MAGNETIC LINEAR BIREFRINGENCE IN RARE EARTH SYSTEMS. II. THIRD-ORDER APPROACH+

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Out of my deep respect and cordial admiration I dedicate this paper to an outstanding Scientist, charming Gentleman and warm Friend – Professor Rudolf Zahradník, on his special birthday, with my best wishes for many years to come.

The theory of linear magnetic birefringence of rare earth ions in crystals is extended here by the contributions that represent a direct perturbing influence of the crystal field potential surrounding the central ion. The basic assumptions of the theoretical model are the same as in the previous analysis of second-order terms. The third-order contributions introduced here break the free ionic system approximation, and they represent the impact due to configuration interaction. The effective operators include the perturbing influence of the excitations from the 4f shell to one-electron states of the same parity (as previously at the second order), and in addition, the excitations to states of opposite parity. All contributing terms are expressed by the effective operators that are defined within the perturbed function approach. The tensorial structure of these operators is discussed, and special attention is directed to newly defined radial integrals. The values of all radial integrals that are necessary for the third-order numerical analysis are presented in the case of all lanthanide ions.
Keywords: Rare earth ions; Lanthanides; Magnetic anisotropy; Polarizability tensor; Effective tensor operators; Perturbation theory; Crystal field potential; Perturbed function approach.

A theoretical model of magnetic linear birefringence in rare-earth-doped materials introduced in the previous paper[1] (hereafter denoted as I) was based on the second-order term of time-dependent perturbation theory applied to the description of the matter-radiation interaction. This formulation was defined within the free ionic system approximation. In order to break this approximation and include in the description the fact that the

+ Previous paper see ref.[1]

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rare earth ion is indeed surrounded by ligands, a perturbing influence of the existing crystal field is taken into account in a direct way. Thus the standard Rayleigh–Schrödinger perturbation theory is applied to the following hamiltonian

$$H = H_0 + \lambda P V_{\mathrm{CF}} Q \,,$$

where H_0 is a zeroth-order hamiltonian that describes the rare earth ion and it is based on a single configuration approximation (H–F model), and the crystal field potential V_{CF}, taken as a perturbation, has a tensorial form

$$V_{\mathrm{CF}} = \sum_{tp} B_p^t \sum_i r_i^t C_p^{(t)}(\vartheta_i, \varphi_i)$$

with B_p^t defined as crystal field parameters.

A particular construction of the perturbing operator, which is accompanied from both sides by the projection operators, prevents inclusion of the same crystal field effects twice. Indeed, here only the inter-shell part of these interactions is taken into account, and the diagonal part $PV_{\mathrm{CF}}P$ associated with the space spanned by the functions of the ground configuration $4f^N$ might be included within the zeroth-order hamiltonian if defined beyond the free ionic system approximation. The particular part of V_{CF} included in the present approach mixes the states of ground and excited configurations of appropriate parity (Q is the orthogonal complement of P). This construction of the perturbing operator reproduces the configuration interactions *via* the crystal field potential, and its effect upon the components of the polarizability tensor is the main aim of the present analysis.

THIRD-ORDER CRYSTAL FIELD APPROACH

The standard expression for the components of the polarizability tensor is modified here by the terms that originate from the improvement of the description of the $4f^N$ configuration. Instead of the zeroth-order wave functions, as used in I, here the functions that are extended by the first-order corrections due to crystal field potential are applied to the evaluation of appropriate matrix elements. In the original expression for the polarizability tensor, for each polarization $\rho_1\rho_2$, there is a sum of two products of matrix elements that differ from each other by the order of operators (apart from energy denominators that are different, see Eq. (*1*) of I). Thus inserting now

into the matrix elements of the original formula the wavefunction in the form

$$4f^N\Psi = \psi + \lambda\psi^{(1)},$$

in general leads to two distinct terms contributing to the polarizability tensor, namely

$$\alpha_{\rho_1\rho_2}(DDV_{CF}) = \sum_{Xx}\left\{\frac{\langle 4f^N\psi|D^{(1)}_{\rho_1}|Xx\rangle\langle Xx|D^{(1)}_{\rho_2}|4f^N\psi^{(1)}\rangle}{(\hbar\omega - \Delta E_{4f^N,X})} - \right.$$
$$\left. - \frac{\langle 4f^N\psi|D^{(1)}_{\rho_2}|Xx\rangle\langle Xx|D^{(1)}_{\rho_1}|4f^N\psi^{(1)}\rangle}{(\hbar\omega + \Delta E_{4f^N,X})}\right\} \qquad (1)$$

$$\alpha_{\rho_1\rho_2}(V_{CF}DD) = \sum_{Xx}\left\{\frac{\langle 4f^N\psi^{(1)}|D^{(1)}_{\rho_1}|Xx\rangle\langle Xx|D^{(1)}_{\rho_2}|4f^N\psi\rangle}{(\hbar\omega - \Delta E_{4f^N,X})} - \right.$$
$$\left. - \frac{\langle 4f^N\psi^{(1)}|D^{(1)}_{\rho_2}|Xx\rangle\langle Xx|D^{(1)}_{\rho_1}|4f^N\psi\rangle}{(\hbar\omega + \Delta E_{4f^N,X})}\right\}, \qquad (2)$$

where Xx are various states of intermediate (singly excited) configurations X of opposite parity to the parity of configuration $4f^N$, and $\psi^{(1)}$ is the first-order correction to the wavefunctions of $4f^N$ configuration that is due to crystal field potential. Using the standard Reyleigh–Schrödinger perturbation theory these corrections are defined in the following way

$$\psi^{(1)} = \sum_{Bb}\frac{\langle Bb|QV_{CF}P|\psi\rangle}{\Delta E_{4f^N\psi,Bb}}|Bb\rangle,$$

where the summation is over all excited configurations B (that belong to Q), and over all their states b, and the energy denominator is the difference of energies of states of $4f^N$ and intermediate configurations B.

The two terms in Eqs (*1*) and (*2*) are distinguished by the different order of operators in triple products of matrix elements ($\psi^{(1)}$ contains matrix elements of V_{CF}), and therefore they are denoted by DDV_{CF} and $V_{CF}DD$. It is seen that the position of the perturbing operator is interchanged in these

expressions, and therefore the coupling schemes of tensor operators are different in each case. Indeed, in a symbolic way the situation is described by the following products of matrix elements

$$\alpha_{\rho_1\rho_2}(DDV_{\mathrm{CF}}) \Rightarrow \langle 4\mathrm{f}^N\psi|D^{(1)}|Xx\rangle\langle Xx|D^{(1)}|Bb\rangle\langle Bb|V_{\mathrm{CF}}|4\mathrm{f}^N\psi\rangle$$

and

$$\alpha_{\rho_1\rho_2}(V_{\mathrm{CF}}DD) \Rightarrow \langle 4\mathrm{f}^N\psi|V_{\mathrm{CF}}|Bb\rangle\langle Bb|D^{(1)}|Xx\rangle\langle Xx|D^{(1)}|4\mathrm{f}^N\psi\rangle ,$$

where the energy denominators (product of two in each case, since these are the terms of the third order) are omitted for simplicity. The parity selection rules for the non-vanishing matrix elements require that

$$p(X) \neq p(4\mathrm{f}^N) \qquad p(X) \neq p(B) \quad \Rightarrow \quad p(B) = p(4\mathrm{f}^N) .$$

The latter conclusion means that only even parts of the crystal field potential are taken into account here, and therefore in the definition of $V_{\mathrm{CF}}t$ is even. Since all the operators in the matrix elements are one-particle objects, the intermediate configurations Xx describe single excited configurations $4\mathrm{f}^{N-1}n'\ell'$ for which, due to the parity conditions, ℓ' is even, and it denotes one-electron states of d and g symmetries. The perturbing influence of these excitations is taken into account at the second-order *via* the interaction of the electric dipole operator, while here their impact is included through the crystal field potential. In addition, the other set of excited configurations taken into account at the third order *via* the crystal field potential, Bb, contains the excitations from the 4f shell to those one-electron states that are of odd value, $\ell'' = \mathrm{p}, \mathrm{f}$. In all cases the excitations to all discrete and also continuum states of given symmetry have to be included. Obviously this requirement makes the numerical calculations at least troublesome, however, this problem is avoided in the present realization by adopting the concept of perturbed function approach (see I). In this approach the problem of performing summations over the complete radial basis sets of one-electron states is replaced by a task of solving differential equations for newly defined functions.

The general expressions for $\alpha_{\rho_1\rho_2}(DDV_{\mathrm{CF}})$ and $\alpha_{\rho_1\rho_2}(V_{\mathrm{CF}}DD)$ presented in Eqs (*1*) and (*2*) are too complex to be used directly for numerical evaluation of the magnitude of the third-order contributions. Therefore, applying the

so-called closure procedure (see I), the triple products of matrix elements, including the energy denominators, are expressed in the terms of effective operators.

In order to be able to perform summations over all quantum numbers of x and b except the one-electron ones, $n\ell$, $n'\ell'$, $n''\ell''$, it is assumed that H_0 is the Fock operator, and the zeroth-order problem is solved for the average energy of configuration $4f^N$. While evaluating the energy of the excited configurations B and X (also an average), the calculations are performed for the frozen core orbitals. This procedure was also used previously, and it might be regarded as a numerical realization of the approximations introduced in the Judd–Ofelt theory of one-photon electric dipole transitions. In fact, these approximations are crucial for the theoretical procedure, since they allow to introduce the effective operators that reproduce the interactions of a given physical mechanism by a new operator that acts only within the $4f^N$ configuration. From a formal point of view, for the first time a concept of Judd–Ofelt theory[2,3] has been applied to the description of magnetic linear birefringence by Nekvasil and co-workers[4]; from a physical point of view, the present analysis is the first attempt made to establish a direct impact of the crystal field upon the magnetic linear birefringence.

As a consequence of the above assumptions, the energy denominators of the third-order contributions are expressed now by a simple difference of orbital energies of appropriate one-electron states. Finally, after coupling of distinct tensor operators and using unit tensor operators, the third-order effective operator that determine the polarizability tensor has the following form

$$\alpha_{\rho_1\rho_2}(DDV) = 2(-1)^{\rho_1+\rho_2} \sum_{tp}^{\text{even}} B_p^t \sum_{kq} (-1)^{k-p} \sum_{\ell'} \boldsymbol{\epsilon}_{\ell'} \sum_{\ell''} \boldsymbol{\epsilon}^*_{\ell''} \mathcal{F}_{qp}^{kt}(\omega\rho_1\rho_2;\ell'\ell'') \\ R^t(\ell'\ell'')\, \mathrm{d}^{1t}(\ell'\ell'') \langle 4f^N\psi | U_q^{(k)} | 4f^N\psi\rangle , \tag{3}$$

where the factor $\mathcal{F}$ of the effective operator contains all the coupling coefficients and additional parity requirements, namely

$$\mathcal{F}_{qp}^{kt}(\omega\rho_1\rho_2;\ell'\ell'') = -\sum_{x,\sigma} X_x^-(\rho_1\rho_2,\omega;\ell')[x] \begin{pmatrix} 1 & 1 & x \\ \rho_1 & \rho_2 & -\sigma \end{pmatrix} \begin{pmatrix} x & t & k \\ \sigma & \mathrm{p} & -q \end{pmatrix} \\ \begin{Bmatrix} 1 & x & 1 \\ \mathrm{f} & \ell' & \ell'' \end{Bmatrix} \begin{Bmatrix} t & k & x \\ \mathrm{f} & \ell'' & \mathrm{f} \end{Bmatrix}, \tag{4}$$

where in general

$$X_x^{\pm}(\rho_1\rho_2,\omega;\ell') = \left[\boldsymbol{\epsilon}_x \pm \boldsymbol{\epsilon}_x^*[1-\delta(\rho_1,\rho_2)]\xi_{\ell'}(\omega)\right]$$

and $\xi_{\ell'}(\omega)$ is an approximate energy factor introduced in I,

$$\xi_{\ell'}(\omega) = \frac{\hbar\omega}{\varepsilon_{n'\ell'} - \varepsilon_{4f}} \cong \frac{\hbar\omega}{\varepsilon_{5\ell'} - \varepsilon_{4f}}$$

In Eq. (*4*), through factor $X_x^{\pm}$, two cases for x = even($\boldsymbol{\epsilon}_x$) and for x = odd($\boldsymbol{\epsilon}_x^*$) are distinguished. These two parts of X are analogs of symmetric and asymmetric contributions discussed at the second order, with the difference that here x is a summation index, and not a rank of effective operator. In fact, x is the rank resulting from a coupling of two electric dipole tensor operators and, together with the rank of crystal field potential operator t in a triangle condition, it determines the rank k of effective operator of Eq. (*3*). The sequence of couplings performed in the derivation of the final expression is clearly presented by the 3*j* and 6*j* symbols of Eq. (*4*).

The radial term of the effective operator is defined by a single integral of two perturbed functions

$$R^t(\ell'\ell'') = \langle \rho^1(4f \rightarrow \ell')|r|\rho^t(4f \rightarrow \ell'')\rangle. \qquad (5)$$

The perturbed function $\rho^1(4f \rightarrow \ell')$ originates from the interaction *via* the electric dipole operator that is present in the original definition of the polarizability tensor, and it is defined by Eq. (*7*) of I. This function contains the impact due to all single excitations from 4f shell to all one-electron states of d and g symmetry. The second in the integral and new in the present approach, is the perturbed function $\rho^t(4f \rightarrow \ell'')$ that represents the perturbing influence of the excited configurations $4f^{N-1}n''p$ and $4f^{N-1}n''f$ taken into account *via* the crystal field potential for all n''. From a formal point of view these particular perturbed functions are defined in the same way as the perturbed functions of the Judd–Ofelt theory. However, for the first time here they are generated by an even part of crystal field potential (therefore ℓ'' is odd), while those of the standard Judd–Ofelt approach originate from the interaction *via* the odd part of crystal field potential (and ℓ' is

even); in fact, from a physical point of view both of these perturbed functions are generated by the same perturbing mechanism.

The angular factor in Eq. (*3*), $d^{1t}(\ell'\ell'')$, is responsible for the equivalence between the spherical tensors and unit tensor operators, and it is defined by the reduced matrix elements

$$d^{1t}(\ell'\ell'') = \langle f||C^{(1)}||\ell'\rangle\langle\ell'||C^{(1)}||\ell''\rangle\langle\ell''||C^{(t)}||f\rangle .$$

The derivation of the effective operator form of the third-order contribution defined by Eq. (*2*) is not so straightforward. As mentioned before, this expression differs from the previous one by the sequence of operators, and therefore it requires coupling and re-coupling of various intermediate ranks. However, making use of the equality between products of 3*j* symbols and 6*j* symbols (see ref.[5], problem 3-1; page 73) it is possible to obtain the effective operator defined also by Eq. (*3*) with the exception of the phase factor. In fact for the $\alpha(VDD)$ contributions factor X_x^- in Eq. (*4*) has to be replaced by X_x^+ and the whole expression in Eq. (*3*) has to be multiplied by the phase factor of $(-1)^k$. Taking these changes into account, both contributions are equal

$$\alpha_{\rho_1\rho_2}(DDV) = \alpha_{\rho_1\rho_2}(VDD)$$

only far the following cases:

if $\rho_1 = \rho_2$ then k = even, x = even, and $X_x^{\pm} = 2\epsilon_x$

if $|\rho_1| \neq |\rho_2|$ then k = odd, x = even, and $X_x^{\pm} = 2\epsilon_x$

or

k = even, x = odd, and $X_x^{\pm} = 2\epsilon_x^*\xi_{\ell'}(\omega)$

otherwise the sum of both terms vanishes. Thus, the third-order contributions due to crystal field potential $\alpha_{\rho_1\rho_2}(DDV + VDD)$ are determined by a modified expression of Eq. (*3*), where the phase factor $(-1)^{\rho_1+\rho_2+k}$ is removed, and the factor $\mathcal{F}$ is changed by replacing X_x^- by $X_x^{\pm}$ in Eq. (*4*) as discussed above.

Finally, when comparing the tensorial structure of second- and third-order contributions it is seen that there are new selection rules for the non-

vanishing matrix elements. Indeed, formally at the second order, the effective operator was of the rank 0,1,2 since it was determined from the coupling of two vectors (operators of rank (1)). At the third order, it is derived from the triangular conditions of Eq. (*4*) that the final rank *k* might be as large as 6 if not limited by the rank of crystal field potential operator *t*. At the same time it should be remembered also that the final rank *k* in both cases, in second- and third-order contributions, has to satisfy the triangular condition for the non-vanishing 3*j* symbol of Wigner–Eckart theorem applied to the evaluation of the matrix elements of operators in Eq. (*3*) and Eq. (*2*) of I.

NUMERICAL ANALYSIS AND CONCLUSIONS

The angular factors of effective operators introduced here are the same for all lanthanide ions, and only the relative importance of various terms associated with the operators with different ranks requires their values to perform any comparison. The electronic structure of a rare earth ion is represented in this approach by the radial integrals that provide individual and distinct properties of each ion to the model. Therefore the most interesting part of numerical analysis is always focused on the newly defined radial integrals.

As presented in I, the radial integrals of the effective operators of second order are of the form $\langle 4f|r|\rho^1(4f \rightarrow d)\rangle$ and $\langle 4f|r|\rho^1(4f \rightarrow g)\rangle$. In the case of third-order terms, the radial integrals contain two perturbed functions. Therefore it is interesting to compare and verify the effect resulting from a substitution of the atomic orbital 4f in the second-order integral by perturbed function that describes the excitations from the 4f shell to one-electron states of f symmetry. In Fig. 1 such a comparison is presented; the values of third-order integrals $\langle \rho^1(4f \rightarrow d)|r|\rho^2(4f \rightarrow f\rangle$ are compared with the second-order ones $\langle \rho^1(4f \rightarrow d)|r|4f\rangle$ and $\langle \rho^1(4f \rightarrow g)|r|\rho^2(4f \rightarrow f\rangle$ are compared with $\langle \rho^1(4f \rightarrow g)|r|4f\rangle$. It is seen from Fig. 1 that in spite the fact that the third-order integrals are different from the second-order ones, their behavior across the lanthanide series is very similar. Taking into account the definitions it is seen that these integrals are indeed different, since the atomic orbital 4f of second-order term is replaced at the third order by the perturbed function that originates from the interactions *via* crystal field potential; this perturbed function represents all the single excitations from 4f to excited orbitals of f symmetry. The perturbed functions through their formal definition as a linear combination of all first-order corrections due to a certain perturbation do not have any physical interpretation. However, it

was concluded from numerical analysis of various kinds of perturbed functions examined in the case of the theoretical description of spectroscopic properties of rare earth ions in various hosts, that in general they behave as the first excited one-electron state of the symmetry to which 4f electron is promoted. Thus, it is expected also here that $\rho^t(4f \rightarrow f)$ behaves as the excited orbital 5f (the number of nodes, for example; for details see ref.[6]). This atomic-like behavior of perturbed functions is then confirmed here as reflected by the changes of radial integrals as presented in Fig. 1.

In Fig. 2 the values of third-order integrals for different ranks of the tensor operator that define the crystal field potential are compared. In order to show on one plot the nature of their changes with the change of the rank of perturbing operator, the values of $\langle \rho^1(4f \rightarrow d)|r|\rho^t(4f \rightarrow g\rangle$ are scaled by 100 and 10 for t = 2 and 4. The most striking feature observed in the changes of values of all radial integrals is their monotonic decrease with increasing Z number; this property is repeated independently of the kind and the number of perturbed functions involved (one or two) in the analyzed integral.

In order to establish the hierarchy of important contributions to the polarizability tensor, the angular factors of all effective operators also have to be evaluated. This means that to demonstrate the dominant role of d-excitations over g-excitations (see Fig. 3 in I), the scaled values of second-order contributions presented in I have to be re-evaluated (in fact only mul-

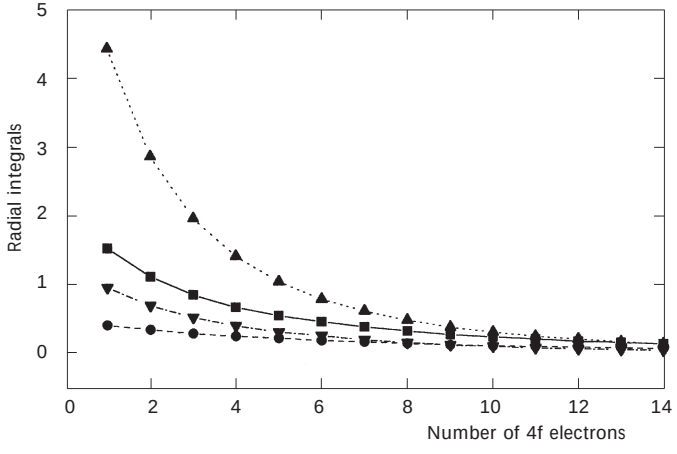

FIG. 1
Values of radial integrals R^2(df) (· · · · ·), R^1(d) (———) and R^2(gf) (– · – · –), R^1(g) (– – – –) for ions across the lanthanide series. ▲ $\langle 4f - d|r|4f - f(2)\rangle$, ■ $\langle 4f - d|r|4f\rangle$, ▼ $\langle 4f - g|r|4f - f(2)\rangle$, ● $\langle 4f - g|r|4f\rangle$

tiplied by the contribution due to g-excitations). Actually, it is interesting to compare at this point the importance of both excitations at second and third order. In I the value of $\eta = R^1(\mathrm{d})/R^1(\mathrm{g})$ (integrals of the second order) decreases from 3.75 for Ce^{3+} to 1.79 for Lu^{3+}; at the third order the ratio of appropriate integrals associated with d- and g-excitations, $R^t(\mathrm{df})/R^t(\mathrm{gf})$ decreases from 4.6 to 2.5 for $t = 2$, and from 4.3 to 2.4 for $t = 4$, for Ce^{3+} and Lu^{3+}, respectively. Again it is seen then that independently of a physical background of the terms of second- and third-order contributions, the d-excitations are the most dominant ones. At the same time, however, as expected by Kolmakova *et al.*[7,8], also at the third order the excitations to the states of g symmetry are not negligible. It should be pointed out that all values of all radial integrals are evaluated for the complete radial basis sets of one-electron states of given symmetry.

To find out the relative importance of second- and third-order terms test calculations have been performed for a particular case of $\rho_1 = \rho_2 = 0$ to simplify the analysis. For this particular case the effective operator of second order has only one rank $k = 2$, due to the conditions for the non-vanishing $3j$ symbol of $\mathcal{A}$ in Eq. (3) of I. The situation is more complex in the case of the third-order contributions, since they depend on the symmetry of the environment of the rare earth ion. In order to compare the numerical results of *ab initio* nature, the contributing terms without the structural parameters are analyzed when possible. At the same time, the final rank of the

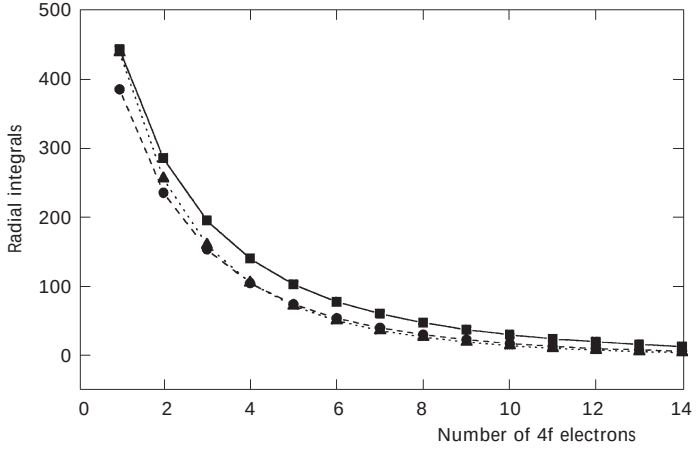

FIG. 2

Comparison of the values of $R^t(\mathrm{df})$ for all lanthanide ions; the values for $t = 2$ (———) and 4 (· · · · ·) are scaled by 100 and 10, respectively. ■ $\langle 4f - d|r|4f - f(2)\rangle \times 100$, ▲ $\langle 4f - d|r|4f - f(4)\rangle \times 10$, ● $\langle 4f - d|r|4f - f(6)\rangle$

effective operator in Eq. (*3*) is also chosen to have value $k = 2$. In this way it is possible to compare just the factors that are state independent, since at both orders the same matrix elements of $U^{(2)}$ is excluded.

The third-order contributions, $\alpha^{kq}_{\rho_1\rho_2}(DDV, B^t_p)$, evaluated for a given rank of crystal field potential have the form

$$\alpha^{20}_{00}(DDV, B^2_0) = B^2_0 \times 10^{-1} \left[4.0988R^2(\mathrm{df}) + 5.4650R^2(\mathrm{gf})\right] U^{(2)}_0$$

$$\alpha^{20}_{00}(DDV, B^4_0) = B^4_0 \times 10^{-1} \left[-3.3845R^4(\mathrm{df}) - 4.5126R^4(\mathrm{gf})\right] U^{(2)}_0 \,.$$

In this particular case, since k = even and x = even, then in order to obtain the whole component due to the crystal field potential $\alpha^{20}_{00}(DDV + VDD)$, the values above have to be multiplied by a factor of 2. It should be pointed out that the above expressions are valid for any of the lanthanide ions, and in order to evaluate the numerical value of this contribution, the radial integrals for certain ion have to be applied. It is obvious, however, that these contributions are behaving across the lanthanide series in the same

TABLE I
Crystal-structure-independent contributions to the components of polarizability tensor originated at the third order from a term *DDV* (for details see the main text)

Ion	*t*	α(d)	α(g)	α(d) + α(g)	κ_d [a]
Ce^{3+}	2	18.20	5.25	23.45	78
	4	–130.68	–40.57	–171.25	76
Eu^{3+}	2	3.28	1.42	4.70	70
	4	–19.02	–8.66	–27.68	69
Gd^{3+}	2	2.58	1.15	3.73	69
	4	–14.35	–6.81	–21.16	68
Tb^{3+}	2	2.05	0.93	2.98	69
	4	–11.07	–5.42	–16.49	67
Yb^{3+}	2	0.66	0.41	1.07	62
	4	–3.11	–2.08	–5.19	60

[a] $\kappa_d = \{\alpha(d)/(\alpha(d) + \alpha(g))\} \times 100\%$.

way as their radial integrals, since the numerical factors, as written above, are common for all ions.

In Table I the crystal-structure-independent contributions to the polarizability tensor are presented for two complementary systems of $Ce^{3+}(4f^1)$ and $Yb^{3+}(4f^{13})$, and for the half-filled shell system $Gd^{3+}(4f^7)$ with two neighbouring ions $Eu^{3+}(4f^6)$ and $Tb^{3+}(4f^8)$. The symbols used in this Table denote particular components, namely $\alpha(\ell') \equiv \alpha_{00}^{20}(\ell'f)$ for ℓ' = d and g, and in the last column the relative importance of d-excitations over g-excitations is presented in percentages. It is seen from this Table that from the very beginning to the very end of the lanthanide series the d-excitations are dominant and their contributions for various ions are not smaller than 60% relative to the contributions caused by g-excitations.

In the case of ions which are characterized by a one electron (hole) in a 4f shell, the effect of the perturbing influence of the crystal field potential is pure in the sense that it is not masked by for example, correlation effects that are very strong in these systems. For two ions, Ce^{3+} and Yb^{3+}, contributions to the component of the polarizability tensor associated with the unit tensor operator $U^{(2)}$, and originated from *VDD* and *DVV*, are defined up to the third order in the following way

for Ce^{3+}

$$\alpha_{00}^{20} = -0.92 + 4.68B_0^2 - 34.26B_0^4$$

for Yb^{3+}

$$\alpha_{00}^{20} = -0.12 + 0.21B_0^2 - 1.04B_0^4 ,$$

where the first value represents the contribution of the second order, and the following ones (those multiplied by the structural parameters) are from the third order.

These two expressions are valid for all symmetries of the environment, since no assumptions are made on the magnitude of the crystal field parameters nor even on the symmetry of the environment. This is also a reason that the numerical results presented here are the results of *ab initio* nature. At the moment of using the values of appropriate crystal field parameters, the calculations are becoming semiempirical, since the parameters are usually evaluated from a fitting procedure. Furthermore, these expressions are also valid for any electronic state of certain ion. Actually, in order to evaluate the value of the component of polarizability tensor, a host has to

be chosen, crystal field parameters have to be known, and in addition the expressions above have to be multiplied by the value of matrix elements of $U^{(2)}$ between appropriate electronic states.

In general, it is demonstrated here that the polarizability tensor depends directly on the strength of the crystal field potential, which is represented by the crystal field parameters. In addition a change of selection rules for the non-vanishing contributions of the third order makes a theoretical model of magnetic linear birefringence more sensitive to the properties of electronic structure of the lanthanide ion.

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