad B_4^0 = A/16 + 5C/16 - D, \qquad B_6^0 = 39A/160 - 91C/160 - 13D/40 \tag{7}$$

and from (4) that

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

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:

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

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 exited state doublets sequence to express energy differences E_{mk} in table 3 through experimental values $\Delta_1 < \Delta_2 < \Delta_3$. Angular parameters φ_6 and φ_7 can take the values $-\pi/2 \le \varphi_6, \varphi_7 \le \pi/2$ independently, the energy scheme does not depend on them. To determine the values of φ_6 and φ_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: φ_6 in the case of Γ_6^t ground state doublet symmetry or φ_7 in the case of Γ_7^t ground state doublet symmetry. But the sign of this angular parameter remain undefined. For doublets with Γ_6^t symmetry it happens because $g_\parallel$ and $g_\perp$ depend only on $\cos\varphi_6$ (tab. 1), and for doublets with Γ_7^t 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 sings 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 φ_6 and φ_7.

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

Ground state	*b*	b_6	b_7
${}^1\Gamma_7^t$	$E_{31} - E_{21} + E_{41}$	$E_{31} - E_{41}$	$-E_{21}$
${}^2\Gamma_7^t$	$E_{32} - E_{12} + E_{42}$	$E_{32} - E_{42}$	E_{12}
${}^3\Gamma_6^t$	$E_{43} - E_{13} - E_{23}$	$-E_{43}$	$E_{13} - E_{23}$
${}^4\Gamma_6^t$	$E_{34} - E_{14} - E_{24}$	E_{34}	$E_{14} - E_{24}$

Table 4. *g-factors values from figure 2 and corresponding values of parameters φ_6 or φ_7 (see tab. 1).*

Compound	*g*-point	$g_\parallel$	$g_\perp$	Ref.	φ_6 or φ_7
$YbRh_2Si_2$	1	− 0.17	− 3.561	[1]*	
	2	− 0.18	− 3.846	[10]	
	3	− 0.169	− 3.794	[9]	$\varphi_7 = -1.2798$
	4	− 0.169	− 3.916	[9]	$\varphi_6 = \pm 0.7769$
	5	− 0.307	− 3.847	[9]	$\varphi_6 = \pm 0.8191$
	6	− 0.20	− 3.897	[10]	$\varphi_6 = \pm 0.787$
$YbIr_2Si_2$	7	− 0.85	− 3.357	[2]*	
	8	− 0.918	− 3.626	[10]	
	9	− 0.887	− 3.558	[10]	$\varphi_6 = \pm 0.9811$
$KMgF_3$	10	1.070	− 4.430	[7]	
	11	0.992	− 4.496	[7]	$\varphi_6 = \pm 0.2576$

* *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 Yb^{3+} ion in $YbRh_2Si_2$ [9,10], $YbIr_2Si_2$ [10] and $KMgF_3$ [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] $YbRh_2Si_2$ compound has been investigated (fig. 2*a*). 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. 2*a*), i.e. correspond to the lowest point from two points for given crystal on figure 1.

In the case of Γ_7^t symmetry of ground state doublet CEF parameters calculated by authors of [9] (tab. 5) correspond to point 3 on figure 2*a*, but it is not the closest point to the experimental one. CEF parameters from [9] could be obtained from our expressions (9) for Δ_i, φ_6, φ_7 and doublets sequence given in table 5. Considering the case of Γ_6^t 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 Γ_6 doublet *g*-factor ($g = 2.67$) than to the absolute value of cubic Γ_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 $^2\Gamma_7^t$ on figure 1. This doublet $^2\Gamma_7^t$ is not originated from the cubic doublet Γ_7 but appears to be a result of the cubic quartet Γ_8 splitting (see above). Moreover, the *g*-curve of doublet $^2\Gamma_7^t$ is closer to the experimental *g*-point than *g*-line of doublet $^4\Gamma_6^t$. The CEF parameters calculated by authors of [9] for the case of Γ_6^t ground state doublet symmetry correspond to the optimal point 5 on the figure 2*a* (the values of parameters are not given in [9]).

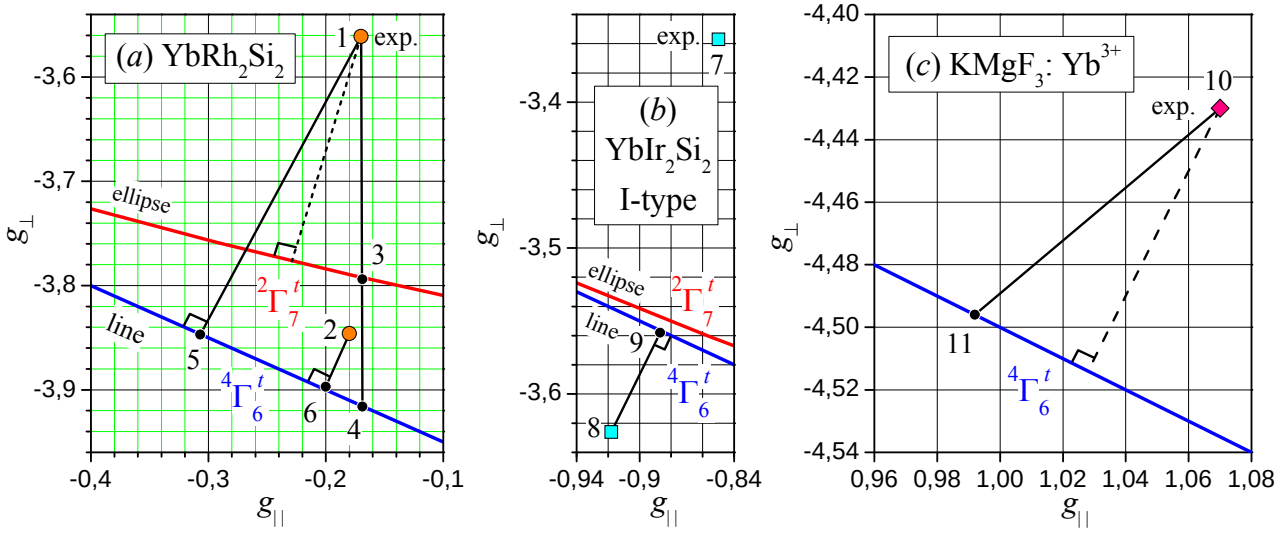

Figure 2. Experimentally measured (tab. 2) and theoretically calculated *g*-factors of Yb^{3+} ion in (*a*) $YbRh_2Si_2$, (*b*) $YbIr_2Si_2$ and (*c*) $KMgF_3$ from [9], [10] and [7]. Numerical values of numbered *g*-points are given in table 4.

Table 5. *Comparison of Yb^{3+} ion CEF parameters in $YbRh_2Si_2$, $YbIr_2Si_2$ and $KMgF_3$ crystals from [9], [10] and [7] with parameters calculated from (9). CEF parameters B_k^q, parameter of the spin-orbit interaction ξ and exited state doublets energies Δ_i are given in meV.*

Compound	$YbRh_2Si_2$						$YbIr_2Si_2$		$KMgF_3$	
Reference	[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
ξ			359.8						360.03	
φ_6		−1.2818		−0.7769		−0.787		−0.9811		−0.2576
φ_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 Γ_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 2*a* 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] $YbRh_2Si_2$ and $YbIr_2Si_2$ 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 $YbRh_2Si_2$ [11] and 18, 25 and 36 meV for $YbIr_2Si_2$ [12]) and g-factors (see point 1 on fig. 2*a* and point 7 on fig. 2*b*) increased at 8 % (see point 2 on fig. 2*a* and point 8 on fig. 2*b*). The authors argue that this increase of the absolute values of g-factors is caused by the interaction with conduction electrons. Γ_6^t symmetry doublet was considered as ground state. The theoretical g-points found in [10] are the optimal points 6 and 9 (fig. 2*a*,*b*). The corresponding CEF parameters coincide with those calculated from expressions (9) (tab. 5).

In paper [7] CEF parameters of Yb^{3+} ion in $KMgF_3$ 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. 2*c*. 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 Γ_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

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

In this case $g_\parallel$ and $g_\perp$ are related by the equation $g_\parallel + 2g_\perp + 8 = 14 p_3^2$, 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 $YbRh_2Si_2$ and $YbIr_2Si_2$ crystals could eliminate the uncertainty in CEF parameters determination (9).

4. CEF parameters for Ce^{3+} ion.

The ground multiplet of free 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 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.*

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

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

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 Γ_7^t and Γ_6^t of the double tetragonal group: $D^{5/2} = 2\Gamma_7^t + \Gamma_6^t$ [4]. Therefore the states of Ce^{3+} in the tetragonal CEF are three Kramers doublets. The decomposition of $D^{5/2}$ includes once Γ_6^t and twice Γ_7^t representations. The doublet with $|\pm 1/2\rangle$ states and energy $\langle \pm 1/2|H|\pm 1/2\rangle$ corresponds to Γ_6^t representation. To find energies and states corresponding to Γ_7^t representation we have to diagonalize two-dimentional matrices

$$\begin{pmatrix} 2A_1 & A_3 \\ A_3 & 2A_2 \end{pmatrix} \tag{12}$$

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:

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

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 $\tan\varphi = A_3/A$, $-\pi/2 \le \varphi \le \pi/2$. 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 Γ_7^t 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 ${}^2\Gamma_7^t$ and ${}^1\Gamma_7^t$ doublets, respectively.

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

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

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:

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

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

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

where b and $\tilde{b}$ are determined in table 7. To use (15) we have to choose the ground state doublet and the exited state doublets sequence to express energy differences E_{mk} in table 7 through experimental values $\Delta_1 < \Delta_2$. The value of angular parameter φ in (15) lies within interval $-\pi/2 \le \varphi \le \pi/2$, the energy scheme does not depend on it. To define the value of φ it is necessary to use other experimental data. In the case of Γ_7^t ground state doublet symmetry the experimental values of g-factors could help to define φ. 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 φ 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 ${}^1\Gamma_7^t$ and ${}^3\Gamma_6^t$ merge into a cubic quartet Γ_8 with energy $E(\Gamma_8) = 16B_4^0/21$ in accordance with expansion $\Gamma_8 = \Gamma_7^t + \Gamma_6^t$ [4]. The doublet ${}^2\Gamma_7^t$ turns into a cubic doublet Γ_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 Yb^{3+} and 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 Yb^{3+} ion the CEF parameters (9) beside the energies of Kramers doublets depend also on angular parameters φ_6 and φ_7, defining wave functions of Γ_6^t and Γ_7^t symmetry doublets correspondingly. Their values are undefined and lie within the interval $-\pi/2 \le \varphi_6, \varphi_7 \le \pi/2$ 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 Yb^{3+} ion in $YbRh_2Si_2$, $YbIr_2Si_2$ and $KMgF_3$ crystals calculated with the use of least squares method could be obtained from our formulas (see tab. 5).

For Ce^{3+} ion the CEF parameters (15) beside the energies of Kramers doublets depend also on angular parameter $-\pi/2 \le \varphi \le \pi/2$, defining wave functions of Γ_7^t symmetry doublets. In case of Γ_7^t 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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