

## Theoretical Calculations of Lanthanide $4f \leftrightarrow 4f$ Intensities. ~~Three Non-Degenerate Wave Processes~~

O. L. MALTA

*Departamento de Química e Departamento de Física da UFPE, Cidade Universitária, Recife, PE. 50000, Brasil*

and

A. A. S. DA GAMA and S. CANUTO

*Departamento de Física da UFPE, Cidade Universitária, Recife, PE 50000, Brasil*

Recebido em 1/6/82

By defining a single average energy denominator,  $\Delta E_{AV}$ , it is shown that a formula for crystal-field induced electric-dipole  $4f \leftrightarrow 4f$  intensities can be obtained which contains contributions of all possible excited configurations of interest and depends on radial integrals involving only  $4f$  wavefunctions. Interference effects between the the Pseudo-Multipolar Field (the mechanism originally proposed by Jørgensen and Judd to account for the high sensitivity of certain  $4f \leftrightarrow 4f$  transitions to changes in the chemical environment) and electric dipole mechanisms are also considered. The theory is then applied to the systems  $Y_2O_3:Nd^{3+}$  and  $LaF_3:Nd^{3+}$ . It is concluded that a reliable value for the average energy denominator,  $\Delta E_{AV}$ , is given by the first opposite parity excited configuration ( $4f^{N-1}5d$ ) and that "core excitations" as well as interference effects give very important contributions.

Através de um denominador energético médio,  $\Delta E_{AV}$ , é demonstrado que uma expressão para intensidades espectrais  $4f \leftrightarrow 4f$  (induzidas por dipolo elétrico na presença de um campo cristalino não centro-simétrico) pode ser obtida na qual todas as configurações excitadas re-

levantas são levadas em consideração e além disso depende de integrais radiais envolvendo unicamente funções  $4f^N$ . Efeitos de interferência entre o Campo Pseudo Multipolar (mecanismo originalmente proposto por Jørgensen e Judd para explicar a enorme sensibilidade de certas transições  $4f^N \leftrightarrow 4f^N$  a mudanças no ambiente químico) e o mecanismo dipolar-elétrico são considerados. Os resultados teóricos são aplicados aos sistemas  $Y_2O_3:Nd^{3+}$  e  $LaF_3:Nd^{3+}$ . Conclui-se que um valor confiável para o denominador energético médio,  $\Delta E_{AV}$ , é dado pela primeira configuração excitada de paridade oposta ( $4f^{N-1}5d$ ) e que excitações de caroço ("core excitations") assim como efeitos de interferência são extremamente importantes.

## 1. INTRODUCTION

Lanthanide  $4f^N \leftrightarrow 4f^N$  intensities is an attractive subject for testing configuration interaction models based on perturbation expansions in which the lanthanide ions are considered to be little perturbed by a chemical environment.

Since 1962, the spectroscopists dispose of a theoretical background for treating the intensities of the sharp lines originated from transitions within the  $4f^N$  configurations. It is known as the Judd-Ofelt theory<sup>1,2</sup>. This theory is based on the following:

In the absence of a center of inversion, the odd part of the crystal field hamiltonian produces, in the lanthanide ion, a mixing of configurations of opposite parities and as a consequence Laporte's rule is relaxed. Perturbation expansions are then used to give nonvanishing electric-dipole matrix elements which are proportional to effective operators depending on the excited configurations of the lanthanide ion as well as the symmetry and the nature of the chemical environment in which the ion is embedded. For each particular excited configuration of interest, there exists a particular effective operator which is found by neglecting the term splittings in comparison with the energy difference between the excited and the ground configurations and by using Racah algebra together with a summation over a complete set of intermediate states<sup>3,4,5</sup>.

$\Theta(t, \lambda)$	$\delta$	0.00	0.25	0.50	0.75	0.90
(1,2)		-0.50	-0.39	-0.18	-0.02	-0.08
(3,2)		0.40	0.34	0.29	0.23	0.20
(3,4)		0.29	0.17	0.06	-0.06	-0.12
(5,4)		-0.26	-0.24	-0.22	-0.20	-0.19
(5,6)		-0.29	-0.15	-0.02	0.12	0.19
(7,6)		0.24	0.24	0.24	0.24	0.24

Table 1 - Values of the angular quantities  $\Theta(t, \lambda)$  for various  $\delta$ 's.

Unfortunately, only very few works have reported on "ab-initio" intensity calculations using the Judd-Ofelt theory<sup>1,6-9</sup>. Instead, workers have given attention to a phenomenological treatment of this theory in which experimental intensities are used to determine a few parameters, in general, with a small mean square deviation. However, it is known that other mechanisms, like the vibronic and the one due to ligand polarization effects<sup>10</sup>, provide contributions to the  $4f^N \rightarrow 4f^N$  intensities which have the same angular dependence as the effective operators given by the Judd-Ofelt theory. Thus, they are completely absorbed in the phenomenological treatment and there is no way to distinguish between the various mechanisms.

The difficulty in dealing with "ab-initio"  $4f^N \rightarrow 4f^N$  intensity calculations, lies on the following points:

i) The crystal-field hamiltonian is based on the point charge electrostatic model which is known to give a weak description of the effects of the chemical environment on the  $4f^N$  states.

ii) Only some the perturbing excited configurations can actually be taken into account, due to the lack of knowledge of both radial excited wavefunctions and energy differences between configurations.

In the present work, we attempt to remedy the second of the above points by introducing a single average energy denominator and a factor,  $\delta$ , which represents the ratio between ratio integrals associated with core excitations and radial integrals involving only  $4f$  wavefunctions. It is then possible to sum over all perturbing configurations.

## 2. THE AVERAGE ENERGY DENOMINATOR

The calculation of second-order energy correction may be performed either by knowledge of the first order correction to the wave function

$$E^{(2)} = \langle \psi_0^{(0)} | V | \psi_0^{(1)} \rangle \quad (1)$$

or by a sum-over-states procedure

$$E^{(2)} = \sum_{n \neq 0} \frac{\langle \psi_0^{(0)} | V | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | V | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \quad (2)$$

where  $V$  is the perturbation and  $|\psi_0^{(0)}\rangle$  is the reference state.

As the solution  $|\psi_0^{(1)}\rangle$  is required in (1) one has often adopted procedure (2). However, the sum in (2) requires an infinite number of terms including integration over the continuum. Nevertheless we can clearly define an average energy such that

$$E^{(2)} = \frac{1}{\Delta E_{AV}} \sum_{n \neq 0} \langle \psi_0^{(0)} | V | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | V | \psi_0^{(0)} \rangle \quad (3)$$

Then by the completeness of the  $\{|\psi_n^{(0)}\rangle\}$  set we have

$$E^{(2)} = \frac{1}{\Delta E_{EV}} [\langle \psi_0^{(0)} | V^2 | \psi_0^{(0)} \rangle - \langle \psi_0^{(0)} | V | \psi_0^{(0)} \rangle^2] \quad (4)$$

In most cases  $\langle \psi_0^{(0)} | V | \psi_0^{(0)} \rangle = 0$  from parity considerations.

In the case of hydrogen,  $\Delta E_{AV}$  can be evaluated exactly. When  $V$  is the electric-dipole operator and the ground state is taken as the reference state we have immediately that  $\langle \psi_0^{(0)} | V | \psi_0^{(0)} \rangle = 0$  and  $\langle \psi_0^{(0)} | V^2 | \psi_0^{(0)} \rangle = 1$  (in atomic units) so that, since  $E^{(2)} = -9/4$ , the average excited state  $E_{AV}^{(0)}$ ,  $\Delta E_{AV} = E_0^{(0)} - E_{AV}^{(0)}$ , lies at the  $n=3$  level.

Hence, for the calculation of ground-state second-order properties such as the polarizability, exact results are obtained with  $E_{AV}^{(0)} = -\frac{1}{18}$  a.u.. The average excited state will obviously depend on the perturbing operator and the reference state.

Bebb and Gold<sup>11</sup> have used the above procedure for treating multiphoton ionization processes in hydrogen and rare-gas atoms. They found that using the first excited state as the average state  $E_{AV}^{(0)}$ , quite satisfactory results may be obtained.

We wish now to use this procedure in the case of lanthanide  $4f \leftrightarrow 4f$  intensities.

### 3. CRYSTAL-FIELD INDUCED ELECTRIC-DIPOLE MATRIX ELEMENTS

The oscillator strength of a transition from a state  $|A\rangle$  to a state  $|B\rangle$ , of an atomic system, due to a spherical component  $q$  of the dipole moment vector is given by

$$P_{AB} = \chi \frac{2m\omega}{\hbar} |\langle A | \sum_i r_i C_q^{(1)}(i) | B \rangle|^2 \quad (5)$$

where  $\omega$  is the angular frequency of the transition,  $\chi$  is the Lorentz local-field correction,  $m$  the electronic mass and  $\hbar$  Planck's constant. The quantities  $C_Q^{(K)}$  are Racah<sup>12</sup> tensor operators of rank  $K$  and the sum over  $i$  runs over all electrons in the atomic system which is to be considered in the presence of a crystal-field.

In order to get nonvanishing matrix elements in eq. (5), we may consider the states  $|A\rangle$  and  $|B\rangle$ , up to first order in perturbation theory, as given by

$$|A\rangle = |4f^N\phi\rangle + \sum_{\phi''} |\phi''\rangle \frac{\langle\phi''|V_{CF}|4f^N\phi\rangle}{[E(\phi)-E(\phi'')]}$$
 (6)

and

$$|B\rangle = |4f^N\phi'\rangle + \sum_{\phi''} |\phi''\rangle \frac{\langle\phi''|V_{CF}|4f^N\phi'\rangle}{[E(\phi')-E(\phi'')]}$$
 (7)

where

$$V_{CF} = \sum_{t,p,i} \gamma_p^t r_i^t C_p^{(t)}(i)$$
 (8)

is the odd part of the crystal-field hamiltonian. We point out that in equation (8), nothing implies that the coefficients  $\gamma_p^t$  are to be given by the usual point charge electrostatic model<sup>13</sup>. Since  $V_{CF}$  is a one-body operator, the only excited configurations of interest are those of the type  $4f^{N-1}n\ell$ , with  $R = f \pm 1$ , and  $(n'\ell')$ <sup>4</sup> $\ell'+1$  $4f^{N+1}$  with  $\ell' = f-1$ , these latter being associated with the so called "core excitations".

Up to second order, we are then interested in the evaluation of the quantity

$$\frac{1}{\Delta E_{AV}} \sum_{t,p,\phi''} \gamma_p^t \langle 4f^N\phi | D_q^{(1)} | \phi'' \rangle \langle \phi'' | D_p^{(t)} | 4f^N\phi' \rangle + \langle 4f^N\phi | D_p^{(t)} | \phi'' \rangle \langle \phi'' | D_q^{(1)} | 4f^N\phi' \rangle$$
 (9)

where we have already replaced energy denominators by the average  $\Delta V_{AV}$  according to the previous section, and the quantities  $D_Q^{(K)}$  stand for  $\sum_i r_i^K C_Q^{(K)}$ .

Since all but the  $4f^{N-1}n\ell$ ,  $\ell=f \pm 1$ , and  $(n'\ell')$ <sup>4</sup> $\ell'+1$  $4f^{N+1}$ ,  $\ell'=f-1$ , configurations give vanishing matrix elements, we may sum over the complete set  $\{|\phi''\rangle\}$  and use closure to bring the operators  $D_q^{(1)}$  and  $D_p^{(t)}$  together. We may then use standard tensor operator techniques<sup>1,4,14</sup> to

couple  $D_g^{(1)}$  and  $D_p^{(t)}$  in order to find an effective operator acting between  $|4f^N\phi\rangle$  and  $|4f^N\phi'\rangle$ . In what follows we merely present the results of this procedure which is well described in a text by Judd<sup>4</sup>.

The quantity in (9) is found to contain the following contributions:

1)  $g$  electrons

$$\sum_{\lambda\rho} (-1)^\rho (2\lambda+1) \langle 4f | r^{t+1} | 4f \rangle \langle f | | c^{(1)} | | g \rangle \langle g | | c^{(t)} | | f \rangle$$

$$\begin{Bmatrix} t & 1 & \lambda \\ p & q & \rho \end{Bmatrix} \begin{Bmatrix} f & 1 & g \\ t & f & \lambda \end{Bmatrix} \langle 4f^N\phi | U_{-\rho}^{(\lambda)} | 4f^N\phi' \rangle \quad (10)$$

and

$$\sum_{\lambda\rho} (-1)^\rho (2\lambda+1) \langle 4f | r^{t+1} | 4f \rangle \langle f | | c^{(t)} | | g \rangle \langle g | | c^{(t)} | | f \rangle$$

$$\begin{Bmatrix} 1 & t & \lambda \\ q & p & \rho \end{Bmatrix} \begin{Bmatrix} f & t & g \\ 1 & f & \lambda \end{Bmatrix} \langle 4f^N\phi | U_{-\rho}^{(\lambda)} | 4f^N\phi' \rangle \quad (11)$$

2)  $d$  electrons

$$\sum_{\lambda\rho} (-1)^\rho (2\lambda+1) \left( \sum_{n>4} \langle 4f | r | nd \rangle \langle nd | r^t | 4f \rangle \right) \langle f | | c^{(1)} | | d \rangle \langle d | | c^{(t)} | | f \rangle$$

$$\begin{Bmatrix} t & 1 & \lambda \\ p & q & \rho \end{Bmatrix} \begin{Bmatrix} f & 1 & d \\ t & f & \lambda \end{Bmatrix} \langle 4f^N\phi | U_{-\rho}^{(\lambda)} | 4f^N\phi' \rangle \quad (12)$$

and

$$\sum_{\lambda\rho} (-1)^\rho (2\lambda+1) \left( \sum_{n>4} \langle 4f | r^t | nd \rangle \langle nd | r | 4f \rangle \right) \langle f | | c^{(t)} | | d \rangle \langle d | | c^{(1)} | | f \rangle$$

$$\begin{Bmatrix} 1 & t & \lambda \\ q & p & \rho \end{Bmatrix} \begin{Bmatrix} f & t & d \\ 1 & f & \lambda \end{Bmatrix} \langle 4f^N\phi | U_{-\rho}^{(\lambda)} | 4f^N\phi' \rangle \quad (13)$$

### 3) Core excitations

$$\begin{aligned}
 & - \sum_{\lambda\rho} (-1)^\rho (2\lambda+1) \left( \sum_{n'=3,4} \langle 4f^t | r^t | n'd \rangle \langle n'd | r | 4f \rangle \right) \langle f || c^{(t)} || d \rangle \\
 & \langle d || c^{(1)} || f \rangle \begin{pmatrix} 1 & t & \lambda \\ q & p & \rho \end{pmatrix} \begin{Bmatrix} f & t & d \\ 1 & f & \lambda \end{Bmatrix} \langle 4f^N \phi | U_{-\rho}^{(\lambda)} | 4f^N \phi' \rangle \quad (14)
 \end{aligned}$$

and

$$\begin{aligned}
 & - \sum_{\lambda\rho} (-1)^\rho (2\lambda+1) \left( \sum_{n'=3,4} \langle 4f | r | n'd \rangle \langle n'd | r^t | 4f \rangle \right) \langle f || c^{(1)} || d \rangle \langle d || c^{(t)} || f \rangle \\
 & \begin{pmatrix} t & f & \lambda \\ p & q & \rho \end{pmatrix} \begin{Bmatrix} f & 1 & d \\ t & f & \lambda \end{Bmatrix} \langle 4f^N \phi | U_{-\rho}^{(\lambda)} | 4f^N \phi' \rangle \quad (15)
 \end{aligned}$$

where the quantities  $\langle | r^K | \rangle$  are radial integrals and  $U_{-\rho}^{(\lambda)}$  is a unit tensor operator of rank  $\lambda$ .

We note that core excitations contribute with an opposite sign. This fact has already been pointed out by Griffith<sup>15</sup> in a theoretical investigation on the intensity theory of open-shell ions and has been, more recently, discussed by Becker<sup>16</sup> from the experimental point of view.

Here, we introduce the factor  $\delta$  defined by

$$\delta = \frac{\sum_{n'=3,4} \langle 4f | r | n'd \rangle \langle n'd | r^t | 4f \rangle}{\langle 4f | r^{t+1} | 4f \rangle} \quad (16)$$

and since for a fixed value of  $\ell$  the radial wavefunctions  $R_{n\ell}$  form a complete set, we must have  $0 < \delta < 1$ . It could be argued that the factor  $\delta$  should depend on the values of  $t$ . However, we have calculated the ratio (16) for some values of  $t$  by assuming hydrogenic wavefunctions and  $\delta$  has shown to be essentially the same in all cases. Therefore, we assume this to be true in the present treatment.



The sum over  $n$  in (12) and (13) may be expressed as

$$\sum_{n>4} \langle 4f | r | nd \rangle \langle nd | r^t | 4f \rangle = \langle 4f | r^{t+1} | 4f \rangle - \sum_{n'=3,4} \langle 4f | r | n' d \rangle \langle n' d | r^t | 4f \rangle \quad (17)$$

Now, owing to the symmetry properties of the 3- $j$  symbols

$$\begin{pmatrix} 1 & t & \lambda \\ q & p & \rho \end{pmatrix} = (-1)^{1+t+\lambda} \begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix}$$

only even values of  $\lambda$  give a total nonvanishing contribution which is therefore

$$2 \sum_{\lambda, \rho} (-1)^\rho (2\lambda+1) \langle 4f | r^{t+1} | 4f \rangle \begin{pmatrix} t & 1 & \lambda \\ p & q & \rho \end{pmatrix} \Theta(t, \lambda) \langle 4f^N \phi | U_{-\rho}^{(\lambda)} | 4f^N \phi' \rangle \quad (18)$$

where

$$\Theta(t, \lambda) \left[ \langle f | | c^{(1)} | | g \rangle \langle g | | c^{(t)} | | f \rangle \begin{Bmatrix} f & 1 & g \\ t & f & \lambda \end{Bmatrix} + (1-2\delta) \langle f | | c^{(1)} | | d \rangle \langle d | | c^{(t)} | | f \rangle \begin{Bmatrix} f & 1 & d \\ t & f & \lambda \end{Bmatrix} \right] \quad (19)$$

If the states  $|4f^N \phi\rangle$  and  $|4f^N \phi'\rangle$  are given by the intermediate coupling scheme<sup>17</sup>, we get the following matrix element

$$\langle A | \sum_i n_z c_q^{(1)}(i) | B \rangle = \frac{2}{\Delta E_{AV}} \sum_{\lambda, \rho, t, p} (-1)^\rho (2\lambda+1) \gamma_p^t \langle 4f | r^{t+1} | 4f \rangle \begin{Bmatrix} t & 1 & \lambda \\ p & q & \rho \end{Bmatrix} \Theta(t, \lambda) \langle 4f^N \psi_{JM_J} | U_{-\rho}^{(\lambda)} | 4f^N \psi_{J'M_{J1}} \rangle \quad (20)$$

It may be useful to note that if we wish to perform intensity calculations between Stark levels, with the inclusion of  $J$ -mixing effects ( $J$  is no longer a good quantum number), we have merely to replace the states

$|4f^N \phi\rangle$  and  $|4f^N \phi'\rangle$  by the appropriate linear combination given by the diagonalization of the even part of the crystal-field hamiltonian. On the other hand, if  $J$ -mixing effects are neglected and we assume an equivalent thermal population of the initial Stark levels, substituting (20) into (5) a summation over  $M_J$  and  $M_{J'}$  weighted by  $\frac{1}{2J+1}$  gives a factor  $\frac{1}{2\lambda+1} \delta_{\lambda\lambda'} \delta_{\rho\rho'}$ . We may therefore carry out the sum over  $\rho$  and  $q$  weighted by  $1/3$ , which is appropriate for isotropic medium<sup>1</sup>, to obtain a factor  $\frac{1}{2t+1} \delta_{tt'} \delta_{pp'}$ . The final result is

$$P_{AB} = \frac{\chi 2m\omega}{3\hbar} \sum_{\lambda} \Omega_{\lambda} \langle 4f^N \psi_{J'} | |U^{(\lambda)}| | 4f^N \psi_{J'} \rangle^2 (2J+1)^{-1} \quad (21)$$

where

$$\Omega_{\lambda} = \frac{4(2\lambda+1)}{\Delta E^2_{AV}} \sum_{t,p} \frac{|Y_p^t|^2}{(2t+1)} \langle 4f^N | r^{t+1} | 4f^N \rangle^2 \Theta^2(t, \lambda) \quad (22)$$

Equations (21) and (22) have exactly the same form as in the Judd-Ofelt theory. However, they differ in that the above equations depend on a single average energy denominator and contain the contributions of all possible excited configurations.

#### 4. THE PSEUDO-MULTIPOLAR FIELD AND INTERFERENCE EFFECTS

The potential energy of the  $4f$  electrons due to an arrangement of dipole moments localized on the ligands may be given by<sup>18</sup>

$$W = -e \sum_{\substack{\lambda q q' q'' \\ \mu j}} (-1)^{\lambda+q+q''} |4\pi(\lambda+1)(2\lambda+1)|^{1/2} \frac{r_j^{\lambda}}{R_{\mu}^{\lambda+2}} \begin{pmatrix} \lambda & 1 & \lambda+1 \\ q & q'' & -q' \end{pmatrix} P_{q''}^{(1)}(\mu) Y_q^{\lambda+1*}(\Omega_{\mu}) C_q^{(\lambda)}(j) \quad (23)$$

where  $P_{q''}^{(1)}(\mu)$  is a spherical component of a dipole moment localized at the  $\mu$ -th ligand whose position is  $\vec{R}_{\mu}$  with respect to a coordinate system centered at the nucleus of the lanthanide ion. These dipole moments are proportional to the net electric field at each ligand

$$\vec{P}(\mu) = \alpha_{\mu} \vec{E}(\mu) \quad (24)$$

where  $\alpha$  is an average polarizability. If, however, the vector  $\vec{E}$  is the electric field of the external electromagnetic radiation, the dipole moments  $\vec{P}(\mu)$  will oscillate producing a resultant field which may induce transitions within a  $4f^N$  configuration. This mechanism has been invoked to explain the phenomenon of "hypersensitivity", that is, the very high sensitivity of certain  $4f \leftrightarrow 4f$  transitions to changes in the chemical environment<sup>1,19-22</sup>. It is considered to be an effect of ligand polarization and is called the Pseudo-Multipolar Field.

This mechanism should then be added to the electric dipole mechanism of the previous section.

The  $4f$  electrons are, therefore, subjected to a total time-dependent interaction of the form

$$W(t) = W^+ e^{i\omega t} + W e^{-i\omega t} \quad (25)$$

Transition probabilities are proportional to the squared matrix elements of  $W^+$  or  $W$ , and interference effects between the two mechanism may occur.

The appropriate matrix element for the electric-dipole mechanism is given by equation (2) while for the Pseudo-Multipolar Field it is given by<sup>21,22</sup>

$$\langle A | W_{P.M.} | B \rangle = \sum_{\lambda \rho \mu} (-1)^{\lambda+\rho} [4\pi(\lambda+1)(2\lambda+1)]^{1/2} \alpha_{\mu} \frac{Y^{\lambda+1*}(\Omega_{\mu})}{R_{\mu}^{\lambda+2}}$$

$$\langle 4f | r^{\lambda} | 4f \rangle \begin{pmatrix} \lambda+1 & 1 & \lambda \\ p & q & \rho \end{pmatrix} \langle f | | C^{(\lambda)} | | f \rangle \langle 4f^N \psi^N M_J | U_{-\rho}^{(\lambda)} | 4f^N \psi^N J' M_{J'} \rangle \quad (26)$$

The sum over the ligands in eq. (26) may be related to point charge lattice sums, , through the equation

$$\sum_{\mu} \frac{\alpha_{\mu} \gamma^{\lambda+1*}(\Omega_{\mu})}{R_{\mu}^{\lambda+2}} = \alpha \left[ \frac{(2\lambda+3)}{4\pi} \right]^{1/2} \frac{\beta^{\lambda+1}}{e^2 g} \quad (27)$$

where  $-ge$  is the net charge on each ligand, and we have assumed  $\alpha_{\mu} = \alpha_V = \dots = \alpha$ .

We get then a contribution to the total oscillator strength, due to interference which is

$$P_{AB}^{int.} = \frac{\chi 2\pi\omega}{3} \sum_{\lambda} \Omega_{\lambda}^{int.} \langle 4f^N \psi_{J'} | U^{(\lambda)} | | 4f^N \psi'_{J'} \rangle^2 (2J+1)^{-1} \quad (28)$$

where

$$\begin{aligned} \Omega_{\lambda}^{int.} &= \frac{2\alpha(1-\sigma_{\lambda})}{ge^2 \Delta E_{AV}} \left[ \frac{(\lambda+1)(2\lambda+1)}{(2\lambda+3)} \right]^{1/2} \langle 4f | r^{\lambda+2} | 4f \rangle \\ &\langle 4f | r^{\lambda} | 4f \rangle \langle f | | C^{(\lambda)} | | f \rangle \Theta(\lambda+1, \lambda) \sum_P (\gamma_P^{\lambda+1} \beta_P^{\lambda+1*} + \\ &+ \gamma_P^{\lambda+1*} \beta_P^{\lambda+1}) \end{aligned} \quad (29)$$

and we have included the factor  $\sigma_A$  to account for shielding effects produced by the external electrons of the lanthanide ion against external multipolar fields<sup>21</sup>.

The Pseudo-Multipolar Field itself gives a contribution to the total oscillator strength which has the same form as equations (21) and (28) but with a coefficient  $\Omega_{\lambda}$  given by

$$\Omega_{\lambda}^{P.M.} = \frac{\alpha^2}{g^2 e^4} (1-\sigma_{\lambda})^2 (\lambda+1) \langle 4f | r^{\lambda} | 4f \rangle^2 \langle f | | C^{(\lambda)} | | f^2 \rangle \sum_P \dots \quad (30)$$

Again, it may be useful to note that formulae to be used in intensity calculations between Stark levels can be easily obtained as described in the previous section.

## 5. COMPARISON WITH EXPERIMENT

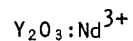
In order to test the results of sections 3 and 4 we decided to concentrate on the systems  $Y_2O_3:Nd^{3+}$  and  $LaF_3:Nd^{3+}$ . Our intention is rather to see and discuss the general features of the theory.

The structure of  $Y_2O_3$  has been established by X-ray and neutron diffraction techniques<sup>23,24</sup> and has been, recently, the subject of a refinement at low temperature<sup>25</sup>. In this host the lanthanide ions may enter in two sites of point symmetries  $C_2$  and  $S_6$  (the ratio of occupied  $C_2$  sites over  $S_6$  being 3:1). Nevertheless, only the formers are of interest, for our purposes, since the  $S_6$  point symmetry possesses a center of inversion and does not allow the existence of odd parity terms in the crystal-field hamiltonian.

The structure of  $LaF_3$  has been determined by Cheetham et al<sup>26</sup>. The lanthanide ion occupies a site with point symmetry  $C_2$  with the binary axis perpendicular to the ternary axis of the lattice. According to classical crystal-field theory, these are typical examples of covalent ( $Y_2O_3$ ) and ionic ( $LaF_3$ ) chemical environments.

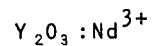
The experimental parameters  $\Omega_\lambda$  for these two systems have been determined by Krupke<sup>6</sup>. To proceed with our purposes, i.e., the application of equations (22), (29) and (30), we need to have a quantitative knowledge of the crystal-field coefficients  $\gamma_Q^K$  (with odd  $K$ 's), the radial integrals  $\langle 4f^N | r^{t+1} | 4f^N \rangle$  and the ligand polarizabilities. Unfortunately, we do not dispose, at present, of more realistic values for the coefficients  $\gamma_Q^K$  than those given by the point charge electrostatic model. Therefore, we have to satisfy ourselves with the latter which are given by Krupke<sup>6</sup> and Leavitt and Morrison<sup>7</sup>.

The appropriate free-ion radial integrals have been recently evaluated by Freeman and Desclaux<sup>27</sup> from a Dirac-Fock calculation (The value of  $\langle 4f^N | r^8 | 4f^N \rangle$  used by us was obtained from an extrapolation). However, other sets of radial integrals have been used in intensity calculations<sup>1,7</sup> and substantial differences arise according to the set used. It seems plausible that the ligand orbitals penetrating the 4 shell produce an expansion of the  $4f$  radial wavefunctions. On the other hand, the



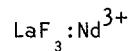
$\delta$	$\Omega_2 (\times 10^{20}) \text{ cm}^2$					$\Omega_4 (\times 10^{20}) \text{ cm}^2$					$\Omega_6 (\times 10^{20}) \text{ cm}^2$				
	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90
E.D.	74.83	46.83	14.63	4.54	3.29	12.59	4.56	0.71	0.62	0.25	0.42	0.12	0.00	0.07	0.17
INT.	13.12	11.21	9.21	7.47	6.61	0.78	0.74	0.68	0.62	0.56	0.07	0.07	0.07	0.07	0.07
P.M.			3.46					0.63					0.21		
TOTAL	92.50	61.50	27.30	15.47	13.36	14.00	5.93	2.02	1.87	1.44	0.70	0.40	0.28	0.35	0.45
EXP.			8.55					5.25					2.89		

Table 2 - Electric dipole (E.D.), interference (INT.) and Pseudo-Multipolar Field (P.M.) contributions, for various  $\delta$ 's, to the  $\Omega_\lambda$  coefficients for the  $\text{Y}_2\text{O}_3:\text{Nd}^{3+}$  system. The radial integrals used are those of Freeman and Desclaux<sup>27</sup>. The lowest row shows the experimental values.



$\delta$	$\Omega_2 (\times 10^{20}) \text{ cm}^2$					$\Omega_4 (\times 10^{20}) \text{ cm}^2$					$\Omega_6 (\times 10^{20}) \text{ cm}^2$				
	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90
E.D.	120.27	75.57	24.61	8.23	5.57	23.84	9.11	1.94	1.69	0.94	3.23	1.47	0.79	1.18	1.88
INT.	22.32	18.94	15.56	12.62	11.17	2.55	2.42	2.22	2.03	1.83	1.56	1.56	1.56	1.56	1.56
P.M.	5.40					1.15					1.23				
TOTAL	147.99	99.91	45.57	26.25	22.14	27.57	12.68	5.31	4.87	3.92	6.02	4.26	3.58	3.97	4.67
EXP.	8.55					5.25					2.89				

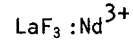
Table 3 - Electric dipole (E.D.), interference (INT.) and Pseudo-Multipolar Field (P.M.) contributions, for various  $\delta$ 's, to the  $\Omega_\lambda$  coefficients for the  $Y_2O_3:Nd^{3+}$  system. The radial integrals used are those given by Judd<sup>1</sup>.



$\delta$	$\Omega_2 (\times 10^{20}) \text{ cm}^2$					$\Omega_4 (\times 10^{20}) \text{ cm}^2$					$\Omega_6 (\times 10^{20}) \text{ cm}^2$				
	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90
E.D.	1.99	1.28	0.51	0.22	0.12	0.81	0.39	0.18	0.13	0.11	0.35	0.10	~0.00	0.06	0.16
INT.	0.66	0.56	0.46	0.37	0.33	0.65	0.62	0.57	0.52	0.47	0.02	0.02	0.02	0.02	0.02
P.M.			0.17					0.53					0.06		
TOTAL	2.82	2.01	1.14	0.76	0.62	1.99	1.54	1.27	1.18	1.21	0.61	0.18	0.08	0.14	0.24
EXP.			0.35					2.57					2.50		

Table 4 Electric dipole (E.D.), interference (INT.) and Pseudo-Multipolar Field (P.M.) contributions, for various  $\delta$ 's, to the  $\Omega_\lambda$  coefficients for the  $\text{LaF}_3:\text{Nd}^{3+}$  system. The radial integrals used are those of Freeman and Desclaux<sup>27</sup>





$\delta$	$\Omega_2 (\times 10^{20}) \text{ cm}^2$					$\Omega_4 (\times 10^{20}) \text{ cm}^2$					$\Omega_6 (\times 10^{20}) \text{ cm}^2$				
	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90	0.00	0.25	0.50	0.75	0.90
E.D.	3.28	2.12	0.89	0.40	0.21	2.24	1.40	0.87	0.68	0.61	2.31	0.85	0.28	0.61	1.20
INT.	1.11	0.95	0.78	0.61	0.56	2.31	2.03	1.86	1.70	1.54	0.45	0.45	0.45	0.45	0.45
P.M.			0.27					0.96					0.35		
TOTAL	4.66	3.34	1.94	1.28	1.04	5.51	4.39	3.69	3.34	3.29	3.11	1.65	1.08	1.41	2.00
EXP.			0.35					2.57					2.50		

Table 5: Electric dipole (E.D.), interference (INT.) and Pseudo-Multipolar Field (P.M.) contributions, for various  $\delta$ 's, to the  $\Omega_A$  coefficients for the  $\text{LaF}_3:\text{Nd}^{3+}$  system. The radial Integrals are those given by Judd<sup>1</sup>.

shielding due to the  $5s5p$  external electrons of the lanthanide ion certainly attenuates this effect and we could expect not a too great departure of radial integral values from the free-ion values. What we feel to be more likely is a combined effect producing changes in both  $\langle 4f | r^K | 4f \rangle$  and  $\gamma_Q^K$  with respect to the free-ion and point charge models. We may anticipate that, in this connection, a study is now being carried out.

The polarizability of the  $F^-$  ion does not seem to vary considerably in different crystals<sup>28</sup> and in our calculations we have assumed the value  $\alpha(F^-) = 1\text{\AA}^3$ . In contrast, the  $O^{--}$  ion shows quite variable polarizability values. In a previous calculation<sup>22</sup> the quoted value of  $\alpha(O^{--}) \approx 3\text{\AA}^3$  in  $Y_2O_3$  seems to have been overestimated; a discussion by Jørgensen<sup>29</sup> excludes this value. He estimates<sup>30</sup> that  $\alpha(O^{--})$  in  $Y_2O_3$  should not be far from  $1.4\text{\AA}^3$ . Within our purposes, we decided to use  $\alpha(O^{--}) = 28$ .

Our basic question now is how to obtain a reliable value for  $\Delta E_{AV}$ . It seems that the only way of estimating  $\Delta E_{AV}$  without having to perform the complete sum over intermediate states, is essentially to proceed by trial and errors like in the work of Bebb and Gold<sup>11</sup>.

If we think only in terms of  $5g-4f$  and  $5d-4f$  radial matrix elements, since the former is expected to be considerably greater than the latter (due to the fact that the  $5d$  radial wavefunctions has two nodes while  $5g$  has none) one would be tempted to say that  $\Delta E_{AV}$  should lie closer to  $\Delta E_{5g}$  than to  $\Delta E_{5d}$ . However, this depends on the  $4d-4f$  matrix element which is also much greater than the  $5d-4f$  one and since core excitations contribute, to the total dipole matrix element, with an opposite sign  $\Delta E_{AV}$  could decrease towards the  $\Delta E_{5d}$  value.

To check this argument we have used equations (22), (29) and (30) to find the value of  $\Delta E_{AV}$  that would best reproduce the values of the best experimentally determined intensity parameters which are  $\Omega_4$  and  $\Omega_6$ . In this procedure we have used the factor  $\delta \approx 0.9$ , as given by the hydrogenic ratio, and the set of radial integrals given by Judd<sup>1</sup>. These radial integrals were calculated from a more expanded  $4f$  wavefunction than the one used by Freeman and Deslaur<sup>27</sup>. They should, therefore, compensate the fact that the point charge electrostatic model of the

crystal-field predicts  $\gamma_{\alpha}^k$  coefficients of high ranks which are in general underestimated<sup>10</sup>.

We finally found  $\Delta E_{AV} \cong \Delta E_5$  ( $=58000 \text{ cm}^{-1}$  for the  $4f^2 5d$  configuration). If we had used the set of radial integrals of Freeman and Desclaux<sup>27</sup> we would have found  $\Delta E_{AV} \ll \Delta E_5$  which is physically unlike.

Our results are shown in tables 2, 3, 4 and 5, the appropriate shielding factors used being  $\sigma_2 = 0.792$ ,  $\sigma_4 = 0.139$  and  $\sigma_6 = 0.109$ . In table 1 we give the values of  $\Theta(t, \lambda)$  for various values of 6. We found it worth to see how the  $\Omega_{\lambda}$  parameters vary as we neglect core excitations.

Our basic assumption is that the factor 6 can be approximately determined by the hydrogenic ratio. It seems reasonable that  $g$  and total  $d$  electrons contribute with opposite signs in order to compensate the fact that both contributions may be overestimated with  $\Delta E_{AV}$  given by the first opposite parity excited configuration.

## 6. CONCLUSION

From the practical point of view, the advantage of using equation (22) in the prediction of  $4f \leftrightarrow 4f$  intensities lies in its conciseness. While it contains contributions of all excited configurations of interest, it depends on a single average energy denominator and on radial integrals involving only  $4f$  wavefunctions.

The present theory lead us to conclude that:

i) Core excitations, hitherto neglected, give important contributions to  $4f \leftrightarrow 4f$  intensities.

ii) The average energy denominator,  $\Delta E_{AV}$ , reproduces, satisfactorily, the experimental intensities if it is given by the first opposite parity excited configuration.

iii) Interference effects are of great importance. Except for the work of Richardson et al<sup>31</sup>, to our knowledge, this is the first time

that interference effects are treated theoretically and included in calculations of  $4f \leftrightarrow 4f$  intensities.

Vibronic as well as magnetic dipole contributions remain to be considered in a full computational treatment. We hope then that the present alternative approach may be useful in the elucidation of the mechanism underlying the main features of lanthanide  $4f \leftrightarrow 4f$  intensities.

The authors express their gratitude to CNPq and FINEP for financial support.

## REFERENCES

1. B.R. Judd, Phys. Rev., 127, 750 (1962).
2. G.S. Ofelt, J.Chem.Phys., 37, 511 (1962).
3. B.R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, N.York, 1963).
4. B.R. Judd, *Second Quantization and Atomic Spectroscopy* (Johns Hopkins University Press, Baltimore, Md., 1967).
5. A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N.Jersey, 1957).
6. W.F. Krupke, Phys. Rev., 145, 325 (1966).
7. R.P. Leavitt and C.A. Morrison, J.Chem.Phys., 73, 749 (1980).
8. C.A. Morrison and R.P. Leavitt, J.Chem. Phys., 74, 25 (1981).
9. A.A.S. da Gama, Thesis (U.F.PE., 1981).
10. R.D. Peacock, Structure and Bonding, 22, 83 (1975).
11. H. Barry Bebb and Albert Gold, Phys. Rev., 143, 1 (1966).
12. G. Racah, Phys. Rev., 62, 438 (1942).
13. D.J. Newman, Adv. Phys., 20, 197 (1971).
14. B.G. Wybourne, J. Chem. Phys., 48, 2596 (1968).
15. J.S. Griffith, Mol. Phys., 3, 477 (1960).
16. P.J. Becker, Phys. Stat. Sol. (b), 43, 583 (1971).
17. B.G. Wybourne, *Spectroscopic Properties of Rare Earths* (John Wiley and Sons, 1965).
18. O.L. Malta, Mol. Phys., 38, 1347 (1979). In equation (23) of this

reference, the correct phase factor should be  $(-1)^{k+q}$ . This has been taken into account in eq. (23) of the present paper.

19. C.K. Jørgensen and B.R. Judd, *Mol. Phys.*, 8, 281 (1964).
20. S.F. Mason, R.D. Peacock and B. Stewart, *Chem. Phys. Lett.*, 29, 149 (1974).
21. B.R. Judd, *J.Chem. Phys.*, 70, 4830 (1979).
22. O.L. Malta, *Mol. Phys.*, 42, 65 (1981).
23. B.H. O'Connor and T.M. Valentine, *Acta Cryst.*, B27, 2140 (1969).
24. M. Bonnet, A. Delapalme and H. Fuess, *Acta Cryst.*, A32, 264 (1975).
25. M. Faucher and J. Pannetier, *Acta Cryst.*, B36, 3209 (1980).
26. A.K. Ctieetham, B.E.F. Fender, H. Fuess and A.F. Wright, *Acta Cryst.*, B32, 94 (1976).
27. A.J. Freeman and J.P. Desclaux, *J. of Mag. and Magnetic Materials*, 12, 11 (1979).
28. J.R. Tessman, A.H. Kahn and W. Shockley, *Phys. Rev.*, 92, 890 (1953).
29. C.K. Jørgensen, *Topics in Current Chem.*, 56, 1 (1975).
30. C.K. Jørgensen, private communication.
31. F.S. Richardson, J.D. Saxe, S.A. Davis and T.R. Faulkner, *Mol. Phys.*, 42, 1401 (1981).