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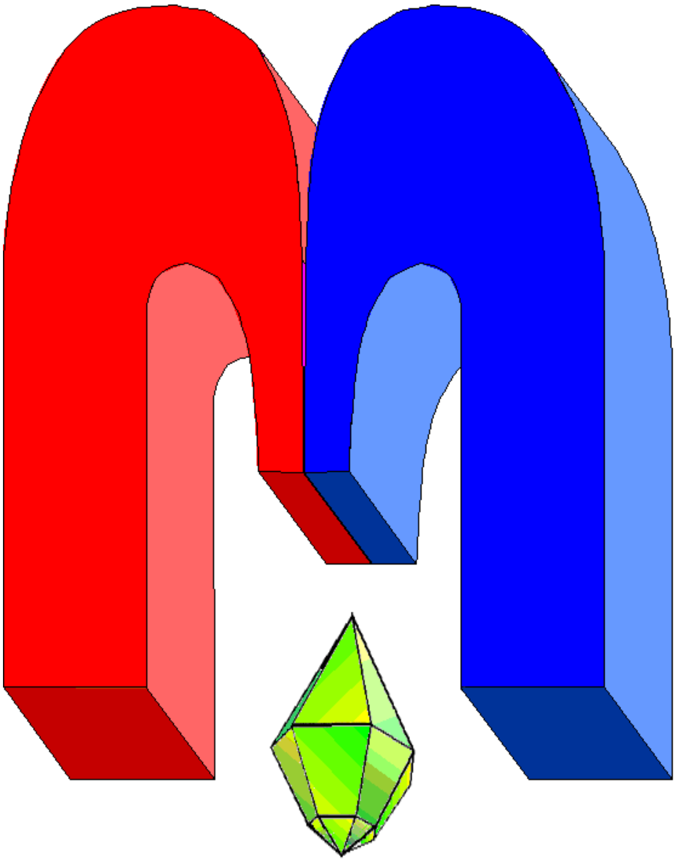

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Calculation of *g*-tensor of rare-earth ions with account of isotropic reduction of orbital momentum

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g-tensor components for a Kramers doublet of an impurity ion doped into dielectric crystal are expressed through coefficients of expansion of the doublet wavefunctions in the basis of full momentum of the impurity ion taking into account isotropic reduction of orbital momentum in Zeeman energy due to covalence. Mixing of terms and multiplets of the impurity ion is considered rigorously in the expansion of doublet wavefunctions. The obtained expressions can be useful in calculations and analysis of *g*-factors dependence on the impurity ion Hamiltonian parameters. The derived formulas are applied to calculation of *g*-factors of the ground Kramers doublet of Ce^{3+} ion doped in $LiYF_4$ crystal. It is shown that considering reduction of orbital momentum of the 4*f* electron of the Ce^{3+} ion in Zeeman energy can significantly improve agreement with experimentally measured *g*-factors for this compound, available in literature.

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1. Introduction

This research was stimulated by theoretical investigation of 4*f* crystal field parameters and *g*-factors of the ground Kramers doublet of Ce^{3+} ion doped in $LiYF_4$ crystal which we conducted earlier [1]. 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. 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 are known in literature [2]. In [1] we considered the Zeeman energy

$$H_{\mathrm{Ze}} = \mu_{\mathrm{B}}\left(2\mathbf{S}+\mathbf{L}\right)\mathbf{H}, \tag{1}$$

where $\mathbf{H}$ is magnetic field, μ_{B} is the Bohr magneton, $\mathbf{S}$ and $\mathbf{L}$ are dimensionless spin and orbital angular momentum of the Ce^{3+} ion 4*f* electron. We found that no reasonable set of 4*f* crystal field parameters can satisfactorily fit the *g*-factors values of the Ce^{3+} ion ground Kramers doublet measured in [2], even if we rigorously consider mixing of the $^2F_{5/2}$ and $^2F_{7/2}$ Ce^{3+} ion multiplets by crystal field. We suggested in [1] that it is necessary to consider reduction of the orbital momentum of the 4*f* electron in the Zeeman energy due to covalency effects, to achieve better agreement with experiment. Let us note, as an argument in favor of considering covalency effects, 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) [3].

In the present study we consider the following rather general case: an impurity ion with an odd number of electrons in lattice crystal field, which can be of an arbitrary point symmetry, but energy level under consideration is a Kramers doublet. We aim to consider rigorously mixing of impurity ion electronic states by crystal field, therefore we consider expansion of the Kramers doublet wavefunctions $|\psi_1\rangle$, $|\psi_2\rangle$ in the basis of full momentum taking into account all terms and multiplets of the impurity ion electronic configuration:

$$\left|\psi_1\right\rangle = \sum_{\gamma SLJM} a_{JM}^{\gamma SL} \left|\gamma SLJM\right\rangle, \tag{2}$$

$$\left|\psi_2\right\rangle = \hat{\theta}\left|\psi_1\right\rangle = \sum_{\gamma SLJM} \left(-1\right)^{J+M} a_{J,-M}^{\gamma SL\,*} \left|\gamma SLJM\right\rangle, \tag{3}$$

where $\hat{\theta}$ is the time reversal operator; quantum number γ allows to differ terms with equal spin and orbital momentum quantum numbers S and L; J and M are quantum numbers of the full momentum of the ion with the usual meaning; complex coefficients $a_{JM}^{\gamma SL}$ satisfy the normalization condition. In many papers only mixing of electronic states within the same multiplet is considered; for example, as for LiYF$_4$:Ce^{3+} crystal, only mixing of states within the ground $^2F_{5/2}$ multiplet was considered in [4,5].

We consider the Zeeman energy

$$H_{\mathrm{Ze}} = \mu_{\mathrm{B}}\mathbf{mH}, \tag{4}$$

$$\mathbf{m} = g_S\mathbf{S} + k\mathbf{L}, \tag{5}$$

where k is isotropic reduction factor for the orbital momentum, g_S is taken as 2.0023 in calculations. Approximation of isotropic reduction factor was introduced in [6] for Tm^{2+} ion doped in CaF$_2$ crystal. A more rigorous analysis of covalent binding by molecular orbital method leads to different reduction factors for orbital momentum matrix elements on wavefunctions, transforming according to different irreducible representations of the impurity ion point symmetry. For example, as for Tm^{2+} ion in CaF$_2$ crystal (cubic point symmetry), two reduction factors have been introduced and calculated in [7,8]. In the case of strong covalent binding (*nd* transition metal ions) reduction factors can sufficiently differ from 1 and from each other for different matrix elements of orbital momentum. However, for the 4*f* electrons of impurity rare-earth ions covalent binding is small, with reduction factors exceeding 0.95, therefore, we can neglect difference between their values and consider isotropic reduction of orbital momentum (5) as an approximation in estimation of its matrix elements.

In the basis of the Kramers doublet states (2), (3) the Zeeman energy can be represented by the effective spin Hamiltonian

$$H_{\mathrm{Ze}}^{\mathrm{eff}} = \mu_{\mathrm{B}}\sum_{\alpha,\beta} H_\alpha g_{\alpha\beta} S_\beta^{\mathrm{eff}}, \tag{6}$$

where α and β denote Cartesian axes; $\mathbf{S}^{\mathrm{eff}}$ is the effective spin operator with $S = 1/2$; $g_{\alpha\beta}$ are components of the g-tensor, which are determined by matrix elements of Cartesian components of the $\mathbf{m}$ operator (5) on the Kramers doublet states as follows:

$$g_{\alpha x} = 2\,\mathrm{Re}\left\langle\psi_1\right|m_\alpha\left|\psi_2\right\rangle,\ \ g_{\alpha y} = -2\,\mathrm{Im}\left\langle\psi_1\right|m_\alpha\left|\psi_2\right\rangle,\ \ g_{\alpha z} = 2\left\langle\psi_1\right|m_\alpha\left|\psi_1\right\rangle. \tag{7}$$

As follows from the above formulas, the set of coefficients $a_{JM}^{\gamma SL}$ determines Kramers doublet wavefunctions (2), (3) and, consequently, values of g-tensor components (7). We find it useful to express g-tensor components explicitly through the $a_{JM}^{\gamma SL}$ coefficients both for calculative reasons and as a tool for analysis of g-tensor dependence on the impurity ion Hamiltonian parameters.

Thus, the purpose of the present study is to establish formulas that would express g-tensor components for a Kramers doublet with account of orbital momentum reduction through the $a_{JM}^{\gamma SL}$ coefficients; as an example of application the derived formulas are used in calculation of g-factors of the ground Kramers doublet of the Ce^{3+} ion in LiYF$_4$ crystal.

The paper is organized as follows. In section 2 we derive formulas for $g_{\alpha\beta}$ expressed through the $a_{JM}^{\gamma LS}$ coefficients that determine the wavefunctions (2), (3) of the Kramers doublet under consideration. In section 3 a particular case of tetragonal local symmetry for the impurity ion is considered. In section 4 a particular case of electronic configuration nl^1 of the impurity ion is considered. Finally, in section 5 we calculate g-factors for a specific system – the Ce^{3+} ion in $LiYF_4$ crystal – and compare results with the known experimental values [2].

2. Formulas for *g*-tensor components expressed through $a_{JM}^{\gamma SL}$ coefficients

For the sake of generality let us consider matrix elements of Cartesian components of the **m** operator (5) between the state $\left|\psi_1\right\rangle$ (2) and an arbitrary state $\left|\varphi\right\rangle$ defined by the following expansion with a set of coefficients $b_{JM}^{\gamma SL}$:

$$\left|\varphi\right\rangle = \sum_{\gamma SLJM} b_{JM}^{\gamma SL}\left|\gamma SLJM\right\rangle. \tag{8}$$

We find it convenient to carry out such transformations that allow to calculate the least possible number of different matrix elements in the right part of the following equation (note that states of the same term γSL appear in matrix elements according to selection rules):

$$\left\langle\psi_1\right|m_\alpha\left|\varphi\right\rangle = \sum_{\gamma SLJMJ'M'} a_{JM}^{\gamma SL^*} b_{J'M'}^{\gamma SL}\left\langle\gamma SLJM\right|m_\alpha\left|\gamma SLJ'M'\right\rangle. \tag{9}$$

For example, it is sufficient to consider only the case $J \geq J'$ in (9), as simultaneous substitutions $J \leftrightarrow J', M \leftrightarrow -M'$ give the term under the sign of summation in (9)

$$\left(-1\right)^{J'-J+M+M'} a_{J',-M'}^{\gamma SL}{}^{*} b_{J,-M}^{\gamma SL}\left\langle\gamma SLJM\right|m_\alpha\left|\gamma SLJ'M'\right\rangle. \tag{10}$$

To obtain (10) one should use the equation

$$\left\langle\gamma SLJM\right|m_\alpha\left|\gamma SLJ'M'\right\rangle = \left(-1\right)^{J+J'-M-M'+1}\left\langle\gamma SLJ',-M'\right|m_\alpha\left|\gamma SLJ,-M\right\rangle, \tag{11}$$

which is actually valid for any time-odd Hermitian operator.

Utilizing (10) we obtain for the z component of operator **m**

$$\begin{aligned}\left\langle\psi_1\right|m_z\left|\varphi\right\rangle = \sum_{\gamma SLJM}\Big[& a_{JM}^{\gamma SL*} b_{JM}^{\gamma SL}\left\langle\gamma SLJM\right|m_z\left|\gamma SLJM\right\rangle + \\ & + \left(a_{JM}^{\gamma SL*} b_{J-1,M}^{\gamma SL} + a_{J-1,-M}^{\gamma SL}{}^{*} b_{J,-M}^{\gamma SL}\right)\left\langle\gamma SLJM\right|m_z\left|\gamma SL,J-1,M\right\rangle\Big].\end{aligned} \tag{12}$$

Property (11) allows to transform the following sum for the x and y components of operator **m**

$$\begin{aligned}\sum_{\{J,J'\}\in D,M,M'} C_{JJ'MM'}^{\gamma SL}\left\langle\gamma SLJM\right|m_{x,y}\left|\gamma SLJ'M'\right\rangle = \sum_{\{J,J'\}\in D,M}\Big(& C_{JJ'M,M-1}^{\gamma SL}\left\langle\gamma SLJM\right|m_{x,y}\left|\gamma SLJ',M-1\right\rangle + \\ & + \left(-1\right)^{J-J'} C_{JJ',-M,1-M}^{\gamma SL}\left\langle\gamma SLJM\right|m_{x,y}\left|\gamma SLJ',M-1\right\rangle^{*}\Big),\end{aligned} \tag{13}$$

where $C_{JJ'MM'}^{\gamma SL}$ are some numerical coefficients, quantum numbers J, J' take values from some fixed set D.

Let us apply (13) to calculation of matrix elements $\left\langle\psi_1\right|m_{x,y}\left|\varphi\right\rangle$: for $J = J'$ in (9) we apply (13) with

$$C_{JJMM'}^{\gamma SL} = a_{JM}^{\gamma SL^*} b_{JM'}^{\gamma SL}; \tag{14}$$

for $J > J'$ in (9) we apply (13) with

$$C_{JJ'MM'}^{\gamma SL} = a_{JM}^{\gamma SL^*} b_{J'M'}^{\gamma SL} + \left(-1\right)^{J'-J+M+M'} a_{J',-M'}^{\gamma SL}{}^{*} b_{J,-M}^{\gamma SL}, \tag{15}$$

according to (10). Thus we obtain, omitting quantum numbers γSL in the matrix elements for brevity:

$$\begin{aligned}\langle\psi_1|m_{x,y}|\varphi\rangle = \sum_{\gamma SLJM}\Big[& a_{JM}^{\gamma SL*} b_{J,M-1}^{\gamma SL}\langle JM|m_{x,y}|J,M-1\rangle + a_{J,-M}^{\gamma SL}{}^{*} b_{J,1-M}^{\gamma SL}\langle JM|m_{x,y}|J,M-1\rangle^{*} + \\ & +\left(a_{JM}^{\gamma SL*} b_{J-1,M-1}^{\gamma SL} - a_{J-1,1-M}^{\gamma SL}{}^{*} b_{J,-M}^{\gamma SL}\right)\langle JM|m_{x,y}|J-1,M-1\rangle + \\ & +\left(a_{J-1,M-1}^{\gamma SL}{}^{*} b_{J,M}^{\gamma SL} - a_{J,-M}^{\gamma SL}{}^{*} b_{J-1,1-M}^{\gamma SL}\right)\langle JM|m_{x,y}|J-1,M-1\rangle^{*}\Big].\end{aligned} \tag{16}$$

Note that formulas (12) and (16) are valid for Cartesian components of any time-odd Hermitian vector operator with matrix elements diagonal in quantum numbers γSL. For time-even Hermitian vector operator analogous formulas can be derived, but terms, which include coefficients with indices $-M$ or $1-M$ (or both), will appear with the opposite signs.

Calculating matrix elements diagonal in J in (12) and (16) we can substitute m_α by equivalent operator

$$g_{\mathrm{L}}(SLJ)\,J_\alpha, \tag{17}$$

where $g_{\mathrm{L}}(SLJ)$ is the Lande *g*-factor modified with account of orbital momentum reduction:

$$g_{\mathrm{L}}(SLJ) = \frac{1}{2}(g_S+k) + (g_S-k)\frac{S(S+1)-L(L+1)}{2J(J+1)}. \tag{18}$$

Calculating matrix elements in (12), (16) between multiplets with different J, we can substitute m_α by equivalent operator $(g_S-k)S_\alpha$. On the basis of the standard formula of algebra of irreducible tensor operators [9] (with Wigner notation for 3*j*- and 6*j*-symbols)

$$\begin{aligned}\langle\gamma SLJM|S_q^{(1)}|\gamma SL,J-1,M'\rangle = (-1)^{2J+S+L-M}\begin{pmatrix} J & 1 & J-1 \\ -M & q & M' \end{pmatrix}\sqrt{(2J+1)(2J-1)}\,\cdot \\ \cdot\begin{Bmatrix} J & 1 & J-1 \\ S & L & S \end{Bmatrix} < S\,\|\,S^{(1)}\,\|\,S >\end{aligned} \tag{19}$$

we can write

$$\langle\gamma SLJM|S_z|\gamma SL,J-1,M\rangle = \frac{1}{2}\lambda(SLJ)\sqrt{J^2-M^2}, \tag{20}$$

$$\langle\gamma SLJM|S_+|\gamma SL,J-1,M-1\rangle = -\frac{1}{2}\lambda(SLJ)\sqrt{(J+M-1)(J+M)}, \tag{21}$$

$$\lambda(SLJ) = \sqrt{\frac{(L+S+J+1)(S-L+J)(L-S+J)(L+S-J+1)}{J^2(2J+1)(2J-1)}}. \tag{22}$$

Thus we can write explicit expressions for matrix elements of m_α operators with the use of coefficients $g_{\mathrm{L}}(SLJ)$ (18) and $\lambda(SLJ)$ (22):

$$\langle\psi_1|m_z|\varphi\rangle = \sum_{\gamma SLJM}\left[g_{\mathrm{L}}(SLJ)M a_{JM}^{\gamma SL*} b_{JM}^{\gamma SL} + \frac{g_S-k}{2}\lambda(SLJ)\sqrt{J^2-M^2}\left(a_{JM}^{\gamma SL*} b_{J-1,M}^{\gamma SL} + a_{J-1,-M}^{\gamma SL}{}^{*} b_{J,-M}^{\gamma SL}\right)\right], \tag{23}$$

$$\begin{aligned}\begin{bmatrix}\langle\psi_1|m_x|\varphi\rangle \\ i\langle\psi_1|m_y|\varphi\rangle\end{bmatrix} = \sum_{\gamma SLJM}\Big[& \frac{1}{2}g_{\mathrm{L}}(SLJ)\sqrt{J(J+1)-M(M-1)}\left(a_{JM}^{\gamma SL*} b_{J,M-1}^{\gamma SL} \pm a_{J,-M}^{\gamma SL}{}^{*} b_{J,1-M}^{\gamma SL}\right) - \frac{1}{4}(g_S-k)\,\cdot \\ & \cdot\lambda(SLJ)\sqrt{(J+M-1)(J+M)}\left(a_{JM}^{\gamma SL*} b_{J-1,M-1}^{\gamma SL} - a_{J-1,1-M}^{\gamma SL}{}^{*} b_{J,-M}^{\gamma SL} \pm a_{J-1,M-1}^{\gamma SL}{}^{*} b_{J,M}^{\gamma SL} \mp a_{J,-M}^{\gamma SL}{}^{*} b_{J-1,1-M}^{\gamma SL}\right)\Big].\end{aligned} \tag{24}$$

Here and further in this section upper signs, if any, are taken for *x*-axis, lower signs – for *y*-axis.

Now let us consider matrix elements of m_α operators on the Kramers doublet states (2), (3). Expressions for diagonal matrix elements can be obtained from (23), (24) by simply putting $b_{JM}^{\gamma SL} = a_{JM}^{\gamma SL}$:

$$\langle\psi_1|m_z|\psi_1\rangle = \sum_{\gamma SLJM}\left[g_{\mathrm{L}}(SLJ)M\left|a_{JM}^{\gamma SL}\right|^2 + (g_S - k)\lambda(SLJ)\sqrt{J^2 - M^2}\,\mathrm{Re}\left(a_{JM}^{\gamma SL*}a_{J-1,M}^{\gamma SL}\right)\right], \tag{25}$$

$$\begin{aligned}\begin{bmatrix}\langle\psi_1|m_x|\psi_1\rangle\\ \langle\psi_1|m_y|\psi_1\rangle\end{bmatrix} = \sum_{\gamma SLJM}\Bigg[& g_{\mathrm{L}}(SLJ)\sqrt{J(J+1)-M(M-1)}\begin{bmatrix}\mathrm{Re}\\ \mathrm{Im}\end{bmatrix}\left(a_{JM}^{\gamma SL*}a_{J,M-1}^{\gamma SL}\right) - \\ & -\frac{1}{2}(g_S - k)\lambda(SLJ)\sqrt{(J+M-1)(J+M)}\begin{bmatrix}\mathrm{Re}\\ \mathrm{Im}\end{bmatrix}\left(a_{JM}^{\gamma SL*}a_{J-1,M-1}^{\gamma SL} - a_{J-1,1-M}^{\gamma SL}{}^{*}a_{J,-M}^{\gamma SL}\right)\Bigg].\end{aligned} \tag{26}$$

Note, that $\langle\psi_2|m_\alpha|\psi_2\rangle = -\langle\psi_1|m_\alpha|\psi_1\rangle$ for the time-odd operator. Expressions for the non-diagonal matrix elements on the states $|\psi_1\rangle$ (2) and $|\psi_2\rangle$ (3) of the Kramers doublet can be obtained from (23), (24) by putting $b_{JM}^{\gamma SL} = (-1)^{J+M}\,a_{J,-M}^{\gamma SL}{}^{*}$:

$$\begin{aligned}\langle\psi_1|m_z|\psi_2\rangle^* = \sum_{\gamma SLJ}\Bigg[& 2\sum_{M>0}(-1)^{J+M}g_{\mathrm{L}}(SLJ)Ma_{JM}^{\gamma SL}a_{J,-M}^{\gamma SL} - \\ & -\sum_{M}(-1)^{J+M}(g_S - k)\lambda(SLJ)\sqrt{J^2-M^2}\,a_{JM}^{\gamma SL}a_{J-1,-M}^{\gamma SL}\Bigg],\end{aligned} \tag{27}$$

$$\begin{aligned}\begin{bmatrix}\langle\psi_1|m_x|\psi_2\rangle^*\\ -i\langle\psi_1|m_y|\psi_2\rangle^*\end{bmatrix} = -\frac{1}{2}\sum_{\gamma SLJ}\Bigg[& (-1)^J g_{\mathrm{L}}(SLJ)\Bigg((-1)^{\frac{1}{2}}\sqrt{J(J+1)+1/4}\left(a_{J,1/2}^{\gamma SL\,2} \mp a_{J,-1/2}^{\gamma SL\,2}\right) + \\ & +2\sum_{M>1/2}(-1)^M\sqrt{J(J+1)-M(M-1)}\left(a_{JM}^{\gamma SL}a_{J,1-M}^{\gamma SL} \mp a_{J,-M}^{\gamma SL}a_{J,M-1}^{\gamma SL}\right)\Bigg) + \\ & +\sum_{M}(-1)^{J+M}(g_S - k)\lambda(SLJ)\sqrt{(J+M-1)(J+M)}\left(a_{JM}^{\gamma SL}a_{J-1,1-M}^{\gamma SL} \pm a_{J,-M}^{\gamma SL}a_{J-1,M-1}^{\gamma SL}\right)\Bigg].\end{aligned} \tag{28}$$

Of course, $\langle\psi_2|m_\alpha|\psi_1\rangle = \langle\psi_1|m_\alpha|\psi_2\rangle^*$. Let us also note for completeness that matrix elements for m_y in (24), (26), (28) can be obtained directly from matrix elements of the m_x operator by rotating corresponding wavefunctions by the angle of $-\pi/2$ around *z*-axis; in the basis $|\gamma SLJM\rangle$ this is equivalent to transformation of the wavefunctions expansion coefficients $a_{JM}^{\gamma SL} \to a_{JM}^{\gamma SL}\exp(iM\,\pi/2)$, $b_{JM}^{\gamma SL} \to b_{JM}^{\gamma SL}\exp(iM\,\pi/2)$.

Calculated matrix elements of the m_α operators (25)–(28) on the Kramers doublet states (2), (3) allow to find components $g_{\alpha\beta}$ of the *g*-tensor according to (7). Rotating Cartesian axes and making unitary transformation in the two-dimensional space of the Kramers doublet states we can always bring the *g*-tensor to diagonal form (we refer to diagonal components as *g*-factors). In the following section we show that for a particular case of tetragonal symmetry of the impurity ion Hamiltonian.

3. Formulas for *g*-factors in the case of tetragonal crystal field

The derived formulas (25)–(28) for *g*-tensor components may be greatly simplified in the case of tetragonal symmetry of the lattice crystal field. If *z*-axis is chosen as the tetragonal symmetry axis, and if expansions (2), (3) of the Kramers doublet wavefunctions $|\psi_1\rangle$, $|\psi_2\rangle$ are obtained by diagonalization of Hamiltonian, which includes spin-orbit and Coulomb interactions and interaction with crystal field, in the basis of full momentum $\left|\gamma SLJM\right\rangle$, then coefficients $a_{JM}^{\gamma SL}$ in (2), (3) can be nonzero only for *M* values that differ by each other by an amount of $4p$, here and further p is integer. Therefore, as seen from (26), (27), $\left\langle\psi_1\right|m_z\left|\psi_2\right\rangle=0$, $\left\langle\psi_1\right|m_{x,y}\left|\psi_1\right\rangle=0$ and, consequently, according to (7):

$$g_{xz}=g_{yz}=g_{zx}=g_{zy}=0. \tag{29}$$

Note, that (29) will be valid for z-axis being the symmetry axis of the second order already.

Moreover, by appropriate numbering of $\left|\psi_1\right\rangle$, $\left|\psi_2\right\rangle$ states we can always obtain nonzero coefficients $a_{JM}^{\gamma SL}$ in (2) only for $M=1/2+2p_0+4p$, where p_0 equals either 0 or 1 (note that expansion (3) of $\left|\psi_2\right\rangle$ will contain terms only with $M=-1/2+2p_0+4p$ in this case). Therefore, in (28) the second terms in all three parentheses will vanish, leading to equality $\left\langle\psi_1\right|m_x\left|\psi_2\right\rangle=i\left\langle\psi_1\right|m_y\left|\psi_2\right\rangle$. The latter means that by appropriate choice of complex phase of the wavefunction $\left|\psi_1\right\rangle$ the *g*-tensor will be directly brought to diagonal form with components $g_{xx}=g_{yy}=g_\perp$, $g_{zz}=g_\parallel$, where *g*-factors derived from (25), (28) equal

$$\begin{aligned}g_\parallel=2\sum_{\gamma SLJp}\Big[&g_\mathrm{L}\left(SLJ\right)\left(1/2+2p_0+4p\right)\left|a_{J,1/2+2p_0+4p}^{\gamma SL}\right|^2+\\&+\left(g_S-k\right)\lambda\left(SLJ\right)\sqrt{J^2-\left(1/2+2p_0+4p\right)^2}\,\mathrm{Re}\left(a_{J,1/2+2p_0+4p}^{\gamma SL}{}^{*}a_{J-1,1/2+2p_0+4p}^{\gamma SL}\right)\Big],\end{aligned} \tag{30}$$

$$\begin{aligned}g_\perp=\Bigg|\sum_{\gamma SLJ}\Bigg[&g_\mathrm{L}\left(SLJ\right)\Bigg(\sqrt{J\left(J+1\right)+1/4}\;a_{J,1/2}^{\gamma SL}{}^2+\\&+2\sum_{p>-p_0/2}\sqrt{J\left(J+1\right)+1/4-\left(2p_0+4p\right)^2}\;a_{J,1/2+2p_0+4p}^{\gamma SL}a_{J,1/2-2p_0-4p}^{\gamma SL}\Bigg)+\\&+\sum_p\left(g_S-k\right)\lambda\left(SLJ\right)\sqrt{\left(J+2p_0+4p\right)^2-1/4}\;a_{J,1/2+2p_0+4p}^{\gamma SL}a_{J-1,1/2-2p_0-4p}^{\gamma SL}\Bigg]\Bigg|.\end{aligned} \tag{31}$$

4. *g*-tensor components in the case of impurity ion electronic configuration *nl*^{1}

In the case of electronic configuration *nl*^{1} of the impurity ion there is only one term $L=l$, $S=1/2$ with two multiplets $J=l\pm\frac{1}{2}$. Wavefunctions $\left|J,M\right\rangle$ of the multiplets components can be expressed through the one-electron wavefunctions $\left|m_l,\sigma\right\rangle$, where m_l and σ denote magnetic and spin quantum numbers of the *nl* electron (below σ values are denoted simply as ‘+’ and ‘–’), with the use of tabulated Clebsch-Gordan coefficients:

$$\begin{aligned}\left|l\pm\frac{1}{2},M\right\rangle&=\sum_{m_l,\sigma}\left\langle\frac{1}{2},l,\sigma,m_l\left|\frac{1}{2},l,l\pm\frac{1}{2},M\right.\right\rangle\left|m_l,\sigma\right\rangle=\\&=\frac{\sqrt{l\pm M+1/2}}{2l+1}\left|M-\frac{1}{2},+\right\rangle\pm\frac{\sqrt{l\mp M+1/2}}{2l+1}\left|M+\frac{1}{2},-\right\rangle.\end{aligned} \tag{32}$$

Coefficients $g_\mathrm{L}\left(SLJ\right)$ (18) and $\lambda\left(SLJ\right)$ (22) for configuration *nl*^{1} take the form (here and further in this section uninformative indices SL are omitted)

$$g_\mathrm{L}\left(l+\frac{1}{2}\right)=\frac{g_S+2kl}{2l+1},\; g_\mathrm{L}\left(l-\frac{1}{2}\right)=\frac{-g_S+2k\left(l+1\right)}{2l+1},\; \lambda\left(l+\frac{1}{2}\right)=\frac{2\left(g_S-k\right)}{2l+1}. \tag{33}$$

Let us consider the example of an *nf* electron ($l=3$). Let us provide only formulas for the matrix elements $\langle\psi_1|m_z|\psi_1\rangle$ (25) and $\langle\psi_1|m_x|\psi_2\rangle$ (28) (in the case of tetragonal symmetry these matrix elements directly define the g-factors as has been shown in the previous section):

$$\begin{aligned}\langle\psi_1|m_z|\psi_1\rangle = \frac{1}{7}\sum_M \Bigg[&(g_S+6k)M\left|a_{\frac{7}{2},M}\right|^2 - (g_S-8k)M\left|a_{\frac{5}{2},M}\right|^2 + \\ &+(g_S-k)\sqrt{49-4M^2}\,\mathrm{Re}\left(a_{\frac{7}{2},M}{}^{*}a_{\frac{5}{2},M}\right)\Bigg],\end{aligned} \tag{34}$$

$$\begin{aligned}\langle\psi_1|m_x|\psi_2\rangle^{*} = -\frac{1}{14}\Bigg[&4(g_S+6k)\left(a^2_{\frac{7}{2},\frac{1}{2}} - a^2_{\frac{7}{2},-\frac{1}{2}}\right) + 3(g_S-8k)\left(a^2_{\frac{5}{2},\frac{1}{2}} - a^2_{\frac{5}{2},-\frac{1}{2}}\right) + \\ &+\sum_{M>1/2}(-1)^{M-\frac{1}{2}}\Bigg((g_S+6k)\sqrt{63-4M(M-1)}\left(a_{\frac{7}{2},M}a_{\frac{7}{2},1-M} - a_{\frac{7}{2},-M}a_{\frac{7}{2},M-1}\right) + \\ &+(g_S-8k)\sqrt{35-4M(M-1)}\left(a_{\frac{5}{2},M}a_{\frac{5}{2},1-M} - a_{\frac{5}{2},-M}a_{\frac{5}{2},M-1}\right)\Bigg) + \\ &+\sum_M(-1)^{M-\frac{1}{2}}(g_S-k)\sqrt{4(3+M)^2-1}\left(a_{\frac{7}{2},M}a_{\frac{5}{2},1-M} + a_{\frac{7}{2},-M}a_{\frac{5}{2},M-1}\right)\Bigg].\end{aligned} \tag{35}$$

5. g-factors of the ground Kramers doublet of the Ce^{3+} ion in $LiYF_4$ crystal

Spectrum of the Ce^{3+} ion $4f^1$ configuration consists of 7 Kramers doublets – $^2F_{5/2}$ (ground) and $^2F_{7/2}$ multiplets splitted by S_4 symmetry crystal field induced by $LiYF_4$ lattice. As has already been mentioned in introduction, g-factors for the ground level of the Ce^{3+} ion in $LiYF_4$ crystal have been found in [2] from EPR measurements:

$$g_{\parallel}^{\exp} = 2.737, \quad g_{\perp}^{\exp} = 1.475. \tag{36}$$

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

$$H_{\mathrm{SO}} = \xi\mathbf{SL}, \tag{37}$$

where ξ is a $4f$ electron spin-orbit coupling constant, and Hamiltonian of interaction with the S_4 symmetry crystal field (in crystallographic axes)

$$H_{\mathrm{CF}} = B_0^2C_0^{(2)} + B_0^4C_0^{(4)} + B_4^4C_4^{(4)} + B_{-4}^4C_{-4}^{(4)} + B_0^6C_0^{(6)} + B_4^6C_4^{(6)} + B_{-4}^6C_{-4}^{(6)}, \tag{38}$$

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 $\mathbf{C}^{(p)}$.

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 (see also expansion (32)). Let us also note that the ground doublet corresponds to irreducible representations Γ_5, Γ_6 of the double S_4 point group in Bethe notation. According to section 3 we choose the wavefunction $|\psi_1\rangle$ (2) to contain the state $\left|\frac{5}{2},\frac{5}{2}\right\rangle$ (this corresponds to $p_0=1$ in section 3;

wavefunction $|\psi_2\rangle$ (3) then contains the $\left|\frac{5}{2},-\frac{5}{2}\right\rangle$ state), which is mixed by crystal field interaction H_{CF} (38) 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 $H = H_{\mathrm{SO}} + H_{\mathrm{CF}}$ with the following matrix elements, which we give here for completeness:

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

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

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

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

$$\left\langle\frac{5}{2},-\frac{3}{2}\right|H\left|\frac{7}{2},-\frac{3}{2}\right\rangle = -\frac{\sqrt{10}}{35}B_0^2 - \frac{8\sqrt{10}}{231}B_0^4 + \frac{5\sqrt{10}}{143}B_0^6,\quad \left\langle\frac{7}{2},\frac{5}{2}\right|H\left|\frac{7}{2},-\frac{3}{2}\right\rangle = \frac{\sqrt{210}}{77}B_4^4 + \frac{5\sqrt{42}}{429}B_4^6. \tag{39}$$

Numerically diagonalizing the matrix with the elements (39) we obtain the wavefunction $|\psi_1\rangle$ (2) of the ground Kramers doublet of the Ce^{3+} ion in LiYF_4; bringing $|\psi_1\rangle$ to the form, suitable for comparison with [1], we may write

$$|\psi_1\rangle = \frac{1}{N}\left(\left|\frac{5}{2},\frac{5}{2}\right\rangle + \alpha\left|\frac{5}{2},-\frac{3}{2}\right\rangle + \beta\left|\frac{7}{2},\frac{5}{2}\right\rangle + \gamma\left|\frac{7}{2},-\frac{3}{2}\right\rangle\right),\quad N = \sqrt{1+|\alpha|^2+|\beta|^2+|\gamma|^2}. \tag{40}$$

Utilizing the formulas (34), (35) for wavefunction (40) we obtain the following expressions for *g*-factors of the ground Kramers doublet of the Ce^{3+} ion in LiYF_4 with account of orbital momentum reduction:

$$g_{\parallel} = \frac{1}{7N^2}\Big((g_S+6k)\big(5|\beta|^2-3|\gamma|^2\big) + (-g_S+8k)\big(5-3|\alpha|^2\big) + 4(g_S-k)\big(\sqrt{6}\,\mathrm{Re}\,\beta + \sqrt{10}\,\mathrm{Re}(\alpha\gamma^*)\big)\Big), \tag{41}$$

$$g_{\perp} = \frac{2}{7N^2}\Big|(g_S+6k)2\sqrt{3}\beta\gamma + (g_S-8k)\sqrt{5}\alpha + (g_S-k)\big(\sqrt{30}\alpha\beta + \sqrt{2}\gamma\big)\Big|. \tag{42}$$

If we put $g_S = 2,\ k = 1$, then (41), (42) transform to the formulas that we obtained earlier in [1] but with the opposite signs of β and γ coefficients, since $\left|\frac{7}{2},M\right\rangle$ states have been taken in [1] with the opposite signs as compared to (32); this also results in the opposite signs of matrix elements cross between $J = \frac{5}{2}$ and $J = \frac{7}{2}$ states in (39) as compared to [1]. If we additionally put $\beta = \gamma = 0$, then we obtain the case, investigated earlier in [4,5], when mixing of the $^2F_{5/2}$ and $^2F_{7/2}$ multiplets by crystal field is not considered.

We use the following crystal field parameters that were exploited in [10] in modeling of the interconfigurational 4*f*–5*d* absorption spectrum of the Ce^{3+} ion in LiYF_4 (in cm^{-1}):

$$B_0^2 = 360,\quad B_0^4 = -1400,\quad B_4^4 = -1240 + i\cdot 751,\quad B_0^6 = -67.2,\quad B_4^6 = -1095 + i\cdot 458. \tag{43}$$

No direct fitting of g-factors or $4f$ crystal field energies has been fulfilled in [10], but signs and orders of magnitude of parameters (43) are in agreement with parameters obtained in literature for trivalent rare earth ions doped in $\mathrm{LiYF_4}$ crystal from fitting experimental data (see, for example, [11]). We also use value $\xi = 625\,\mathrm{cm}^{-1}$ from [10] for the spin-orbit coupling constant, this value also being in agreement with the common in literature (for example, $615\,\mathrm{cm}^{-1}$ in [11] and $628\,\mathrm{cm}^{-1}$ in [12]). Diagonalization of matrix (39) with the Ce^{3+} ion Hamiltonian parameters given above leads to the following g-factors of the ground Kramers doublet of the Ce^{3+} ion, calculated without taking orbital momentum reduction into account [1] (i.e. for $k = 1$ in (41), (42)):

$$g_{\parallel} = 2.845, \quad g_{\perp} = 1.551, \tag{44}$$

with a root-mean-square deviation from experimental values (36) equal to 0.132. Calculations show [1] that large $B_{\pm 4}^{6}$ values ($\left|B_{\pm 4}^{6}\right| \approx 2000\ \mathrm{cm}^{-1}$) could, in principle, solve the problem of this discrepancy with experiment, but such large values are at least one and a half times greater than expected, as follows from trends of parameters commonly used in literature for trivalent rare earth ions doped in double fluoride crystals [11, 13], and do not seem reasonable.

In order to improve agreement with experiment we consider reduction of the orbital momentum of the $4f$ electron of the Ce^{3+} ion. For $k = 0.97$ the obtained formulas (41), (42) lead to the following g-factors of the ground Kramers doublet of the Ce^{3+} ion in $\mathrm{LiYF_4}$:

$$g_{\parallel} = 2.734, \quad g_{\perp} = 1.487, \tag{45}$$

with a root-mean-square deviation from experimental values (36) equal to 0.013, that is 10 times less than without taking orbital momentum reduction into account (44).

Thus, we have shown that considering reduction of the orbital momentum of the Ce^{3+} ion $4f$ electron in the Zeeman energy could improve agreement with g-factors obtained from experiment. However, the result (45) should not be considered as final yet. First of all, one must keep in mind that a more thorough determination of crystal field parameters in $\mathrm{LiYF_4{:}Ce^{3+}}$ remains a problem. Correct $4f$ energy levels for this compound should be provided. Recently infrared absorption spectrum of the $\mathrm{LiYF_4{:}Ce^{3+}}$ crystal corresponding to $^2\mathrm{F}_{5/2} \rightarrow {}^2\mathrm{F}_{7/2}$ intra-$4f$ transitions have been measured at 10 K [14], providing energies of the excited $4f$ ($^2\mathrm{F}_{7/2}$) levels. Another attempt [15] was made to determine several of the Ce^{3+} excited $4f$ crystal field levels from analysis of low-temperature $5d$–$4f$ luminescence spectrum in $\mathrm{LiYF_4{:}Ce^{3+}}$ crystal: microscopic modeling of vibrational structure of the luminescence spectrum based on the exchange charge model [16] allowed to distinguish electron-vibrational peaks observed in the spectrum from zero-phonon lines corresponding to transitions from the lowest $5d$ state to different $4f$ levels of the Ce^{3+} ion. The total of five known for the present moment excited $4f$ energy levels need to be reproduced by modeling of crystal field in $\mathrm{LiYF_4{:}Ce^{3+}}$, consistent with modeling of g-factors.

6. Conclusions

Analytical expressions have been derived for g-tensor components of a Kramers doublet of an impurity ion doped into dielectric crystal with account of orbital momentum reduction due to covalence: g-tensor components are expressed explicitly through coefficients of expansion of the doublet wavefunctions in the basis of full momentum of the impurity ion. The obtained expressions can be useful in calculations and analysis of g-tensor dependence on the impurity ion Hamiltonian parameters. Additionally, a particular case of tetragonal symmetry of crystal field and a case of the electronic configuration nl^1 of the impurity ion have been considered. For completeness, expressions are provided for matrix elements of the impurity ion magnetic moment on arbitrary wavefunctions defined by expansions in the basis of full momentum with account of orbital momentum reduction.

The derived formulas have been used in calculation of g-factors of the ground Kramers doublet of the Ce^{3+} ion doped in $\mathrm{LiYF_4}$ crystal. It was shown that taking into account reduction of the orbital momentum of the Ce^{3+} ion $4f$ electron in the Zeeman energy can significantly improve agreement with g-factors measured experimentally. Further progress can be achieved by going beyond the approximation of isotropic reduction factor, estimation of reduction of orbital momentum matrix elements by molecular orbital method, and, on the other hand, by consistent modeling of $4f$ crystal field energies. Safe values of $4f$ crystal field parameters for the Ce^{3+} ion in $LiYF_4$ crystal are absent in literature, though certain progress have been recently achieved in determining crystal field energies from measurements for this compound. A thorough investigation of possible $4f$ crystal field parameters in $LiYF_4:Ce^{3+}$ in the context of both g-factor values of the ground Kramers doublet and $4f$ energy levels, established in literature for the present moment, is planned to be conducted in future.

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