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Abstract. The two-photon odd-parity vibronic transitions in centrosymmetric systems have been described by a simple model based on the third-order mechanisms. The use of symmetry-adaptation techniques and Racah–Wigner calculus has led to the expression for transition intensity, including magnetic and vibronic components as well as the polarization factor. This expression has been used for calculations of intensity strengths of two-photon vibronic transitions between the ground state ($[^8S_{7/2}]|$) and one of the excited J multiplets $|[^6P_{5/2}]$) of the Gd^{3+} ion in surroundings of octahedral symmetry.

1. Introduction

It has been known since the 1930s that the selection rules governing the two-photon (TP) transitions are complementary to those governing one-photon spectra and may serve as an additional source of information not accessible with classical one-photon methods. The construction of lasers made possible the first experimental observations of TP absorption spectra [1]. Further development in laser technology, in particular the introduction of tunable dye lasers, offered new possibilities. At the beginning of the 1980s very precise TP spectra of Gd^{3+} impurities in LaF$_3$ were registered [2] using those lasers. Within the theoretical analysis of the reported results it appeared that the second-order theory [3] based on the Judd–Ofelt approach to one-photon f–f transitions in rare-earth (RE) ions [4] was insufficient for the description of observed TP spectra. New mechanisms had to be introduced in order to give satisfactory agreement between experiment and theory. An avalanche of experimental [5–7] and theoretical [8–13] papers followed the first report [2]. Different ions in different crystals were examined, but the Gd^{3+} ion, an object of the first paper in the series, remained the case of special interest. The reasons are twofold. First, a large energy gap between the ground and first excited states excludes the 4f states as intermediate ones, so resonance effects are absent. Secondly, the diagonal matrix elements of $U^{(k)}$ operators disappear for the half-filled 4f^7 configuration, and hence the second-order contributions to the TP transition intensities for the Gd^{3+} ion are much weaker than expected and the higher-order effects can manifest their importance.

The first exhaustive analysis of the Gd^{3+} ion in LaF$_3$ and aqueous solution [9] was followed by measurements of TP spectra of this ion in GdCl$_3$, Gd(OH)$_3$ [14], gadolinium diglycolate [15] and Cs$_2$NaGdCl$_6$ [16, 17]. The experimental set-ups and the means of theoretical analysis of experimental results were rather similar in all investigated cases. The reported calculations generally confirmed the importance of spin–orbit and crystal-field third-order mechanisms of two-photon absorption (TPA) introduced in the first papers of a

series [8, 9] in describing the observed spectra properly. However, the improved model was still not perfect and its inaccuracy was usually explained by the ligand-polarizability effect [10, 11] or other mechanisms [12], but no detailed calculations had been carried out.

Recent measurements of TPA of Gd^{3+} in elpasolites [16, 17] have brought qualitatively new features to the field. First, the highly symmetric surroundings (O_h site symmetry) are something new, since in former cases only systems of low symmetry were investigated: D_{3h} [9], C_{3h} [14], D_3 [15]. In those symmetries the totally resolved J levels could be characterized in most cases by a single magnetic quantum number M, while for O_h symmetry this approach is no longer sufficient. The second novelty is the TP vibronic lines observed for the first time in RE ions [18]. This new feature is absent or too weak to be observed in RE spectra in other systems, but quite common in transition-metal TPA spectra [19].

In the present paper we are going to report the theoretical analysis of the TP vibronic spectra in terms of the symmetry-adaptation technique. The proposed approach makes the calculations of the transition intensities trivial, even in highly symmetric systems, where the eigenstates have several comparable M components. Moreover, within the analysis of vibrational normal modes, the symmetry adaptation is just inevitable.

The observed vibronic spectra [18] contain exclusively lines induced by odd-parity modes, so the standard even-parity mechanism [3] cannot describe this unusual kind of vibronic transition. The theory developed will then focus on a new mechanism of TP transitions accompanied by odd-parity vibrational excitations. Within the presented model the general formula for the intensity of TP vibronic transitions will be derived. It will be next applied to calculations of transition intensities of the Gd^{3+} ion in octahedral symmetry.

2. General theoretical framework

In order to describe the vibronic transitions we will use the perturbation approach with the crude adiabatic wavefunctions

$$|\Psi\rangle = |\psi_{vib}(R)\rangle|\psi_{el}(r, R_0)\rangle \tag{1}$$

as the zero-order states. The electronic part $|\psi_{el}(r, R_0)\rangle$ is the eigenstate of the lanthanide electronic system corrected by the static potential $V_0(r, R_0)$ produced by the ligands fixed at the equilibrium position R_0. To obtain the electronic wavefunction we will start with the free-ion intermediate-coupling states calculated by Carnall *et al* [20]. They are given as a linear combination of LS coupling states:

$$|\psi_{\alpha J}\rangle = \sum_{S,L} c(\alpha, S, L, J)|\alpha\, SL\, JM\rangle \tag{2}$$

where S, L and J are the spin, orbital and total angular momentum quantum numbers, while α includes all other necessary labels. In the case of rare-earth ions the expansion (2) usually contains the leading term $|S_0 L_0 J_0\rangle$, which serves as a label of the eigenstate. Some examples of expansion (2) can be found in table 1, where the ground state $|[^8S_{7/2}]\rangle$ and the lowest excited states $|[^6P_J]\rangle$ of a free Gd^{3+} ion within the intermediate-coupling scheme have been listed [20].

For a free ion the eigenstates (2) are classified by J, which is a good quantum number owing to the spherical symmetry of the system. Each of the levels is degenerate with multiplicity $[J] = 2J + 1$ and their components are marked by $|JM\rangle$. When an ion is put into a crystal of local symmetry G, its levels split owing to the interaction with the

Table 1. The leading components of the ground state and two excited states of a free Gd^{3+} ion within the intermediate-coupling scheme (according to Carnall *et al* [20]).

	$|[^8S_{7/2}]\rangle$	$|[^6P_{7/2}]\rangle$	$|[^6P_{5/2}]\rangle$
^{8}S	−0.9860	−0.1559	—
^{6}P	−0.1651	0.8672	−0.9105
^{6}D	0.0125	−0.3633	0.3735
^{6}F	−0.0011	0.0645	−0.0574
^{4}D1	−0.0141	0.1852	−0.1046
^{4}D2	−0.0002	0.0099	−0.0087
^{4}D3	−0.0011	0.0468	−0.0399
^{4}D4	0.0030	−0.0464	0.0280
^{4}D5	−0.0002	0.0051	−0.0032
^{4}D6	−0.0143	0.1972	−0.1112

surrounding ions and the JM quantum numbers do not classify the eigenstates properly any more. However, in the case of the RE ions, it has been proved on many examples that the J mixing does not introduce any significant changes to transition intensities [21], and hence in this paper we will neglect this phenomenon. Nevertheless, the magnetic quantum number M completely loses its value as an eigenstate label and, especially for highly symmetric systems, it has to be replaced by the irreducible representation (irrep) label Γ of the point group G, and the index γ, which numbers the base vectors of degenerate representations. The multiplicity index τ is necessary when the representations of the same dimension appear more than once in the irrep J. Finally, the electronic eigenstates are labelled by $|\alpha[SL]J\tau\Gamma\gamma\rangle$.

The vibrational wavefunction ψ_{vib} of equation (1) depends on the position of nuclei creating the system under study. Since we are interested in vibrations localized on the RE ion and its surroundings, we will use here the molecular approach and will focus our considerations on the limited number of nuclei creating the complex.

The wavefunction ψ_{vib} is assumed to be an eigenstate of the harmonic oscillator. This is possible when we limit the expansion of the potential to the quadratic terms and pass from the nuclear displacements R to normal coordinates. The Hamiltonian of nuclear vibrations is diagonalized and the vibrational wavefunctions can be expressed as

$$\psi_{vib} = \prod_i \chi_{v_i}^m(Q_i^m) \tag{3}$$

where $\chi_{v_i}^m$ is a harmonic oscillator function with the occupation number v_i for the ith normal mode of the mth electronic state. Normal modes can be classified in the same way as the electronic states. They are marked by $Q_{\tau\Gamma\gamma}$ where the indices $\tau\Gamma\gamma$ have the same meaning as for the electronic case.

The general expression (3) can be further simplified if we assume that the electronic potential surfaces of the initial and final states are identical, so the index m is not necessary. The above assumption is usually satisfied quite well by the RE systems. Moreover, we will consider vibrational states with only one, singly excited mode. In this case we may label this state by $|0\rangle$ when it is phononless, and by $|Q_{\tau\Gamma\gamma}\rangle$ when the mode $Q_{\tau\Gamma\gamma}$ is excited.

The vibronic transitions between the wavefunctions (1) are caused by the light beam and the vibrations of the complex. Within the perturbation theory the TP transition probability between the ground state $\langle g|$ and the final state $|f\rangle$ of type (1) is proportional to:

$$P_{vib}^{TP} = \left| \sum_{m,n} [\langle g|V_{vib}|n\rangle\langle n|V_{1-m}|m\rangle\langle m|V_{1-m}|f\rangle E_{gn}^{-1}(E_{gm} - \hbar\omega)^{-1} \right.$$

$$+ \langle g|V_{l-m}|n\rangle\langle n|V_{vib}|m\rangle\langle m|V_{l-m}|f\rangle(E_{gn} - \hbar\omega)^{-1}(E_{gm} - \hbar\omega)^{-1}$$

$$+ \langle g|V_{l-m}|n\rangle\langle n|V_{l-m}|m\rangle\langle m|V_{vib}|f\rangle(E_{gn} - \hbar\omega)^{-1}E_{fm}^{-1}] + \ldots \Big|^2 \tag{4}$$

where $E_{gn} = E_g - E_n$ are the energy denominators, V_{l-m} is the light–matter interaction and V_{vib} is the vibronic potential. In principle, more perturbing potentials can be of some importance in TP vibronic transitions (e.g. spin–orbit or crystal-field interaction within the excited configuration), but in order to avoid higher-order perturbation terms we will treat those contributions in an effective way, the details of which will be given later.

The vibronic potential V_{vib} appears within the expansion of the electron–nucleon interaction in powers of the normal coordinates Q [22]:

$$H_{en} = V_0(r, R_0) + \sum_{\Gamma\gamma} V_{vib}(\Gamma\gamma)Q_{\Gamma\gamma} + \ldots = V_0(r, R_0) + V_{vib} + \ldots. \tag{5}$$

The expansion coefficients $V_{vib}(\Gamma\gamma)$ are purely electronic operators and $Q_{\Gamma\gamma}$ are one-phonon operators dependent only on nuclear vibrational coordinates.

The light–matter interaction V_{l-m} is given by [23]:

$$V_{l-m} = (i\bar{\omega}/c)A_0(\omega)[\hat{\epsilon} \cdot \boldsymbol{D} + (\hat{k} \times \hat{\epsilon}) \cdot \boldsymbol{m}] \tag{6}$$

where $\hat{\epsilon}$ is the light polarization unit vector, $\hat{k}$ is a unit vector directed along the light beam and $\bar{\omega} = E_{if}/\hbar$. $\boldsymbol{D}$ is an electric dipole operator, $\boldsymbol{D} = e\boldsymbol{r}$, and $\boldsymbol{m}$ is the magnetic dipole operator defined by:

$$\boldsymbol{m} = (e/2mc)(\boldsymbol{l} + 2\boldsymbol{s}). \tag{7}$$

Combining equations (4) and (6) we obtain the third-order expression for the amplitude of TP vibronic transitions, limited to the leading electric–electric and electric–magnetic terms:

$$P_{vib}^{TP} = -\sum_{m,n} \frac{\bar{\omega}^2 A_0^2}{c^2(E_{gm} - \hbar\omega)(E_{gn} - \hbar\omega)}[\langle g|\hat{\epsilon} \cdot \boldsymbol{D}|m\rangle\langle m|V_{vib}|n\rangle\langle n|\hat{\epsilon} \cdot \boldsymbol{D}|f\rangle$$

$$+ \langle g|\hat{\epsilon} \cdot \boldsymbol{D}|m\rangle\langle m|V_{vib}|n\rangle\langle n|(\hat{k} \times \hat{\epsilon}) \cdot \boldsymbol{m}|f\rangle + \ldots]. \tag{8}$$

Let us note that, for wavefunctions of defined parity (which is the case here), the first term (electric–electric) gives non-zero contributions only for even-parity vibrations while the second term (electric–magnetic) works only for odd-parity modes. This happens owing to the odd character of operator $\boldsymbol{D}$ and even character of $\boldsymbol{m}$. Moreover, we demand V_{vib} to be a scalar of point symmetry group, which implies that the electronic operator $V_{vib}(\Gamma\gamma)$ of (5) has to have the same symmetry as the vibronic mode taking part in the transition. The above symmetry considerations suggest that the electric–magnetic mechanism represented by the second term of (8) may be responsible for the odd-parity vibronic spectra mentioned in the introduction [18]. However, the transition intensity analysis is necessary to make the proposed mechanism more convincing, so the next few pages will be devoted to direct calculations of the intensities of TP vibronic $^8S_{7/2} \rightarrow {}^6P_{5/2}$ transitions in the Gd^3 ion in symmetry O_h. The question why the electric–magnetic vibronic transitions can be stronger than electric–electric ones is a separate problem, which will also be discussed shortly in the next section.

3. Transition intensity

If we assume the mixed electric–magnetic dipole character of TP vibronic transitions, then equation (8) gives the following expression for the transition amplitude:

$$f_{\mathrm{vib}}^{\mathrm{TP}} = -\sum_{m,n} \frac{\bar{\omega}^2 A_0^2}{c^2} \left[\frac{\langle g|\hat{\epsilon}' \cdot \boldsymbol{m}|m\rangle}{E_m - \hbar\omega} \left(\frac{\langle m|V_{\mathrm{vib}}|n\rangle\langle n|\hat{\epsilon} \cdot \boldsymbol{D}|f\rangle}{E_n - \hbar\omega} + \frac{\langle m|\hat{\epsilon} \cdot \boldsymbol{D}|n\rangle\langle n|V_{\mathrm{vib}}|f\rangle}{E_n - 2\hbar\omega} \right) \right. \tag{9}$$

$$+ \langle g|\hat{\epsilon} \cdot \boldsymbol{D}|m\rangle\langle m|\hat{\epsilon}' \cdot \boldsymbol{m}|n\rangle\langle n|V_{\mathrm{vib}}|f\rangle (E_m - \hbar\omega)^{-1}(E_n - 2\hbar\omega)^{-1}$$

$$+ \langle g|V_{\mathrm{vib}}|m\rangle\langle m|\hat{\epsilon}' \cdot \boldsymbol{m}|n\rangle\langle n|\hat{\epsilon} \cdot \boldsymbol{D}|f\rangle E_m^{-1}(E_n - \hbar\omega)^{-1} \tag{10}$$

$$+ \left. \left(\frac{\langle g|V_{\mathrm{vib}}|m\rangle\langle m|\hat{\epsilon} \cdot \boldsymbol{D}|n\rangle}{E_m} + \frac{\langle g|\hat{\epsilon} \cdot \boldsymbol{D}|m\rangle\langle m|V_{\mathrm{vib}}|n\rangle}{E_m - \hbar\omega} \right) \frac{\langle n|\hat{\epsilon}' \cdot \boldsymbol{m}|f\rangle}{E_n - \hbar\omega} \right] \tag{11}$$

where $\hat{\epsilon}' = \hat{k} \times \hat{\epsilon}$.

Let us note that, owing to the even parity of the magnetic dipole operator and odd parity of $\boldsymbol{D}$, one of the intermediate configurations of (9) and (11) is a ground configuration 4f^N, while in (10) both intermediate states $|m\rangle$ and $|n\rangle$ belong to the configuration of the parity opposite to the ground state. This means that both of the energy denominators of (10) are of the order of 150 000 cm^{-1}, while one of the energy denominators of (9) and (11) is an order of magnitude smaller. Therefore we will neglect the term (10) in our further considerations.

Examining the expressions in large parentheses in (9) and (11) we observe that they describe one-photon vibronic transitions and can be replaced by matrix elements of an effective electric-dipole one-photon vibronic operator $V_{\mathrm{vib}}^{(1)} (= V_{\mathrm{vib}})$ defined for the general case by Reid and Richardson [24]:

$$V_{\mathrm{vib}}^{(1)} = \sum_{\nu} V_{\mathrm{vib}}^{(1)}(\nu) Q_\nu \tag{12}$$

where ν is a normal mode index containing group theoretical labels $\Gamma\gamma$ (as in (5)).

The new, simplified expression for TP vibronic transition amplitude is given by

$$f_{\mathrm{vib}}^{\mathrm{TP}} = -\sum_m \frac{\bar{\omega}^2 A_0^2}{c^2(E_m - \hbar\omega)} (\langle g|\hat{\epsilon}' \cdot \boldsymbol{m}|m\rangle\langle m|\hat{\epsilon} \cdot V_{\mathrm{vib}}|f\rangle + \langle g|\hat{\epsilon} \cdot V_{\mathrm{vib}}|m\rangle\langle m|\hat{\epsilon}' \cdot \boldsymbol{m}|f\rangle). \tag{13}$$

Before we pass on to further simplifications and detailed calculations of $f_{\mathrm{vib}}^{\mathrm{TP}}$ let us first briefly analyse the electric–electric term of equation (8), responsible for vibronic transitions induced by even vibrations. Following the procedure already applied to the electric–magnetic term we can obtain the electric–electric counterpart of formula (13):

$$f_{\mathrm{vib}}^{\mathrm{TP}}(\mathrm{e\text{-}e}) = -\sum_m \frac{\bar{\omega}^2 A_0^2}{c^2(E_m - \hbar\omega)} (\langle g|H_{\mathrm{eff}}^{\mathrm{TP}}|m\rangle\langle m|V_{\mathrm{vib}}|f\rangle + \langle g|V_{\mathrm{vib}}|m\rangle\langle m|H_{\mathrm{eff}}^{\mathrm{TP}}|f\rangle) \tag{14}$$

where $H_{\mathrm{eff}}^{\mathrm{TP}}$ is an effective TP operator defined [25] by

$$H_{\mathrm{eff}}^{\mathrm{TP}} = \sum_{k=1,2} C_k ((\epsilon_1^{(1)}\epsilon_2^{(1)}) \cdot U^{(k)}). \tag{15}$$

Let us compare respective matrix elements of equations (13) and (14). First, we should note that the vibrational components of both equations are, within our assumptions, of the

same form $\langle 0|Q_\nu|Q_\nu\rangle$. Extracting this component we can state, within a very rough analysis, that the one-photon vibronic matrix element $\langle g|\hat{e}\cdot V_{\text{vib}}|m\rangle$ and TP matrix element $\langle g|H_{\text{eff}}^{\text{TP}}|m\rangle$ should be of the same order of magnitude owing to their quadrupole character and similar origin. Similarly, if we compare the magnetic dipole matrix element $\langle g|\hat{e}\cdot m|m\rangle$ and even vibronic matrix element $\langle g|V_{\text{vib}}|m\rangle$, we may conclude that the former should not be smaller than the latter, since its electronic part is a sum of quadrupole and higher-rank even-parity multipole operators.

This very crude analysis suggests that the two mechanisms considered should produce comparable transition intensities, and for some special cases the magnetic–electric vibronic transitions can dominate. This encouraging conclusion supports our effort to develop equation (13) into a form that can be used in direct calculations of transition intensities.

Further simplifications may be introduced in formula (13) if we specify the initial and final states we are considering. The available experimental data [18] made us focus on the transition between the Gd^{3+} ground state $|[^8S_{7/2}]\rangle$ and one of the lowest excited states $|[^6P_{5/2}]\rangle$ (both of them listed in table 1). If we note that

  (i) the magnetic dipole operator m acts exclusively within the LS term,
  (ii) the final state $|[^6P_{5/2}]\rangle$ does not contain any admixture of $|^8S_{7/2}\rangle$, and
  (iii) the most important component of the initial state, apart from $|^8S_{7/2}\rangle$, is $|^6P_{5/2}\rangle$

then we can conclude that most of the transition intensity defined by (13) comes from the $|[^6P_J]\Gamma\gamma\rangle$ intermediate states, which means that we need the electronic matrix elements of the form

$$\langle[^6P_J]|V_{\text{vib}}^{(1)}(\nu)|[^6P_{5/2}]\rangle \qquad \langle[^8S_{7/2}]|V_{\text{vib}}^{(1)}(\nu)|[^6P_J]\rangle. \tag{16}$$

To obtain reliable values for those elements we would have to carry out a separate theoretical analysis including higher-order effects, espcially an effect of spin–orbit interaction in excited intermediate configurations, which proved to be of great importance for the description of TP spectra [9]. Also the one-photon crystal-field-induced transitions have been recently reinvestigated with special stress on the same mechanisms [26]. Owing to the formal similarity, the one-photon vibronic transitions in centrosymmetric systems could be investigated within the same scheme, but it would lead us far away from our main topic and would probably be sufficient for a separate paper. In the present paper we will assume that the matrix elements (16) are comparable. In this case we may further simplify our calculations if we notice that the ground state contains only a very small admixture of the state $|^6P_{7/2}\rangle$, so the magnetic part of the first term of (13) is much smaller than that of the second term and hence we may assume that the second term dominates. It gives the final formula for the TP vibronic transition amplitude:

$$f_{\text{vib}}^{\text{TP}} = -\sum_{J,\Gamma,\nu} \frac{\bar{\omega}^2 A_0^2}{c^2(E_{J\Gamma} - \hbar\omega)}$$
$$\times \langle[^8S_{7/2}]|\hat{e}\cdot V_{\text{vib}}(\nu)|[^6P_J]\rangle\langle[^6P_J]|\hat{e}'\cdot m|[^6P_{5/2}]\rangle\langle 0|Q_\nu|Q_\nu\rangle. \tag{17}$$

3.1. Calculations

Our goal is to calculate an expression of a general form:

$$f_{\Gamma\gamma\to\Gamma''\gamma''}^{(2)} = \sum_{J',\Gamma',\gamma'} \langle\alpha J\Gamma\gamma|\epsilon_1\cdot P|\beta J'\Gamma'\gamma'\rangle$$
$$\times \langle\beta J'\Gamma'\gamma'|\epsilon_2\cdot Q|\delta J''\Gamma''\gamma''\rangle(E_{\beta J'\Gamma'} - \hbar\omega)^{-1}. \tag{18}$$

Within the standard approach the summation over intermediate states is replaced by unity, so that the tensor operators can be recoupled, creating an effective operator acting between initial and final states. This procedure is based on the closure approximation, which can be applied only when the intermediate states constitute a complete set of states and are far enough from the ground state to make the assumption that they are energetically degenerate realistic. In our case, however, the intermediate states belong to the ground configuration, so assuming the configuration's degeneracy would be too crude an approximation. However, we may assume that the $|SLJ\rangle$ manifolds are degenerate, which leads to replacing $E_{\beta J'\Gamma'}$ of equation (18) with $E_{\beta J'}$. In crystals doped with RE ions the crystal-field splitting is of the order of a few tens of cm^{-1}, so it is much smaller than $E_{\beta J'} - \hbar\omega$ and our approximation is fully justified. Owing to this approximation we will be able to simplify the calculations considerably and take advantage of using the symmetry-adaptation methods.

To carry out the summation over $\Gamma'\gamma'$ we first have to express the scalar products of equation (18) in terms of the tensor's components, according to the definition

$$A^{(k)} \cdot B^{(k)} = (-1)^k [k]^{1/2} (A^{(k)} B^{(k)})_0^{(0)} = (-1)^k [k]^{1/2} \sum_{\Gamma\gamma} A_{\Gamma\gamma}^{(k)} B_{\Gamma^*\gamma^*}^{(k)} \langle k\Gamma\gamma, k\Gamma^*\gamma^* | 00\rangle$$

$$= (-1)^k \sum_{\Gamma\gamma} \begin{pmatrix} k \\ \Gamma \\ \gamma \end{pmatrix} A_{\Gamma\gamma}^{(k)} B_{\Gamma^*\gamma^*}^{(k)} \tag{19}$$

and apply the Wigner–Eckart theorem to matrix elements of (18):

$$f_{\Gamma\gamma\to\Gamma''\gamma''}^{(2)} = \sum_{J'} \sum_{\Gamma_1\gamma_1,\Gamma_2\gamma_2} \left[\sum_{\Gamma'\gamma'} \begin{pmatrix} J \\ \Gamma \\ \gamma \end{pmatrix} \begin{pmatrix} J' \\ \Gamma' \\ \gamma' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ \Gamma^* & \Gamma_1 & \Gamma' \\ \gamma^* & \gamma_1 & \gamma' \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ \Gamma'^* & \Gamma_2 & \Gamma'' \\ \gamma'^* & \gamma_2 & \gamma'' \end{pmatrix} \right]$$

$$\times \begin{pmatrix} 1 \\ \Gamma_1 \\ \gamma_1 \end{pmatrix} \begin{pmatrix} 1 \\ \Gamma_2 \\ \gamma_2 \end{pmatrix} \epsilon_{1\Gamma_1^*\gamma_1^*}^{(1)} \epsilon_{2\Gamma_2^*\gamma_2^*}^{(1)} \frac{\langle \alpha J \| P^{(1)} \| \beta J' \rangle \langle \beta J' \| Q^{(1)} \| \delta J'' \rangle}{(E_{\beta J'} - \hbar\omega)}. \tag{20}$$

The

$$\begin{pmatrix} J \\ \Gamma \\ \gamma \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} J & 1 & J' \\ \Gamma & \Gamma_1 & \Gamma' \\ \gamma & \gamma_1 & \gamma' \end{pmatrix}$$

symbols are the $2jm$ and $3jm$ symbols [27] of a chain of groups SO$_3$–G–H. G is a symmetry group of a system and H is its subgroup with exclusively one-dimensional irreps, necessary to define partners γ of G irreps Γ. In our case G $\equiv$ O$_h$ and H may be C$_3$ or C$_4$, depending on the choice of a basis. The branching labels in (20) are omitted in order to simplify the notation. However, the summation over $\Gamma\gamma$ is understood as also including the branching multiplicity. Fortunately, the coupling multiplicity labels are not necessary for SO$_3$ and H, as long as the latter is a cyclic group.

The summation over $\Gamma'\gamma'$ can be carried out [27] and the content of the square brackets of (20) gives:

$$\sum_{\lambda} (-1)^{-J-J''} [\lambda] \begin{Bmatrix} \lambda & 1 & 1 \\ J' & J'' & J \end{Bmatrix} \begin{pmatrix} J \\ \Gamma \\ \gamma \end{pmatrix} \begin{pmatrix} J & \lambda & J'' \\ \Gamma^* & \Gamma_3^* & \Gamma'' \\ \gamma^* & \gamma_3^* & \gamma'' \end{pmatrix} \begin{pmatrix} \lambda \\ \Gamma_3 \\ \gamma_3 \end{pmatrix} \begin{pmatrix} \lambda & 1 & 1 \\ \Gamma_3 & \Gamma_1 & \Gamma_2 \\ \gamma_3 & \gamma_1 & \gamma_2 \end{pmatrix}. \tag{21}$$

If we put (21) into (20) and rearrange the resulting expression, the transition amplitude will take the form

$$
f^{(2)}_{\Gamma\gamma\to\Gamma''\gamma''} = \sum_{J'}\sum_{\lambda\Gamma_3}(-1)^{-J-J''}[\lambda]\begin{Bmatrix}\lambda & 1 & 1\\ J' & J'' & J\end{Bmatrix}\begin{pmatrix}J\\ \Gamma\\ \gamma\end{pmatrix}\begin{pmatrix}J & \lambda & J''\\ \Gamma^* & \Gamma_3^* & \Gamma''\\ \gamma^* & \gamma_3^* & \gamma''\end{pmatrix}
$$

$$
\times\left[\sum_{\Gamma_1\gamma_1,\Gamma_2\gamma_2}\begin{pmatrix}1\\ \Gamma_1\\ \gamma_1\end{pmatrix}\begin{pmatrix}1\\ \Gamma_2\\ \gamma_2\end{pmatrix}\begin{pmatrix}\lambda\\ \Gamma_3\\ \gamma_3\end{pmatrix}\begin{pmatrix}1 & 1 & \lambda\\ \Gamma_1 & \Gamma_2 & \Gamma_3\\ \gamma_1 & \gamma_2 & \gamma_3\end{pmatrix}\epsilon^{(1)}_{1\Gamma_1^*\gamma_1^*}\epsilon^{(1)}_{2\Gamma_2^*\gamma_2^*}\right]
$$

$$
\times\frac{\langle\alpha J\|P^{(1)}\|\beta J'\rangle\langle\beta J'\|Q^{(1)}\|\delta J''\rangle}{(E_{\beta J'}-\hbar\omega)}. \tag{22}
$$

Making use of properties and definition of $3j$ symbols [27] we may transform the content of the square brackets of (22) to

$$
\sum_{\Gamma_1\gamma_1,\Gamma_2\gamma_2}\begin{pmatrix}1\\ \Gamma_1\\ \gamma_1\end{pmatrix}\begin{pmatrix}1\\ \Gamma_2\\ \gamma_2\end{pmatrix}\begin{pmatrix}\lambda\\ \Gamma_3\\ \gamma_3\end{pmatrix}\begin{pmatrix}1 & 1 & \lambda\\ \Gamma_1 & \Gamma_2 & \Gamma_3\\ \gamma_1 & \gamma_2 & \gamma_3\end{pmatrix}\epsilon^{(1)}_{1\Gamma_1^*\gamma_1^*}\epsilon^{(1)}_{2\Gamma_2^*\gamma_2^*}
$$

$$
=\sum_{\Gamma_1\gamma_1}\sum_{\Gamma_2\gamma_2}\begin{pmatrix}1 & 1 & \lambda\\ \Gamma_1^* & \Gamma_2^* & \Gamma_3^*\\ \gamma_1^* & \gamma_2^* & \gamma_3^*\end{pmatrix}\epsilon^{(1)}_{1\Gamma_1^*\gamma_1^*}\epsilon^{(1)}_{2\Gamma_2^*\gamma_2^*}
$$

$$
=[\lambda]^{-1/2}\begin{pmatrix}\lambda\\ \Gamma_3\\ \gamma_3\end{pmatrix}\langle1\Gamma_1^*\gamma_1^*,1\Gamma_2^*\gamma_2^*|\lambda\Gamma_3\gamma_3\rangle\epsilon^{(1)}_{1\Gamma_1^*\gamma_1^*}\epsilon^{(1)}_{2\Gamma_2^*\gamma_2^*}
$$

$$
=[\lambda]^{-1/2}\begin{pmatrix}\lambda\\ \Gamma_3\\ \gamma_3\end{pmatrix}(\epsilon^{(1)}_1\epsilon^{(1)}_2)^{(\lambda)}_{\Gamma_3\gamma_3}. \tag{23}
$$

Now, the transition amplitude is given by

$$
f^{(2)}_{\Gamma\gamma\to\Gamma''\gamma''} = \sum_{J'}\sum_{\lambda\Gamma_3}(-1)^{-J-J''}[\lambda]\begin{Bmatrix}\lambda & 1 & 1\\ J' & J'' & J\end{Bmatrix}\begin{pmatrix}J\\ \Gamma\\ \gamma\end{pmatrix}\begin{pmatrix}J & \lambda & J''\\ \Gamma^* & \Gamma_3^* & \Gamma''\\ \gamma^* & \gamma_3^* & \gamma''\end{pmatrix}
$$

$$
\times\begin{pmatrix}\lambda\\ \Gamma_3\\ \gamma_3\end{pmatrix}(\epsilon^{(1)}_1\epsilon^{(1)}_2)^{(\lambda)}_{\Gamma_3\gamma_3}\frac{\langle\alpha J\|P^{(1)}\|\beta J'\rangle\langle\beta J'\|Q^{(1)}\|\delta J''\rangle}{(E_{\beta J'}-\hbar\omega)}. \tag{24}
$$

The intensity strength

$$
S^{(2)}_{\Gamma\to\Gamma''} = \sum_{\gamma,\gamma''}|f^{(2)}_{\Gamma\gamma\to\Gamma''\gamma''}|^2 \tag{25}
$$

can be calculated in a standard way [25], by employing the factorization property of $3j$ symbols and the coupling factor orthonormality:

$$
S^{(2)}_{\Gamma\to\Gamma''} = \sum_{\lambda,\lambda'}\sum_{\Gamma_3\gamma_3}\sum_{r}\chi[\lambda\Gamma_3,\Gamma\Gamma'';r]\chi[\lambda'\Gamma_3,\Gamma\Gamma'';r]^*
$$

$$
\times\begin{pmatrix}\lambda\\ \Gamma_3\\ \gamma_3\end{pmatrix}(\epsilon^{(1)}_1\epsilon^{(1)}_2)^{(\lambda)}_{\Gamma_3\gamma_3}\left[\begin{pmatrix}\lambda'\\ \Gamma_3\\ \gamma_3\end{pmatrix}(\epsilon^{(1)}_1\epsilon^{(1)}_2)^{(\lambda')}_{\Gamma_3\gamma_3}\right]^* \tag{26}
$$

where χ coefficients are given by

$$\chi[\lambda\Gamma_3, \Gamma\Gamma''; r] = \sum_{J'}(-1)^{-J-J''}\left(\frac{[\lambda]}{[\Gamma_3]}\right)^{1/2}\begin{Bmatrix}\lambda & 1 & 1 \\ J' & J'' & J\end{Bmatrix}\begin{pmatrix}J & \lambda & J'' \\ \Gamma^* & \Gamma_3^* & \Gamma''\end{pmatrix}_r$$

$$\times \frac{\langle\alpha J\|P^{(1)}\|\beta J'\rangle\langle\beta J'\|Q^{(1)}\|\delta J''\rangle}{(E_{\beta J'} - \hbar\omega)} \tag{27}$$

and r are the coupling multiplicity labels of group G.

3.2. The intensity of the $|[^8S_{7/2}]\rangle \rightarrow |[^6P_{5/2}]\rangle$ TP vibronic transition

The formalism described in section 3.1 will now be used in calculations of intensities of TP vibronic transitions between the ground state $|[^8S_{7/2}]\rangle$ and one of the excited states $|[^6P_{5/2}]\rangle$ of the Gd^{3+} ion situated in a neighbourhood of octahedral symmetry. In order to specify equations of section 3.1 to our case we have to put $\epsilon_1 = \hat{\epsilon}$ and $\epsilon_2 = \hat{k} \times \hat{\epsilon}$ ($\hat{k}$ perpendicular to $\hat{\epsilon}$), while operators P and Q should be replaced by $V_{vib}(\nu)$ and m, respectively. This can be done on the previously suggested assumption that the second term of equation (13) gives the leading contribution to the process.

Since there are no common irreps of group O for $\lambda = 1$ and $\lambda = 2$ ((1) $= T_1$, (2) $= E \otimes T_2$) there will be no cross-terms with respect to λ, λ' in equation (26). Hence, it may be simplified to

$$S_{\Gamma\rightarrow\Gamma''}^{(2)}(\nu) = \sum_{\lambda=1,2}\sum_{\Gamma_3}\sum_r|\chi[\lambda\Gamma_3, \Gamma\Gamma''; r; \nu]|^2 E_{\Gamma_3}^{(\lambda)} \tag{28}$$

where the polarization factor $E_{\Gamma_3}^{(\lambda)}$ is defined by

$$E_{\Gamma_3}^{(\lambda)} = \sum_{\gamma_3}|(\epsilon_1^{(1)}\epsilon_2^{(1)})_{\Gamma_3\gamma_3}^{(\lambda)}|^2 \tag{29}$$

and its explicit form for octahedral symmetry will be calculated below.

First, let us note that the scalar term $(\epsilon_1^{(1)}\epsilon_2^{(1)})^{(0)}$ is equal to zero, since ϵ_1 is by definition perpendicular to ϵ_2. The first-rank tensor $(\epsilon_1^{(1)}\epsilon_2^{(1)})^{(1)}$ can be expressed in terms of the vector product [28]:

$$(A^{(1)}B^{(1)})^{(1)} = (i/\sqrt{2})A \times B \tag{30}$$

and we obtain

$$(\epsilon_1^{(1)}\epsilon_2^{(1)})^{(1)} = (i/\sqrt{2})\epsilon_1 \times \epsilon_2 = (i/\sqrt{2})[\hat{\epsilon} \times (\hat{k} \times \hat{\epsilon})] = (i/\sqrt{2})\hat{k}. \tag{31}$$

The second-rank tensor can be obtained by direct coupling of spherical components of the polarization vectors. For $\hat{k}$ directed along the z axis and $\hat{\epsilon}$ making an angle ϕ with axis x we get:

$$(\epsilon_1\epsilon_2)_{\pm 2}^{(2)} = \pm(i/2)e^{\pm i2\phi}$$

$$(\epsilon_1\epsilon_2)_{\pm 1,0}^{(2)} = 0. \tag{32}$$

Both polarization tensors should be now transformed to the symmetry-adapted form by means of the formula

$$(\epsilon_1\epsilon_2)^{(\lambda)}_{\Gamma_3\gamma_3} = \sum_{q=-\lambda}^{\lambda} (\epsilon_1\epsilon_2)^{(\lambda)}_q (\lambda q|\lambda\Gamma_3\gamma_3). \tag{33}$$

To define the symmetry-adapted components $\Gamma_3\gamma_3$ we choose the chain $SO_3 \supset O \supset D_4 \supset C_4$. The reduction coefficients $(\lambda q|\lambda\Gamma(O)\Gamma(D_4)\Gamma(C_4))$ are then given by [27]:

$$(10|1T_1A_2\Gamma_1) = 1$$

$$(11|1T_1E\Gamma_3) = -1$$

$$(1-1|1T_1E\Gamma_4) = -1$$

$$(20|2EA_1\Gamma_1) = -1$$

$$(22|2EB_1\Gamma_2) = -1/\sqrt{2}$$

$$(2-2|2EB_1\Gamma_2) = -1/\sqrt{2} \tag{34}$$

$$(22|2T_2B_2\Gamma_2) = 1/\sqrt{2}$$

$$(2-2|2T_2B_2\Gamma_2) = -1/\sqrt{2}$$

$$(21|2T_2E\Gamma_3) = -1$$

$$(2-1|2T_2E\Gamma_4) = 1.$$

From equations (31)–(34) we get the polarization factors of equation (28) for the particular case of octahedral symmetry:

$$E^{(1)}_{T_1} = \sum_{\gamma_3} |(\epsilon_1\epsilon_2)^{(1)}_{T_1\gamma_3}|^2 = \tfrac{1}{2}$$

$$E^{(2)}_{E} = \sum_{\gamma_3} |(\epsilon_1\epsilon_2)^{(2)}_{E\gamma_3}|^2 = \tfrac{1}{2}\sin^2(2\phi) \tag{35}$$

$$E^{(2)}_{T_2} = \sum_{\gamma_3} |(\epsilon_1\epsilon_2)^{(2)}_{T_2\gamma_3}|^2 = \tfrac{1}{2}\cos^2(2\phi).$$

Having calculated the polarization factors we can rewrite equation (28) in a form containing explicit dependence of intensity strength on the direction of the polarization vector with respect to the crystal axes:

$$S^{(2)}_{\Gamma\to\Gamma''}(\nu) = \sum_{\lambda\Gamma_3} S^{(\lambda)}_{\Gamma_3}(\Gamma\Gamma''; \nu)E^{(\lambda)}_{\Gamma_3} = \tfrac{1}{2}S^{(1)}_{T_1}(\Gamma\Gamma''; \nu) + S^{(2)}_{E}(\Gamma\Gamma''; \nu)\tfrac{1}{2}\sin^2(2\Theta)$$

$$+ S^{(2)}_{T_2}(\Gamma\Gamma''; \nu)\tfrac{1}{2}\cos^2(2\Theta) \tag{36}$$

where we have introduced, for the sake of clarity, an auxiliary factor $S^{(\lambda)}_{\Gamma_3}(\Gamma\Gamma''; \nu)$:

$$S^{(\lambda)}_{\Gamma_3}(\Gamma\Gamma''; \nu) = \sum_r |\chi[\lambda\Gamma_3, \Gamma\Gamma''; r; \nu]|^2. \tag{37}$$

Table 2. The oscillator strength $P^{el}_{J \to J'}$ of electronic transitions [30], approximate values of the ratio $g_{J \to J'}(\nu)$ defined by equation (40), estimated from spectra of [29], and values of reduced matrix elements of $V^{(1)}_{vib}$ defined by equation (41).

Transition	$P^{el}_{J \to J'}$ $(\times 10^8)$	$g_{J \to J'}(\nu_4)$	$\langle i \| V^{(1)}_{vib}(\nu_4) \| f \rangle$ $(\times 10^{12} \text{ cm})$	$g_{J \to J'}(\nu_6)$	$\langle i \| V^{(1)}_{vib}(\nu_6) \| f \rangle$ $(\times 10^{12} \text{ cm})$
$^8S_{7/2} \to {}^6P_{7/2}$	4.13	0.2	4.4	0.15	2.8
$^8S_{7/2} \to {}^6P_{5/2}$	2.33	0.1	3.1	0.1	2.3

Parameters χ defined by equation (27) are, in our particular case, given by

$$\chi[\lambda\Gamma_3, \Gamma\Gamma''; r; \nu] = \sum_{J'=7/2,5/2} \left(\frac{[\lambda]}{[\Gamma_3]}\right)^{1/2} \begin{Bmatrix} \lambda & 1 & 1 \\ J' & 5/2 & 7/2 \end{Bmatrix} \begin{pmatrix} 7/2 & \lambda & 5/2 \\ \Gamma^* & \Gamma_3^* & \Gamma'' \end{pmatrix}_r$$

$$\times \frac{\langle 4f^7[^8S_{7/2}] \| V^{(1)}_{vib}(\nu) \| 4f^7[^6P_{J'}]\rangle \langle 4f^7[^6P_{J'}] \| m^{(1)} \| 4f^7[^6P_{5/2}]\rangle}{(E_{J'} - \hbar\omega)} \tag{38}$$

where $\Gamma \in \{\Gamma_6, \Gamma_7, \Gamma_8\}$ and $\Gamma'' \in \{\Gamma_7, \Gamma_8\}$.

The reduced matrix elements of the magnetic dipole operator can be calculated directly from the definition of m (equation (7)). Using the intermediate-coupling eigenfunctions presented in table 1 and equation (7) we obtain for $J' = 7/2$ and $5/2$ values of $\langle [^6P_{J'}] \| m \| [^6P_{5/2}]\rangle$ equal to 5.0×10^{-11} cm and 25.7×10^{-11} cm, respectively.

Evaluation of the vibronic reduced matrix elements is much more complicated. The semiempirical approach seems to be the most effective way of doing it. Comparing the theoretical expression for the oscillator strength of one-photon vibronic transition between multiplets $\alpha J \to \beta J'$ [4]

$$P^{vib}_{J \to J'}(\nu) = \sum_{\Gamma_J, \Gamma_{J'}} f^{vib}_{J \to J'}(\Gamma_J, \Gamma_{J'}, \nu) = \frac{4\pi mc\sigma_{J \to J'}}{3\hbar(2J+1)} |\langle \alpha J \| V^{(1)}_{vib}(\nu) \| \beta J'\rangle|^2 \tag{39}$$

with the measured one, we may obtain the values of $|\langle i \| V^{(1)}_{vib}(\nu) \| f\rangle|^2$. Here $\sigma_{J \to J'}$ is the energy difference between multiplets αJ and $\beta J'$, expressed in cm^{-1}. Γ_J, $\Gamma_{J'}$ are the crystal-field components of J multiplet and ν marks the considered normal mode.

Since in our case the experimental values of the vibronic oscillator strength are not available [29] we may estimate them by means of the ratio

$$g_{J \to J'}(\nu) = P^{vib}_{J \to J'}(\nu)/P^{el}_{J \to J'}. \tag{40}$$

Experimental values of $g_{J \to J'}(\nu)$ can be roughly estimated from [29] and are presented in table 2. The oscillator strengths of electronic transitions $P^{el}_{J \to J'}$ calculated by Carnall *et al* [30] are equal to 4.13×10^{-8} and 2.33×10^{-8} for transitions from the ground state to $^6P_{7/2}$ and $^6P_{5/2}$, respectively.

Combining (39) with (40) we get

$$|\langle [^8S_{7/2}] \| V^{(1)}_{vib}(\nu) \| [^6P_{J'}]\rangle|^2 = \frac{(2J+1)3\hbar g_{J \to J'}(\nu) P^{el}_{J \to J'}}{4\pi mc\sigma_{J \to J'}}$$

$$= 2.3 \times 10^{-15} \text{ cm}^2 \, g_{7/2 \to J'}(\nu) P^{el}_{7/2 \to J'} \tag{41}$$

which produces values of $\langle [^8S_{7/2}] \| V^{(1)}_{vib}(\nu) \| [^6P_{J'}]\rangle$ collected in table 2.

To calculate the intensity strength defined by equation (36) we have to sum $S^{(2)}_{\Gamma \to \Gamma''}(\nu)$ with respect to three degenerate components Γ_n ($n = 6, 7, 8$) of the ground state. Numerical values of $\sum_n S^{(\lambda)}_{\Gamma_3}(\Gamma_n \Gamma''; \nu)$ for crystal-field components $\Gamma'' = \Gamma_7$ and Γ_8, and vibrations $\nu_4(T_{1u})$ and $\nu_6(T_{2u})$ have been calculated and presented in table 3. The data collected in this table suggest that the term $(1, T_1)$ of equation (36) is of secondary importance, and dominant terms $(2, E)$ and $(2, T_2)$ are comparable. However, we should remember that their relative contributions to the intensity strength (equation (36)) depend on the crystal orientation with respect to the light polarization vector. For example, for the particular case of $\hat{\epsilon}$ directed along the edge of a cube, the term $(2, E)$ is not active at all.

Within the experimental studies [18] of the discussed transitions, all of them were observed but the line $\Gamma_7 \nu_6$ was too weak to establish its relative intensity. Moreover, lines $\Gamma_7 \nu_4$ and $\Gamma_8 \nu_6$ overlapped, so only the ratio σ between the integrated intensity $I_{\Gamma_7 \nu_4} + I_{\Gamma_8 \nu_6}$ and $I_{\Gamma_8 \nu_4}$ could be measured and was equal to 1.85. The fourth column of table 3 for the transition $\Gamma_7 \nu_6$ gives intensities at least two times smaller than for other transitions, which justifies its low experimental value. If we sum columns 2 and 5 and compare with the third column we get the ratio $\sigma = 1.1$, which is not very close to the measured one. However, owing to the imperfections of the investigated crystal [18] it was difficult to establish its orientation with respect to the laser beam and hence the comparison of the theory and experiment cannot be very precise. More experimental data are necessary in order to carry out a real test of the presented theory.

Table 3. Numerical values of $\sum_n S^{(\lambda)}_{\Gamma_3}(\Gamma_n \Gamma''; \nu)$ defined by equation (37) for $\Gamma'' = \Gamma_7$ and Γ_8, and for active vibrating modes $\nu_4(T_{1u})$ and $\nu_6(T_{2u})$.

$\lambda \Gamma_3$	$\sum_n S^{(\lambda)}_{\Gamma_3}(\Gamma_n \Gamma_7; \nu_4)$ $(\times 10^{54})$	$\sum_n S^{(\lambda)}_{\Gamma_3}(\Gamma_n \Gamma_8; \nu_4)$ $(\times 10^{54})$	$\sum_n S^{(\lambda)}_{\Gamma_3}(\Gamma_n \Gamma_7; \nu_6)$ $(\times 10^{54})$	$\sum_n S^{(\lambda)}_{\Gamma_3}(\Gamma_n \Gamma_8; \nu_6)$ $(\times 10^{54})$
$\lambda = 1, \Gamma_3 = T_1$	3.7	1.3	2.25	0.8
$\lambda = 2, \Gamma_3 = E$	28.4	43.1	14.8	22.6
$\lambda = 2, \Gamma_3 = T_2$	20.8	50.7	10.9	26.5

4. Conclusions

The main purpose of the present paper was to develop a simple theoretical model describing TP vibronic transitions in RE^{3+} ions in crystals. The model is based on mechanisms arising within the third-order perturbation theory, including electric dipole–electric dipole electronic transitions as well as electric dipole–magnetic dipole ones. It has been roughly estimated that the two mechanisms give comparable contributions to transition intensities and, since the available TP spectra [18] exhibit only the presence of vibronic lines induced by odd vibrations, we have focused our interest on the latter, electric–magnetic, mechanism responsible for this kind of transition.

To develop the general expression for the transition intensity, we have extensively used the symmetry-adaptation techniques and Racah–Wigner calculus for point groups. Applying these methods we were able to carry out a summation over the components of J multiplets of intermediate configuration, which significantly simplified further calculations. Moreover, the use of the symmetry-adapted form of electronic and vibrational parts of eigenstates and interaction Hamiltonians has given a consistent and uniform description of the phenomena considered, including details of the dependence of intensity strength on the light polarization.

The general expression for TP vibronic electric–magnetic transitions has been used for calculations of intensity strength of transitions between the ground state $\langle[^8S_{7/2}]|$ and one of the excited J multiplets $|[^6P_{5/2}]\rangle$ of the Gd^{3+} ion in surroundings of octahedral symmetry. First, the explicit dependence of transition intensites on the direction of the polarization vector with respect to the axes of a cubic crystal has been established. Within further analysis the set of intermediate states has been limited to the single term ^6P of configuration $4f^7$, which made the calculations relatively simple, in comparison to the ignored electric–electric term. The magnetic dipole reduced matrix elements between the states of the term ^6P have been calculated from first principles with use of free-ion eigenstates provided by Carnall *et al* [20]. However, in order to avoid much more complicated *ab initio* calculations of the vibronic part, which would involve many uncertain quantities, we have used a semiempirical approach, so that the reduced matrix elements of the effective vibronic operator have been estimated from available one-photon spectra of the considered system [29] and theoretical values of one-photon electronic oscillator strengths [30]. It should be noted, however, that the accuracy of the proposed method would be even better if experimental values of vibronic oscillator strengths were available.

The theoretical investigations of TP vibronic transitions presented in this paper are far from being complete. The detailed *ab initio* analysis of vibronic terms would demand the inclusion of higher-order effects, and would eventually lead to a more satisfactory theoretical model. However, the experimental evidence of TP vibronic transitions in RE ions is so poor that we decided to take a more pragmatic view and focus our effort on a particular mechanism and the simplest way of calculating the transition intensity, which could explain existing results.

One important question is still left unanswered: where are the TP vibronic lines to be found? Within the simple model of TP electric–electric vibronic transitions [31] it can be shown that the vibronic factor depends on R^{-4}, where R is the distance between the metal ion and the ligand. The respective one-photon vibronic operator [32] active in an electric–magnetic mechanism depends on R^{-3}. Hence, we can suggest that the even-parity vibronic lines should be sought in systems with relatively strong TP electronic transitions and ligands situated close to the central ion. The odd-parity vibronic transitions can be observed in cases where the magnetic transitions within the excited or ground LS terms are strong and TP electronic transitions are relatively weak. The Gd^{3+} ion, well known for its very small reduced matrix elements of $U^{(k)}$ operators, is a perfect case where this rule can be applied.

Acknowledgments

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