

**BORROWING INTENSITY IN RARE EARTH DOPED MATERIALS;
MAGNETIC DIPOLE TRANSITIONS**Brian G. WYBOURNE^{a,+}, Lidia SMENTEK^{a,b,*} and Andrzej KĘDZIORSKI^{a1}^a Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Toruń, Poland;e-mail: ¹ tecumseh@phys.uni.torun.pl^b Department of Chemistry, Vanderbilt University, Nashville, U.S.A.; e-mail: smentek1@aol.com

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This paper is dedicated to Professor Joe Paldus – a GIANT in both scientific and human scales – with the confidence that Brian Wybourne would have repeated these words.

A theoretical model of magnetic dipole transitions in crystals doped by the lanthanide ions is based on the fourth-order perturbation theory applied for the Hamiltonian in which two perturbing mechanisms are taken into account. Namely, the impact due to the crystal field potential and also spin-orbit interaction operator is included in the transition amplitude. The analysis is performed in the language of Racah algebra applied for the formulation of the effective operators expressed in terms of unit double tensor operators. The radial integrals of the terms contributing at the fourth order are defined within the perturbed function approach, due to which their values are evaluated for the complete radial basis sets of one-electron states of given symmetry. The numerical analysis performed for the Eu^{3+} ion provides the information on the relative importance of various effective operators and allows one to establish a hierarchy of important terms contributing to the transition amplitude. The results of the analysis lead also to the verification of possible importance of magnetic dipole transitions in the description of $0 \leftrightarrow 0$ and $0 \leftrightarrow 1$ electric dipole transitions via the so-called borrowing mechanism introduced by Wybourne.

Keywords: Hamiltonian; Magnetic dipoles; Lanthanides; Spin-orbit interaction; Racah algebra; Borrowing mechanism; Double perturbation theory.

The so-called hypersensitive transitions in lanthanide ions are not the only ones for which a theoretical model of their description is not yet established. The second class of transitions that are at the center of attention are $0 \leftrightarrow 0$ and $0 \leftrightarrow 1$ that are observed for Eu^{3+} and Sm^{2+} in various hosts. Al-

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though many papers have already been devoted to their description, still in the literature of the field there is a discussion performed in light of various physical mechanisms that might be important in their understanding and reproduction. There are at least two reasons for further investigations that would solve the puzzle definitively and without doubt. The outstanding applications of these transitions as spectroscopic tools for the diagnosis of cancerous tissues in various organs inspire this basic research. At the same time, from a purely scientific point of view, the fact that still their origins are not fully known and their properties are not completely understood, defines a challenge for all involved in the field.

In 1997 a theoretical analysis based on the third-order model was performed in the case of the transitions observed in Eu^{3+} in a host with C_{2v} symmetry¹. In this approach, in addition to the perturbing influence of the crystal field potential, also the impact due to the electron correlation effects was taken into account. In fact, the inclusion of electron correlation (represented by scalar operators) does not change the selection rules for the non-vanishing transition amplitude. The two-particle nature of the Coulomb interaction leads to new two-particle effective operators that contribute to the transition amplitude of these unusual transitions. In the case of the transitions allowed by the selection rules of the standard Judd-Ofelt theory, the major part of the transition amplitude is due to one-particle effective operators, while the two-particle ones are relatively negligible. However, when the single particle part of the parametrization scheme is vanishing, the only nonzero contributions to the transition amplitude are determined by two-particle effective operators. This was the concept applied for the calculations in the case of the unusual transitions observed in Eu^{3+} ion in C_{2v} symmetry. The results of *ab initio* calculations are presented in detail in ref.¹ together with the basic definitions of the approach. An extensive and very precise discussion of these numerical results performed in the context of observations, and also on the background of the impact which is due to other physical mechanisms, is presented in a very elegant and complete way by Kushida and Tanaka. Their contribution to the understanding of these transitions is outstanding²⁻⁹, however, at the same time, other publications like refs^{10,11}, and references in all the papers cited here, should not be overlooked in the discussion.

It is common practice, when analyzing these unusual transitions, to expect that their amplitudes are enhanced by the borrowing mechanism suggested by Wybourne. It should be realized however, that there is a wide class of distinct physical interactions that might provide the contribution to the transition amplitude and realize the borrowing intensity mechanism.

It is possible to regard this mechanism as the borrowing of the intensity from the transitions or interactions via the perturbing operators among the excited states of the ground configuration of lanthanide ion. This is the most common practical interpretation of this mechanism. It is also possible to reinforce the transition amplitude by the contributions that result from the intershell interactions via certain operators (like crystal field potential, electron correlation operator and spin-orbit interaction operator). This is the interaction that includes the perturbing influence of all excited configurations of appropriate parity. In this particular case, the forced closure procedure guarantees that all the energy states of the excited configurations are taken into account (summation over the complete set of energy states). At the same time, in order to perform *ab initio* calculations, one has to include all the excitations from the $4f^N$ shell to one-electron states of l' symmetry for all n' , including the states from the continuum. This is the requirement of taking into account the complete radial basis sets of one-electron functions, and it is satisfied if the perturbed function approach is applied.

The borrowing mechanism of Wybourne might also be understood in the way as discussed recently by him in a series of lectures that were devoted to magnetic dipole transitions. Namely, it is expected that the amplitude of the unusual transitions is gaining the value from the magnetic dipole transition in the following sense,

$$S(7F_0 \leftrightarrow 5D_0) = S_{ed}(0 \leftrightarrow 0) + S_{md}(0 \leftrightarrow 0)$$

where S_{ed} is the electric dipole contribution and S_{md} denotes the term due to the magnetic dipole origin. This particular borrowing mechanism is verified in the present paper. In order to have a deeper insight into the problem of the theoretical description of the magnetic dipole transitions, a numerical analysis is performed here also for the transition $0 \leftrightarrow 1$. Thus, the present analysis is a continuation of a still vivid discussion devoted to the unusual transitions, and might be treated as a new addition to the knowledge presented previously in ref.¹ and in the series of papers by Kushida and his collaborators²⁻⁹.

THEORETICAL MODEL

In the previous paper devoted to the magnetic dipole transitions between the energy levels of rare earth ions doped in crystals¹², a detailed theoretical

model of their description was introduced. The approach was based on double perturbation theory applied for the following Hamiltonian

$$H = H_0 + \lambda V_{\text{CF}} + \mu(PV_{\text{so}}Q + QV_{\text{so}}P + QV_{\text{so}}Q) \quad (1)$$

where the operators P projects onto the space associated with the configuration $4f^6$ of Eu ion and Q is its orthogonal complement. The zeroth-order Hamiltonian in Eq. (1) describes the free ion at the level of Hartree-Fock model implemented by the intrashell spin-orbit interactions

$$H_0 = h_{\text{HF}} + PV_{\text{so}}P. \quad (2)$$

The inclusion of the intrashell spin-orbit interaction into the unperturbed Hamiltonian H_0 implies the intermediate coupling scheme of the zeroth-order functions ψ .

In the present analysis the amplitude of magnetic dipole transition is defined up to the fourth order and it is expressed in terms of effective operators that represent the perturbing influence of crystal field potential and spin-orbit interaction.

The perturbation expansion applied for initial Ψ_i and final Ψ_f states of a transition in a matrix element of magnetic dipole operator produces the following terms of various orders (see ref.¹²)

– first-order contributions to the magnetic dipole transition between the states ψ and ψ' of zeroth order,

$$\langle 4f^6\psi | (L + g_s S)_q^{(1)} | 4f^6\psi' \rangle \equiv D_{\text{MD}}(\psi, \psi'); \quad (3)$$

– second-order contributions caused by the crystal field potential, and associated with λ

$$\Gamma_{\lambda} = D_{\text{MD}}(\psi, x)V_{\text{CF}}(x, \psi') + V_{\text{CF}}(\psi, x)D_{\text{MD}}(x, \psi') \quad (4)$$

where ψ , ψ' and x denote states of the ground configuration $4f^6$, and the summation is performed over all intermediate states x ;

– intrashell third-order contributions associated with $\lambda\mu$

$$\Gamma_{\lambda\mu} = D_{\text{MD}}(\psi, x)F_2(x, \psi') + F_2(\psi, x)D_{\text{MD}}(x, \psi') \quad (5)$$

where the effective operator F_2 represents the intershell interactions via $PV_{\text{so}}QV_{\text{CF}}P$, and its tensorial form is presented in Eq. (A1) of Appendix;

– fourth-order contributions associated with $\lambda^2\mu$, where the crystal field potential occurs twice in the perturbing expressions together with V_{so} , namely

$$\Gamma_{\lambda^2\mu}^1 = D_{MD}(\psi, \mathbf{x})V_{CF}(x, y)F_2(y, \psi') + V_{CF}(\psi, \mathbf{x})F_2(x, y)D_{MD}(y, \psi') \quad (6)$$

$$\Gamma_{\lambda^2\mu}^2 = D_{MD}(\psi, \mathbf{x})F_2(x, y)V_{CF}(y, \psi') + F_2(\psi, \mathbf{x})V_{CF}(x, y)D_{MD}(y, \psi') \quad (7)$$

$$\Gamma_{\lambda^2\mu}^3 = F_2(\psi, \mathbf{x})D_{MD}(x, y)V_{CF}(y, \psi') + V_{CF}(\psi, \mathbf{x})D_{MD}(x, y)F_2(y, \psi') \quad (8)$$

$$\Gamma_{\lambda^2\mu}^4 = D_{MD}(\psi, \mathbf{x})F_4(x, \psi') + F_4(\psi, \mathbf{x})D_{MD}(x, \psi') \quad (9)$$

$$\Gamma_{\lambda^2\mu}^5 = D_{MD}(\psi, \mathbf{x})F_5(x, \psi') + F_5(\psi, \mathbf{x})D_{MD}(x, \psi') . \quad (10)$$

The new effective operators F_4 and F_5 above correspond to the intershell interactions $PV_{CF}QV_{so}QV_{CF}P$ and $PV_{CF}QV_{CF}QV_{so}P$, respectively. These two sequences of perturbing operators lead to two different effective operators that are defined by Eqs (A2) and (A3) of Appendix.

It is seen from the structure of Eqs (6)–(10) that all the fourth-order contributions are caused by a double action of the crystal field potential, and therefore they are multiplied by the product of two structural parameters of appropriate orders (see effective operators in ref.¹²). It should also be pointed out that in the derivation of the tensorial structure of all effective operators, the radial terms are evaluated separately. This is the reason that instead of standard crystal field parameters A_p^t , here the structural parameters are applied. The relation between them is the following (see the definition of the crystal field potential in Eq. (3) of ref.¹²),

$$A_p^t = B_p^t \langle r^t \rangle_{4f} .$$

The symbolic product of the operators in the case of all contributions above denotes in fact the product of their matrix elements including the energy denominator, for example

$$D_{MD}(\psi, \mathbf{x})V_{CF}(x, \psi') = \sum_x \langle \psi | D_{MD} | \mathbf{x} \rangle \langle \mathbf{x} | V_{CF} | \psi' \rangle / (E_{\psi'} - E_x) . \quad (11)$$

In all matrix elements that determine the transition amplitude only the energy states of the ground configuration are involved. In this sense the op-

erators in Eqs (6)–(10) are effective as acting between the states of $4f^N$ configuration. For the clarity of presentation, the energy denominators that are specific for all the perturbing expressions are omitted in the presented expressions.

The crystal structure independent analysis of the tensorial structure of all the operators contributing to the magnetic dipole transition amplitude has been performed in detail previously¹². The analysis presented there was based on the results of *ab initio* calculations since the angular factors and the radial integrals of distinct contribution, were evaluated in an exact way. Indeed, the radial integrals as expressed in terms of the perturbed functions were evaluated for the complete radial basis sets of one-electron functions of a given symmetry¹³.

In order to find out the importance of various contributions to the so-called “borrowing mechanisms” introduced by Wybourne, and to find the hierarchy of the physical mechanisms that are represented by various effective operators, numerical calculation has been performed for the Eu^{3+} ion in LaCl_3 of C_{3h} symmetry.

NUMERICAL ANALYSIS

The magnetic dipole transitions occur between the energy states of given configuration. As a consequence, every higher-order contribution to their amplitude has the form of product of matrix elements $D_{\text{MD}}(\psi, x)O(x, \psi')$, where ψ , ψ' and x in the case of Eu^{3+} ion are the energy states of $4f^6$ (see contributions (4)–(10)). The mechanisms represented in general by O are responsible for the so-called borrowing of intensity. The importance of these mechanisms contributing to the amplitude of $0 \leftrightarrow 0$ and $1 \leftrightarrow 0$ transitions is established in this work. The comparison of various contributions is performed up to the fourth order as indicated above.

The radial integrals of all effective operators contributing to the transition amplitude were evaluated within the perturbed function approach, and their values are collected in Tables I and II of ref.¹² The angular factors of new effective operators F_2 , F_4 and F_5 were also analyzed previously¹². The conclusions derived there were based on the analysis of the results of *ab initio* quality, since no adjusted parameters were taken into account in the numerical procedure. Only in the present investigations are the matrix elements of double tensor operators evaluated with the adjusted coefficients of the wave functions defined within the intermediate coupling scheme. In addition, for the final analysis of various contributions also the semi-empirical values of the structural parameters are applied here.

$0 \leftrightarrow 0$ Transition

Due to the selection rules the only possible non-vanishing contributions to the $0 \leftrightarrow 0$ transition amplitude are the fourth-order terms that consist of the product of three distinct matrix elements $\Gamma_{\lambda^2\mu}^1$, $\Gamma_{\lambda^2\mu}^2$, $\Gamma_{\lambda^2\mu}^3$ as defined in Eqs (6)–(8), for example

$$\Gamma_{\lambda^2\mu}^1 ([^5D]_0 \rightarrow [^7F]_0) = D_{MD} ([^7F]_0, x) V_{CF}(x, y) F_2(y, [^5D]_0) + V_{CF}([^7F]_0, x) F_2(x, y) D_{MD}(y, [^5D]_0) \quad (12)$$

where x, y denote the states which belong to the ground configuration and the contributions are summed up over these intermediate states. F_2 of these contributions describes effectively the intershell interactions via $PV_{so}QV_{CF}P$. It is necessary to include all possible sequences of operators that determine the fourth-order contributions, namely

$$D_{MD} V_{CF} F_2 \quad (13)$$

$$D_{MD} F_2 V_{CF} \quad (14)$$

$$V_{CF} D_{MD} F_2 \quad (15)$$

$$F_2 D_{MD} V_{CF} \quad (16)$$

$$V_{CF} F_2 D_{MD} \quad (17)$$

$$F_2 V_{CF} D_{MD} \quad (18)$$

Each contribution has the form of a product of the angular part independent of directions in space (independent of angular momentum projection numbers), radial integrals and 3- j symbols that result from coupling of angular momenta and from the Wigner–Eckart theorem (see in ref.¹²). The part of the contribution that is independent of the direction in space is expressed by the product of reduced matrix elements, of the general form

$$\sum_{SLJ, S'L'J'} \langle [^7F]_0 || O_1 || [SL]J \rangle \langle [SL]J || O_2 || [S'L']J' \rangle \langle [S'L']J' || O_3 || [^5D]_0 \rangle (\Delta\Delta')^{-1} \quad (19)$$

where each term contains the components of the operators D_{MD} , F_2 and V_{CF} in an appropriate order as defined in Eqs (13)–(18). The direction-dependent coefficients in all expressions are expressed by the 3- j symbol,

$$[t, 1]^{-\frac{1}{2}} \begin{pmatrix} 1 & t & t \\ q & p_1 & p_2 \end{pmatrix}. \quad (20)$$

In the case of contributions (15) and (16) however, the factor at the 3- j symbol is replaced by $-[t]^{-1}$. The form of this symbol is simplified by the selection rules that are valid for the particular transition $0 \leftrightarrow 0$.

In the case of all contributions to the amplitude of this particular transition, due to the symmetry properties of 3- j symbols, the sum over the appropriate components p_1 and p_2 of a given crystal field potential vanishes. Indeed, an odd permutation of the two last columns for $p_1 = p_2$ gives a negative sign $((-1)^{1+t+t})$, while the 3- j symbol remains the same. For $p_1 \neq p_2$, in the summation there are always pairs of the 3- j symbols of the same value but of the opposite sign for $(p_1 p_2)$ and $(p_2 p_1)$.

Thus, there are no contributions of fourth order to the amplitude of $0 \leftrightarrow 0$ transition. This conclusion is valid for any symmetry of a crystalline lattice. It should be mentioned that also third-order terms in the particular case of the $0 \leftrightarrow 0$ transition are vanishing. Indeed, for example the intrashell crystal field effect, Γ_{λ^2} , is determined by the following sequence of matrix elements,

$$\langle [{}^7\text{F}]_0 | D_{\text{MD}} \leftrightarrow P V_{\text{CF}} P \leftrightarrow P V_{\text{CF}} P | [{}^5\text{D}]_0 \rangle \quad (21)$$

where the arrows denote that there are also remaining terms with the positions of operators interchanged. In this particular case the expression for the transition amplitude is also associated with the same 3- j symbol as before, and therefore these terms also vanish.

Similarly, the intershell crystal field effect represented by $P V_{\text{CF}} Q V_{\text{CF}} P$ also does not contribute to the amplitude of the $0 \leftrightarrow 0$ transition. In this case the third-order contribution, $\Gamma_{\lambda^2}^2$, has the form of product of matrix elements

$$\Gamma_{\lambda^2}^2 = D_{\text{MD}} ([{}^7\text{F}]_0, \mathbf{x}) F_{\text{CF}} (\mathbf{x}, [{}^5\text{D}]_0) \quad (22)$$

where a new effective operator of third order, F_{CF} , is defined as follows

$$F_{\text{CF}} (\mathbf{x}, [{}^5\text{D}]_0) = \sum_{t_1 p_1}^{p(t_1)=p(t_2)} \sum_{t_2 p_2} B_{p_1}^{t_1} B_{p_2}^{t_2} \times$$

$$\begin{aligned}
& \times \sum_{I'} \langle 4f | r^{t_1} | \rho^{t_2} (4f \rightarrow I') \rangle \langle f || C^{(t_1)} || I' \rangle \langle I' || C^{(t_2)} || f \rangle \times \\
& \times \sum_{\lambda \mu} (-1)^{\lambda - \mu + t_2 - t_1} [\lambda] \begin{pmatrix} t_1 & t_2 & \lambda \\ p_1 & p_2 & -\mu \end{pmatrix} \begin{Bmatrix} t_1 & t_2 & \lambda \\ f & f & I' \end{Bmatrix} \times \\
& \times \langle 4f^6 x | U_{\mu}^{(\lambda)}(ff) | [^5D]_0 \rangle. \tag{23}
\end{aligned}$$

Comparing the tensorial structure of this new operator with those introduced previously (F_2 , F_4 and F_5 in Appendix), it is clearly seen that the radial integrals and also the angular parts in all cases are very similar. However, the main difference between them is such that now the effective operator is associated with the unit tensor operator $U^{(\lambda)}$, while the previously analyzed objects are defined by the double tensor operators acting within the spin-orbital space. In the particular case of the $0 \leftrightarrow 0$ transition, only operator $U^{(1)}$ in Eq. (23) contributes to its amplitude (the intermediate state x in the matrix element of $U^{(\lambda)}$ is identified by $J=1$ due to the selection rules for the product of matrix elements in $\Gamma_{\lambda^2}^2$). Taking into account only the direction-dependent part of Eq. (22) one can write

$$\Gamma_{\lambda^2}^2 \sim \sum_{p_1 p_2} B_{p_1}^t B_{p_2}^t \begin{pmatrix} t & t & 1 \\ p_1 & p_2 & -\mu \end{pmatrix}. \tag{24}$$

The right-hand side vanishes for the same reasons as in the previous cases discussed above.

This means that up to the fourth order there is no nonzero contributions to the amplitude of the $0 \leftrightarrow 0$ magnetic dipole transition. Thus, in general it is found that in the case of the electric dipole $0 \leftrightarrow 0$ transition there is no borrowing intensity from the magnetic dipole transition.

1 ↔ 0 Transition

The other unusual transition that is observed in the case of Eu ion in various hosts is $^5D_1 \leftrightarrow ^7F_0$. It is the aim of present analysis to verify whether its intensity is reinforced by the borrowing mechanism from the interactions via V_{CF} and V_{SO} between the multiplets of $4f^6$ configuration.

Introduction of the spin-orbit interaction into the zeroth-order Hamiltonian H_0 makes it possible to obtain non-vanishing first-order

contributions defined in Eq. (3) between the states in the intermediate coupling scheme. In the particular case of the transition analyzed here, the first-order contribution has the following value

$$D_{\text{MD}}([{}^7\text{F}]00, [{}^5\text{D}]10) = -9.570 \times 10^{-2} \quad (25)$$

where the coefficients of linear combinations of wave function for the Eu^{3+} are taken from ref.¹⁴

In this particular case the values of the second-order (Eq. (4)) and third-order contributions (Eq. (5)) are the following,

$$\Gamma_{\lambda} (\equiv D_{\text{MD}} V_{\text{CF}} + V_{\text{CF}} D_{\text{MD}}) = 6.7950 B_0^2 \quad (26)$$

$$\Gamma_{\lambda\text{H}} (\equiv D_{\text{MD}} F_2 + F_2 D_{\text{MD}}) = 2.6059 B_0^2 \quad (27)$$

and they are measured in the units of a common structural parameter B_0^2 .

The results presented above indicate that the second-order contribution is of the same order of magnitude as the third one. In order to evaluate the absolute values of various contributions one has to apply the semi-empirical values of crystal field parameters A_q^k . In the present analysis the values found in ref.¹⁵ for LaCl_3 are used, and the structural parameters B_p^t are obtained with the radial integrals presented in ref.¹² In Table I the structural parameters evaluated in this way are collected. For the simplicity of the preliminary analysis it is assumed that, due to the fact that all the structural parameters of even rank are of the same order of magnitude, the order of their values is fixed for further analysis of the importance of various contributions to 10^{-4} a.u.

TABLE I
Crystal field parameters A_p^t and structural parameters B_p^t for Eu^{3+} in LaCl_3 (ref.¹⁵)

t	p	$A_p^{t\text{a}}, \text{cm}^{-1}$	$B_p^t \times 10^4, \text{a.u.}$
2	0	178	9.6897
4	0	-304	-8.5307
6	0	-816	-5.9161
6	6	521	3.7773

^a $A_p^t = B_p^t \langle r^t \rangle_{4f}$.

Consequently, the first-order contribution from Eq. (25) is two orders of magnitude greater than the second- and third-order contributions. The situation is much more complex in the case of the fourth-order terms where in addition to the variety of various terms there is also an explosion of intermediate states that have to be taken into account not to mention the double summation over the products of structural parameters.

In Table II the values are collected of fourth-order contributions determined by the sequences of operators that involve the effective operator F_2 , and which are associated with the products of various structural parameters. The first three columns of the numbers represent the terms defined by Eqs (6)–(8). In the last column the total contribution is presented for the pairs of indices $t_1(p_1)t_2(p_2)$ that contribute to the amplitude of the $0 \leftrightarrow 1$ transition. With the assumption made above that the order of magnitude of all structural parameters is the same, it is easy to compare the results and establish their relative importance.

From the definition of $\Gamma_{\lambda^2\mu}^{1,2,3}$ in Eqs (6)–(8) it is seen that each term is summed over all possible intermediate states that describe the excited states of $4f^6$ configuration. In Table III ten (of 44) dominant contributions caused by F_2 are presented together with the specification of the source of the term (the sequence of matrix elements), and also with information about the symmetry of the intermediate states. All values presented in that Table are associated with the structural parameters $B_0^4 B_0^4$, as an example. It is seen from this Table that it is rather difficult to establish the hierarchy of important terms and to define the physical origin of the most important contribution. At the same time however it is seen that the most important inter-

TABLE II
Comparison of the fourth-order contributions determined by the effective operator F_2 and associated with the products of structural parameters B'_p

Structural parameters	$\Gamma_{\lambda^2\mu}^1$	$\Gamma_{\lambda^2\mu}^2$	$\Gamma_{\lambda^2\mu}^3$	Total
$B_0^2 B_0^2$	-320.10	-153.51	491.99	18.383
$B_0^2 B_0^4$	18.094	712.59	-308.45	422.23
$B_0^4 B_0^4$	-92.643	-15.578	130.66	22.443
$B_0^4 B_0^6$	-1961.9	3415.7	225.42	1679.26
$B_0^6 B_0^6$	-13506.	4700.7	1702.9	-7102.76
$B_6^6 B_6^6$	50891.	-99638.	-12741.	-61488.

mediate state for the first step of borrowing intensity is 7F_4 . In the case of second intermediate states there are various states, involved in the process of gaining intensity, and among them 7F_2 and excited state 7F_3 are the dominant. This means that the magnetic dipole transition ${}^7F_0 \leftrightarrow {}^5D_1$ is borrowing the intensity from the transitions ${}^7F_2({}^7F_3) \leftrightarrow {}^5D_1$ and in majority of cases this is reinforced by the interaction via F_2 or V_{CF} between the initial state 7F_0 and 7F_4 . It should be mentioned that in general, for all the other products of the structural parameters with various ranks, the most important contributions are due to the terms that involve interactions between the components of the initial state 7F_j , for various values of J , while the impact due to other symmetries of the terms is negligible.

In order to find the most important contributions of fourth order, the terms caused by the effective operators F_4 and F_5 ($\Gamma_{\lambda^2\mu}^4$ from Eq. (9) and $\Gamma_{\lambda^2\mu}^5$ from Eq. (10)) have to be evaluated and analyzed. These contributions associated with certain structural parameters are collected in Table IV. In this Table attention is directed to the symmetry of one-electron states l' to which the 4f electron is promoted in the excited configuration. The effective operators F_4 and F_5 (and also F_2 in the analysis above) represent the intershell interactions via certain perturbing operator. In particular, as mentioned before (see also ref.¹²), the operator F_4 represents the intershell

TABLE III

Ten dominant contributions of the fourth-order terms determined by the effective operator F_2 and associated with the structural parameters $B_0^4 B_0^4$ for various intermediate states

Value	Sequence ^a	x	y
88.14	$F_2 V_{CF} D_{MD}$	7F_4	7F_2
-86.58	$V_{CF} F_2 D_{MD}$	7F_4	7F_2
70.36	$V_{CF} D_{MD} F_2$	7F_4	7F_3
-51.02	$F_2 V_{CF} D_{MD}$	7F_4	5D_0
39.31	$F_2 D_{MD} V_{CF}$	7F_4	7F_3
-36.50	$V_{CF} F_2 D_{MD}$	7F_4	5D_0
-35.74	$D_{MD} F_2 V_{CF}$	7F_1	5G_3
-32.80	$V_{CF} D_{MD} F_2$	7F_4	7F_5
29.71	$V_{CF} F_2 D_{MD}$	7F_4	5D_2
21.70	$F_2 D_{MD} V_{CF}$	7F_4	5G_2

^a For example $F_2 V_{CF} D_{MD} \equiv \langle 4f^6 {}^7F_0 | F_2 | 4f^6 x \rangle \langle 4f^6 x | V_{CF} | 4f^6 y \rangle \langle 4f^6 y | D_{MD} | 4f^6 {}^5D_1 \rangle$.

interactions via crystal field potential (taken into account twice), while F_5 represents the intershell interaction via crystal field potential and also the spin-orbit interaction operator. This is why in the first column of Table IV the values of I from the excited configurations $4f^5n'I$ are specified. Here the intermediate states x of Eqs (9) and (10) describe the energy levels of $4f^6$ ground configuration of Eu^{3+} ion, while the excited states of the excited configurations $4f^5n'd$, $4f^5n'f$, $4f^5n'g$, for all n' , are included within the effective operators F_4 and F_5 . The last column of Table IV presents the relative importance of $\Gamma_{\lambda^2\mu}^4(F_4)$ and $\Gamma_{\lambda^2\mu}^5(F_5)$.

It is seen from Table IV that again the situation is not very clear, and it is rather difficult to derive a definite conclusion about the importance of particular terms. The values of terms that are caused by the excitations to the one-electron states of f symmetry, $4f^5n'f$, are increasing together with the increase of the rank of the crystal field potential. At the same time, almost for all ranks of crystal field potential the most dominant are the contributions $\Gamma_{\lambda^2\mu}^5$ for $I = f$; thus for these excitations the other contributions that are due to F_4 are relatively negligible. However, in the case of the excitation to the orbitals of d and g symmetry the situation is not clear, as it is seen from the comparison of the terms associated with the structural parameters of odd ranks. In the case of the d excitations, the most dominant is the

TABLE IV
Fourth-order contributions $\Gamma_{\lambda^2\mu}^4$ and $\Gamma_{\lambda^2\mu}^5$ in the units of product of structural parameters

I	$B_{p_1}^{t_1} B_{p_2}^{t_2}$	$\Gamma_{\lambda^2\mu}^4$ ^a	$\Gamma_{\lambda^2\mu}^5$ ^a	$\kappa_{p_1 p_2}^{t_1 t_2}(I)^b$, %
3	$B_0^2 B_0^2$	0.7157	-2.3176	-45
	$B_0^2 B_0^4$	-1.5224	14.159	-12
	$B_0^4 B_0^4$	-4.1017	-29.582	12
	$B_0^4 B_0^6$	38.138	518.99	7
	$B_0^6 B_0^6$	138.41	4403.2	3
	$B_0^6 B_0^6$	-794.43	-49133.	2
2	$B_0^1 B_0^1$	13.966	0.4476	97
	$B_1^1 B_3^3$	-36.007	-20.914	63
4	$B_0^1 B_0^1$	-0.0239	-0.4390	5
	$B_1^1 B_3^3$	-1.5143	-17.388	8

^a $\Gamma_{\lambda^2\mu}^n \equiv D_{\text{MD}} F_n + F_n D_{\text{MD}}$. ^b $\kappa_{p_1 p_2}^{t_1 t_2}(I) = [\Gamma_{\lambda^2\mu}^4 / (\Gamma_{\lambda^2\mu}^4 + \Gamma_{\lambda^2\mu}^5)] \times 100\%$.

term $\Gamma_{\lambda^2\mu}^4$ while in the case of the g excitations, the most important is the term $\Gamma_{\lambda^2\mu}^5$. Again in deriving these conclusions it is assumed that all the structural parameters are of the same order of magnitude. Although there is an evidence that this assumption is correct in the case of even rank parameters (see Table I), its validity is only predicted for the case of odd parameters, since it is impossible to estimate them in a reliable way.

In Table V the summary of the fourth-order contributions to the amplitude of magnetic dipole transition ${}^7F_0 \leftrightarrow {}^5D_1$ in Eu^{3+} ion in the LaCl_3 host is presented. All values collected in this Table are scaled by 10^4 (the values of the structural parameters are included), and they are numbered by the pairs of the ranks of crystal field potential. For each entry, there are three sources of the contribution, namely F_2 , F_4 and F_5 . The underlined values for $B_6^6 B_6^6$ are the largest, and they are of the same order of magnitude as second- and third-order contributions as presented in Eqs (26) and (27). Thus the most important terms are caused by the interactions via F_2 and F_5 ; the remaining terms presented there are at least one order of magnitude smaller.

TABLE V

Summary of the fourth-order contributions to the amplitude of magnetic dipole transition ${}^5D_1 \leftrightarrow {}^7F_0$ in Eu^{3+} in LaCl_3 host; terms are caused by the effective operators F_2 , F_4 , F_5 and their values are scaled by factor 10^4

$\times 10^4$		(<i>tp</i>) = 20	40	60	66
(<i>tp</i>)	F_2	0.0937	0.4222		
20	F_4	0.0000	-0.0001		
	F_5	-0.0002	0.0014		
40	F_2		0.0022	0.1680	
	F_4		-0.0030	0.0038	
	F_5		-0.0004	0.0519	
60	F_2			-0.7105	
	F_4			0.0138	
	F_5			0.4404	
66	F_2				<u>-6.1487</u>
	F_4				0.0794
	F_5				<u>-4.9132</u>

CONCLUSIONS

The total contributions of various orders to the amplitude of the transition ${}^7F_0 \leftrightarrow {}^5D_1$ are presented in Table VI. The first-order terms describe the direct transition between the initial and final states, and their values are modified by terms of various orders. Second-order terms involve the interactions between the excited states of $4f^N$ configuration via crystal field potential; this is the borrowing mechanism from the interactions within the multiplet. At the third order, intershell interactions via crystal field and spin-orbit interaction operator are taken into account. The fourth-order contributions are determined by interactions within the multiplet via the perturbing operators and the intershell interactions via the crystal field potential (included twice) and the spin-orbit interaction operator.

It is seen from Table VI that all higher-order contributions, although of the same order, are two orders of magnitude smaller than the amplitude defined in a standard way at the first order. The latter is evaluated with the free ion functions in the intermediate coupling scheme. Thus, it has to be concluded that in the particular case of the $0 \leftrightarrow 1$ magnetic dipole transition the borrowing intensity mechanism does not play an important role in the understanding of its origin and reproduction of its intensity. It is interesting to recall that in ref.¹ this very transition has been analyzed as electric dipole in origin, understanding that its intensity is an effect of combination of electric and magnetic dipole radiations. That approach was based on the alternative formulation of the Judd-Ofelt theory in which the velocity form (instead of the length form of the standard formulation) of the electric dipole radiation operator was applied. Although the symmetry of the host of the Eu ion was different (C_{2v}), assuming that within a good approximation the order of the crystal field parameters is the same as in the present analysis ($\sim 10^{-4}$), it is evidently seen from Table II of ref.¹ that the contribution to the transition amplitude of $0 \leftrightarrow 1$, the part which is due to the electric dipole mechanism, is of the same order of magnitude as those of

TABLE VI
Total contributions of various orders to the amplitude of ${}^5D_1 \leftrightarrow {}^7F_0$ transition

Order	Contribution
1st	-9.57×10^{-2}
2nd	6.80×10^{-4}
3rd	2.61×10^{-4}
4th	-1.11×10^{-3}

second-, third- and fourth-order terms of the magnetic dipole radiation. At the same time it is two orders of magnitude smaller than the major contribution of the first order, as presented in Table VI. This means that the $0 \leftrightarrow 1$ transition is primarily of the magnetic dipole origin as stated by Kushida and his collaborators.

In summary it is concluded that contributions to the magnetic dipole transition ${}^5D_1 \leftrightarrow {}^7F_0$ are of the following relative importance

$$V_{CF} F_2 \approx F_2 V_{CF} \approx F_5 (f) > F_4 (f)$$

$$F_4 (d) > F_5 (d) > F_5 (g) \gg F_4 (g)$$

where in parentheses the symmetry of one-electron excited states is displayed to which the 4f electron is promoted in the excited configurations.

The possibility of the importance of the mechanisms of borrowing intensity for the ${}^5D_0 \leftrightarrow {}^7F_0$ magnetic dipole transition has also been checked. The detailed inspection of the tensorial form of various effective operators has proved that none of the considered mechanisms reinforce this transition, since all the contributions analyzed here vanish due to the selection rules. Thus, at this point of the analysis the only non-zero contribution is of electric dipole origin, and it is determined by the third-order two-particle effective operators representing the perturbing influence of the crystal field potential and also the electron correlation effects. Since such a description of this unusual transition is not precise enough as discussed by Kushida, as a next step of the investigations it is planned to formulate a model in which three major interactions simultaneously are taken into account as perturbations, namely: the crystal field potential, electron correlation effects and spin-orbit interaction. As a consequence of the inclusion of the spin-orbit interaction the transition amplitude will be expressed in the terms of double tensor operators, and therefore completely new selection rules for the non-vanishing contributions to the amplitude of the $0 \leftrightarrow 0$ transition are expected. Work along this line is in progress.

APPENDIX. EFFECTIVE OPERATORS THAT CONTRIBUTE TO THE AMPLITUDE OF MAGNETIC DIPOLE TRANSITIONS

The third-order contributions are determined by the effective operator which present intershell interactions via $PV_{CF}QV_{so}P$. Using the assumptions of the standard Judd-Ofelt theory about the energy denominators it is possible to perform the partial closure and derive the effective operator of the following form

$$F_2(x, \psi') = \frac{2}{\sqrt{3}} \sum_{tp}^{\text{even}} (-1)^{t+1} [t]^{-\frac{1}{2}} B_p^t \langle 4f | r^{-3} | \rho^t (4f \rightarrow f) \rangle a_{so}(f) \langle f || C^{(t)} || f \rangle$$

$$\sum_k^{\text{even}} [k] \begin{Bmatrix} t & k & 1 \\ f & f & f \end{Bmatrix} \langle 4f^6 x | W_p^{(1k)t} (ff) | 4f^6 \psi' \rangle. \quad (A1)$$

In this particular case the perturbing influence of the excited configurations $4f^{N-1}n'f$, for all n' , is taken into account.

The fourth-order contributions that contain the intershell interactions are determined by two different effective operators. The operator F_4 represents the interaction $PV_{CF}QV_{so}QV_{CF}P$ and it has the following effective form

$$F_4(x, \psi') = \frac{2}{\sqrt{3}} \sum_{t_1 p_1}^{p(t_1)=p(t_2)} \sum_{t_2 p_2} B_{p_1}^{t_1} B_{p_2}^{t_2} \sum_{I'} \langle \rho^{t_1} (4f \rightarrow I') | r^{-3} | \rho^{t_2} (4f \rightarrow I') \rangle$$

$$\langle f || C^{(t_1)} || I' \rangle \langle I' || C^{(t_2)} || f \rangle a_{so}(I') \sum_k^{\text{odd}} [k] \sum_{\lambda \mu} (-1)^{t_1 - \mu + \lambda} [\lambda]^{-\frac{1}{2}}$$

$$\begin{pmatrix} t_1 & t_2 & \lambda \\ p_1 & p_2 & -\mu \end{pmatrix} \begin{Bmatrix} 1 & k & \lambda \\ I' & f & t_2 \\ I' & f & t_1 \end{Bmatrix} \langle 4f^6 x | W_{\mu}^{(1k)\lambda} (ff) | 4f^6 \psi' \rangle. \quad (A2)$$

In this case the intrashell interactions within the excited configurations via the spin-orbit interaction are taken into account ($QV_{so}Q$). When the order of physical mechanisms in the triple product is different, namely in the case of $PV_{CF}QV_{CF}QV_{so}P$, the effective operator has the form

$$F_5(x, \psi') = \frac{2}{\sqrt{3}} \sum_{t_1 p_1}^{p(t_1)=p(t_2)} \sum_{t_2 p_2} B_{p_1}^{t_1} B_{p_2}^{t_2} \sum_{I'} \langle \rho^{t_1} (4f \rightarrow I') | r^{t_2} | \rho^{-3} (4f \rightarrow f) \rangle$$

$$\langle f || C^{(t_1)} || I' \rangle \langle I' || C^{(t_2)} || f \rangle a_{so}(f) \sum_k^{\text{even}} \sum_{\lambda \mu} (-1)^{k-\mu} [\lambda]^{-\frac{1}{2}}$$

$$\begin{pmatrix} t_1 & t_2 & \lambda \\ p_1 & p_2 & -\mu \end{pmatrix} \begin{Bmatrix} t_2 & \lambda & t_1 \\ f & I' & f \end{Bmatrix} \begin{Bmatrix} 1 & k & \lambda \\ f & f & f \end{Bmatrix}$$

$$\langle 4f^6 x | W_{\mu}^{(1k)\lambda} (ff) | 4f^6 \psi' \rangle. \quad (A3)$$

The effective operators contributing at the fourth order, F_4 and F_5 , represent the perturbing influence of pairs of excited configurations. Namely, for the even part of the crystal field potential the impact of $4f^{N-1}n'f$ via V_{CF} and V_{so} is included. For the odd parts of the crystal field, F_4 represents interactions between $4f^N - 4f^{N-1}n'd$, $4f^{N-1}n'g$ via V_{CF} potential. F_5 with odd part of V_{CF} represents interactions between $4f^N$ and $4f^{N-1}n'd$, $4f^{N-1}n'g$ via V_{CF} , and $4f^N - 4f^{N-1}n'f$ via V_{so} .

In the case of all these effective operators, the radial integrals are expressed in terms of the perturbed functions¹³. Therefore, in the numerical calculations the impact due to the excitations to the one-electron states from the complete set is taken into account.

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