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On Crystal Field Parameters: A Comparative Study for Eu^{3+} in KLu_3F_{10} and KY_3F_{10}

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The irreducible tensor method for a chain of finite subgroups of the three-dimensional full rotation group O_3 is briefly described in connection with crystalline-field effects in solids. Emphasis is put on crystal-field parameters adapted to a chain of groups starting from O_3. The material is applied to the interpretation of emission and excitation spectra of Eu^{3+} in KLu_3F_{10} recently investigated by Valon, Gacon, Vedrine, and Boulon (*J. Solid State Chem.* **21**, 357 (1977)). Crystal-field parameters for $KLu_3F_{10}:Eu^{3+}$ are obtained with and without J-mixing within the ground term ^7F of Eu^{3+}. The results are paralleled with the corresponding ones for $KY_3F_{10}:Eu^{3+}$ previously determined by Porcher and Caro (*J. Chem. Phys.* **65**, 89 (1976)).

1. Introduction

Rare-earth-doped compounds have received considerable attention (spectroscopic, magnetic, and thermal studies), both from an experimental and theoretical point of view, during the last 15 years. The Eu^{3+}-doped compounds turn out to be of particular importance in solid-state chemistry and solid-state physics due to their interesting luminescent and magnetic properties and their interest as laser materials. Emission and excitation spectra of Eu^{3+} in KLu_3F_{10} have been recently measured at 4.4, 77, and 295°K by Valon *et al.* (*1*). The obtained spectra present numerous similarities with the fluorescence spectrum for Eu^{3+} in KY_3F_{10} investigated by Porcher and Caro (*2*).

It is one goal of this paper to determine crystal-field parameters for $KLu_3F_{10}:Eu^{3+}$ and to compare them to the parameters derived in (*2*) for $KY_3F_{10}:Eu^{3+}$.

In recent years there has been an increasing interest in irreducible tensor methods and chains of groups around ligand field theory and related phenomena. [For a review, see (*3*).] In Section 2 we present, in the language of Wigner–Racah algebra for a chain of groups, some of the basic elements useful for a theoretical approach to energy level splittings of ions in solids. These basic elements are applied in Section 3 to the determination of crystal-field parameters for Eu^{3+} in KLu_3F_{10} and KY_3F_{10}.

2. Theory

Let us begin with some general considerations concerning the theoretical derivation of the electronic levels of an nl^N ion embedded in a molecular, crystalline, or biological matrix. In the case where the ion remains a sufficiently localized system when introduced in the matrix, we may describe the ion and its surroundings by the Hamiltonian $H_{fl} + H_{im}$, where H_{fl} is the Hamiltonian of the corresponding free ion and H_{im} the crystal-field Hamiltonian describing the (static) in-

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teraction between the ion and the matrix. To obtain the first-order energy levels arising from the configuration nl^N (single-configuration approximation), it is necessary to set up the matrix of general element

$$\langle nl^N p | \mathscr{H}_{fi} + \mathscr{H}_{im} | nl^N q \rangle,$$

where $|nl^N p\rangle$ stands for a state vector of the configuration nl^N, $\mathscr{H}_{fi}$ is the part of H_{fi} that does not contain the (restricted) Hartree–Fock contribution, and $\mathscr{H}_{im}$ the part of H_{im} corresponding to the interaction between the N electrons and the matrix under consideration. The most important contributions to $\mathscr{H}_{fi}$ are the electrostatical repulsion Hamiltonian $\mathscr{H}_e$ between the N electrons and the spin–orbit Hamiltonian $\mathscr{H}_{so}$ for the N electrons. The dimension of the $\mathscr{H}_{fi} + \mathscr{H}_{im}$ matrix is clearly

$$\binom{4l+2}{N} = (4l+2)!/N!(4l+2-N)!,$$

which is the dimension of the space $\varepsilon(nl^N)$ spanned by the $\binom{4l+2}{N}$ state vectors $|nl^N p\rangle$ of the configuration nl^N. Different bases

$$\left\{ |nl^N p\rangle : p \text{ ranging on } \binom{4l+2}{N} \text{ labels} \right\}$$

of $\varepsilon(nl^N)$ may be used to build the $\mathscr{H}_{fi} + \mathscr{H}_{im}$ matrix. Each basis directly depends on the coupling scheme chosen for the state vectors $|nl^N p\rangle$. There are thus (at least) $3! = 6$ different bases corresponding to the 3! coupling schemes we can form with $\mathscr{H}_e$, $\mathscr{H}_{so}$, and $\mathscr{H}_{im}$. The different bases are, of course (formally), connected through a unitary matrix (which is in general not easily obtainable), so that the spectrum of the operator $\mathscr{H}_{fi} + \mathscr{H}_{im}$ within $\varepsilon(nl^n)$ does not depend on the basis chosen. Different bases generally present different physical and/or mathematical advantages. Among the principal bases, we have: (i) the strong-field basis[1] corresponding to the coupling scheme $[[[\mathscr{H}_{im}]\otimes\mathscr{H}_e]\otimes\mathscr{H}_{so}]$, physically adapted to the strong-field case $\mathscr{H}_{im} > \mathscr{H}_e > \mathscr{H}_{so}$; (ii) the medium-field basis corresponding to the coupling scheme $[[[\mathscr{H}_e]\otimes\mathscr{H}_{im}] \otimes \mathscr{H}_{so}]$, physically adapted to the medium-field case $\mathscr{H}_e > \mathscr{H}_{im} > \mathscr{H}_{so}$; and (iii) the weak-field basis[1] corresponding to the coupling scheme $[[[\mathscr{H}_e] \otimes \mathscr{H}_{so}] \otimes \mathscr{H}_{im}]$, physically adapted to the weak-field case $\mathscr{H}_e > \mathscr{H}_{so} > \mathscr{H}_{im}$. Insofar as we do not want to truncate the space $\varepsilon(nl^N)$, the most interesting basis from a mathematical point of view is a weak-field basis adapted to the point symmetry group G of $\mathscr{H}_{im}$ or its double group G^* according to whether N is even or odd. In addition, in the case where S, L, and J retain their significance to a reasonable extent (as is the case for the lanthanides), a symmetry-adapted weak-field basis may be physically suitable when the space $\varepsilon(nl^N)$ is restricted to a direct sum of subspaces associated with some of the lowest terms of the configuration nl^N. For these last two reasons and in view of application to the Eu^{3+}-doped fluorides we deal with in this work, we now concentrate on weak-field bases adapted to a subgroup G (G^*) of the single (double) three-dimensional full rotation group O_3 (O_3^*).[2]

A typical state vector belonging to a symmetry-adapted weak-field basis is $|nl^N \alpha SLJa\Gamma\gamma\rangle$. We adopt the notations, cf. (*3–7*), developed in the irreducible tensor theory for a chain $O_3^* \supset G^*$. The symbol Γ stands[3] for an irreducible representations class (IRC) of G^*; we shall use $\Gamma(G^*)$ in place of Γ where necessary. Further, when necessary, γ is a row–column label for the irreducible representation matrix D^Γ associated to the IRC Γ and spanned by the set

$$\{|nl^N \alpha SLJa\Gamma\gamma\rangle : \gamma \text{ ranging}\}.$$

[1] The strong- (weak-) field basis proved to be very useful for the ions of the iron (rare-earth) group.

[2] If G only contains proper rotations, O_3 may be replaced by the three-dimensional proper rotation group SO_3. In that case, the double (or spinor) group SO_3^* of SO_3 is isomorphic with SU_2, the so-called two-dimensional special unitary group.

[3] Indeed, Γ stands for an IRC of G or G^* depending upon the parity of N. However, it is sufficient to deal with G^* only since G^* covers G.

Finally, when necessary, a is an external or branching multiplicity label to classify the various subspaces spanning the a_Γ identical representations D^Γ of G^* contained in the irreducible representation matrix of O_3^* spanned by the set

$$\{|nl^N \alpha SLJM\rangle : M = -J(1)J\}.$$

For classification or descending symmetry purposes, it is interesting to characterize, at least partially, the label a by an IRC $\Gamma(G_a{}^*)$ of a subgroup $G_a{}^*$ of $O_3{}^*$ that contains G^* (*5*). In similar fashion, it is interesting to characterize, at least partially, the label γ by an IRC $\Gamma(G_\gamma{}^*)$ of a subgroup $G_\gamma{}^*$ of G^* (*5*). This yields chains of groups of type $O_3{}^* \supset G_a{}^* \supset G^* \supset G_\gamma{}^*$. For the purposes of describing descent in symmetry and establishing selection rules, it may be worth introducing $\Gamma(G_a{}^*)$ and/or $\Gamma(G_\gamma{}^*)$ even in the cases where the a and/or γ labels are not indispensable. The $O_3{}^* \supset G^*$ symmetry-adapted state vector $|nl^N \alpha SLJa\Gamma\gamma\rangle$ is connected to the $|nl^N \alpha SLJM\rangle$'s (which are $O_3{}^* \supset O_2{}^*$ symmetry-adapted state vectors) via

$$|nl^N \alpha SLJa\Gamma\gamma\rangle = \sum_{M=-J(1)J} |nl^N \alpha SLJM\rangle \;(JM|Ja\Gamma\gamma),$$

where $(JM|Ja\Gamma\gamma)$ is the $M - a\Gamma\gamma$ element of the unitary matrix which decomposes the irreducible representation matrix of $O_3{}^*$ spanned by the set.

$$\{|nl^N \alpha SLJM\rangle : M = -J(1)J\}$$

into the direct sum $\bigoplus_\Gamma a_\Gamma D^\Gamma$.

The matrix of $\mathscr{H}_{\rm fi}$ in an $O_3{}^* \supset G^*$ symmetry-adapted weak-field basis readily follows from the corresponding matrix for the free ion. As an illustration, by retaining only the contribution $\mathscr{H}_{\rm e} + \mathscr{H}_{\rm so}$ in $\mathscr{H}_{\rm fi}$, we have

$$\begin{aligned}&\langle nl^N \alpha' S'L'J'a'\Gamma'\gamma'|\mathscr{H}_{\rm fi}|nl^N \alpha SLJa\Gamma\gamma\rangle \\ &= \delta(S'S)\delta(L'L)\delta(J'J)\delta(a'a)\delta(\Gamma'\Gamma)\delta(\gamma'\gamma) \\ &\quad \langle nl^N \alpha' SL|\mathscr{H}_{\rm e}|nl^N \alpha SL\rangle \\ &\quad +\delta(J'J)\delta(a'a)\delta(\Gamma'\Gamma)\delta(\gamma'\gamma) \\ &\quad \langle nl^N \alpha' S'L'J|\mathscr{H}_{\rm so}|nl^N \alpha SLJ\rangle. \end{aligned} \tag{1}$$

To easily evaluate the matrix of $\mathscr{H}_{\rm im}$ in an $O_3{}^* \supset G^*$ symmetry-adapted weak-field basis, it is convenient to adapt $\mathscr{H}_{\rm im}$ to the chain $O_3{}^* \supset G^*$. This is achieved by developing $\mathscr{H}_{\rm im}$ in terms of irreducible tensor operators adapted to the chain $O_3 \supset G$. Following (*4–6*), we have:

$$\mathscr{H}_{\rm im} = \sum_{\substack{k=2(2)2l \\ a_0}} D[ka_0\Gamma_0]\, U^k_{a_0\Gamma_0\gamma_0},$$

as far as matrix elements of $\mathscr{H}_{\rm im}$ within $\varepsilon(nl^N)$ are concerned. In this effective Hamiltonian, the $D[ka_0\Gamma_0]$'s are $O_3 \supset G$ symmetry-adapted crystal-field parameters (*4–6*).[4] Further, $U^k_{a_0\Gamma_0\gamma_0}$ is a Racah unit tensor component transforming as the identity IRC Γ_0 of G; in other words[5]:

$$U^k_{a_0\Gamma_0\gamma_0} = \sum_{q=-k(1)k} U^k_q (kq|ka_0\Gamma_0\gamma_0),$$

where U^k_q is the qth $O_3 \supset O_2$ symmetry-adapted component of the Racah unit tensor U^k (*4–6*). The parameter $D[ka_0\Gamma_0]$, or $D[ka_0]$ for short, is proportional to the parameter A_{ka_0} of (*5*):

$$D[ka_0] = (-1)^l(2l+1)\left(\frac{2k+1}{4\pi}\right)^{1/2} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} A_{ka_0}.$$

The $O_3 \supset G$ symmetry-adapted parameters $D[ka_0]$ may be expanded in terms of $O_3 \supset O_2$ symmetry-adapted parameters $A^q_k\langle r^k\rangle$ (*10*)

[4] The parameters $D[ka_0\Gamma_0]$ parallel, to some exent, the popular parameters Dq, Ds, and Dt (*8, 9*). The cubical parameter Dq writes $Dq = (1/6\ (30)^{1/2})\ D[4A_1]$ in function of the parameter $D[k\Gamma_0(O)] \equiv D[4A_1]$ adapted to the chain $SO_3 \supset O$. The tetragonal parameters Ds, Dq, and Dt are connected to some specific parameters $D[k\Gamma(O)\ \Gamma_0(D_4)]$ adapted to the chain $SO_3 \supset O \supset D_4$. More precisely: $D[2EA_1] = (70)^{1/2}\, Ds$, $D[4A_1\ A_1] = 6\ (30)^{1/2}\, Dq - 7(15/2)^{1/2}\, Dt$, and $D[4EA_1] = 5(21/2)^{1/2}\, Dt$.

[5] The tensor $U^k_{a_0\Gamma_0\gamma_0}$ is related, on $\varepsilon(nl^N)$, to the G harmonics $y^k_{a_0\Gamma_0\gamma_0}(\theta_i, \varphi_i)$ by $\sum_{i=1}^{N} y^k_{a_0\Gamma_0\gamma_0}(\theta_i, \varphi_i) = (-1)^l(2l+1)\,((2k+1)/4\pi)^{1/2} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} U^k_{a_0\Gamma_0\gamma_0}$.

or B^k_q (*11*, *12*). To be specific, we have

$$D[ka_0] = (-1)^l (2l+1) \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \sum_{q=-k(1)k} B^k_q (kq|ka_0\Gamma_0\gamma_0)^*. \quad (2)$$

The interest in the $D[ka_0]$ parametrization is fourfold: (i) the matrix elements of the $O_3 \supset G$ symmetry-adapted tensors $U^k_{a_0\Gamma_0\gamma_0}$ in any $O_3^* \supset G^*$ symmetry-adapted basis are readily obtainable (*3–7*), (ii) in particular, the reduced matrix elements $(nl^N \alpha' S' L' J' \| U^k \| nl^N \alpha SLJ)$, cf. Eq. (3) below, easily follow from Racah's work (*13*), (iii) the $U^k_{a_0\Gamma_0\gamma_0}$'s are unit tensors so that the $D[ka_0]$'s give a true measure of the relative importance of each $U^k_{a_0\Gamma_0\gamma_0}$, and (iv) the $D[ka_0]$ parametrization is particularly appropriate for decomposing $\mathscr{H}_{\text{im}}$ as

$$\mathscr{H}_{\text{im}} = \mathscr{H}_{\text{im}}(G_s) + \mathscr{H}_{\text{im}}(G),$$

where $\mathscr{H}_{\text{im}}(G_s)$ is invariant under a supergroup G_s of G ($G_s \supset G$) and $\mathscr{H}_{\text{im}}(G)$ is G-invariant without being G_s-invariant. Such a decomposition may be very useful in perturbation theory. In addition, G_s may play the role of a group of type G_a. It is easily seen (*5*) that the center-of-gravity rule applies to the entire spectrum of $\mathscr{H}_{\text{im}}(G_s) + \mathscr{H}_{\text{im}}(G)$ as well as to each $\mathscr{H}_{\text{im}}(G_s)$-level perturbed by any component of $\mathscr{H}_{\text{im}}(G)$. It should be remembered that this rule does not hold for the cubical levels perturbed by a tetragonal distortion expressed in the *Ds-Dt* parametrization (*9*).

We are now in a position to set up the matrix of $\mathscr{H}_{\text{im}}$ in an $|nl^N \alpha SLJa\Gamma\gamma\rangle$ basis. The Wigner–Eckart theorem for the chain $O_3^* \supset G^*$ (*4*) leads to

$$\begin{aligned} &\langle nl^N \alpha' S' L' J' a' \Gamma' \gamma' | \mathscr{H}_{\text{im}} | nl^N \alpha SLJa\Gamma\gamma \rangle \\ &= \delta(S'S)\,\delta(\Gamma'\Gamma)\,\delta(\gamma'\gamma)\,(-1)^{S+L+J'} \\ &\cdot ((2J'+1)(2J+1))^{1/2} \sum_{\substack{k=2(2)2l \\ a_0}} \\ &\cdot \begin{Bmatrix} L' & k & L \\ J & S & J' \end{Bmatrix} (l^N \alpha' SL' \| U^k \| l^N \alpha SL) \\ &\cdot f\begin{pmatrix} J' & J & k \\ a'\Gamma & a\Gamma & a_0\Gamma_0 \end{pmatrix} D[ka_0], \end{aligned} \quad (3)$$

where $\{\ \}$ is a 6-j symbol for the group SU_2 (*13–15*), $(\|\ \|)$ a reduced matrix element for the Racah unit tensor U^k (*13*, *15*, *16*), and $f(\ )$ a coupling coefficient for the chain $O_3 \supset G$ (*4*, *5*). Therefore, the matrix of $\mathscr{H}_{\text{im}}$ in an $|nl^N \alpha SLJa\Gamma\gamma\rangle$ basis can be constructed once we have tables and/or programs of 6-j symbols, reduced matrix elements, and f coefficients at our disposal. Extensive tables of 6-j symbols $\begin{Bmatrix} j_1 j_2 j_3 \\ j_4 j_5 j_6 \end{Bmatrix}$ were published by Rotenberg *et al.* (*14*). Further, the reduced matrix elements $(l^N \alpha' SL' \| U^k \| l^N \alpha SL)$ were tabulated by Nielson and Koster for $l = p, d$, and f (*16*). Finally, f coefficients for various chains of groups of interest in ligand field theory are now available (*4–7*). In particular, analytical formulas for the f coefficients relative to the chain $SU_2^* \supset D_\infty^* \supset D_4^* \supset D_2^*$ have been derived (*7*); by using elementary group-theoretical arguments, these formulas may be transcribed to the chains $O_3^* \supset D_{\infty h}^* \supset D_{4h}^* \supset D_{2h}^*$, $O_3^* \supset C_{\infty v}^* \supset C_{4v}^* \supset C_{2v}^*$, and $O_3^* \supset D_{\infty h}^* \supset D_{2d}^* \supset D_2^*$. Since the matrix of $\mathscr{H}_{\text{im}}$ on $\varepsilon(nl^N)$ has been obtained, we may check it owing to the sum rule[6]

$$\begin{aligned} &\text{tr}_{\varepsilon(nl^N)} (U^{k'\dagger}_{a_0'\Gamma_0\gamma_0} U^k_{a_0\Gamma_0\gamma_0}) = \delta(k'k)\delta(a_0'a_0) \\ &\cdot \frac{1}{2k+1} \sum_{\alpha'\alpha SL'L} \\ &\cdot (2S+1)|(l^N \alpha' SL' \| U^k \| l^N \alpha SL)|^2, \end{aligned}$$

where $\text{tr}_{\varepsilon(nl^N)}$ means trace operation on $\varepsilon(nl^N)$.

The matrix of $\mathscr{H}_{\text{fi}} + \mathscr{H}_{\text{im}}$ in an $O_3^* \supset G^*$ symmetry-adapted weak-field basis exhibits a bloc form, each bloc being associated to an IRC of G^*. Each bloc depends on various independent parameters, namely, (i) for $\mathscr{H}_{\text{fi}}$: the interelectron repulsion parameters $F^{(k)}$ of Slater, Condon, and Shortley, the spin–orbit coupling parameter ζ_{nl}, the interconfiguration

[6] This sum rule follows from the orthogonality relation (*4*) $\text{tr}_{\varepsilon(ij)} (T^{k'\dagger}_{a'\Gamma'\gamma'} T^k_{a\Gamma\gamma}) = \delta(k'k)\ \delta(a'a)\ \delta(\Gamma'\Gamma)\ \delta(\gamma'\gamma)\ |(ij \| T^k \| ij)|^2/(2k+1)$, where $\varepsilon(ij)$ is the space spanned by the set $\{|ija\Gamma\gamma\rangle : a\Gamma\gamma$ ranging over $(2j+1)$ labels$\}$. The preceding equation expresses the fact that $T^{k'}_{a'\Gamma'\gamma'}$ and $T^k_{a\Gamma\gamma}$ are mutually orthogonal on $\varepsilon(ij)$.

parameters of Trees, the three-particles parameters of Judd, etc.; and (ii) for $\mathscr{H}_{\mathrm{im}}$: the crystal-field parameters $D[ka_0]$. It is well known that ab initio calculation of these parameters leads generally to levels in very poor agreement with the experimental ones. In fact, these parameters have to be considered as phenomenological parameters to be determined by an iterative fitting procedure (least-square-fitting procedure, for example) from the experimental levels. Such an approach accounts for various effects in a collective manner. In particular, the fact of considering the $D[ka_0]$'s as adjustable parameters globally takes into account: electrostatic contributions, (anti)shielding effects, configuration interaction (*12*), covalency and overlap effects, etc. The whole matrix is diagonalized several times by iteratively varying the empirical parameters to minimize a deviation between computed and experimental levels. One generally chooses to minimize the quadratic mean deviation (or root-mean-square deviation)

$$\sigma = \left(\sum_{i=1}^{E} \omega_i \Delta_i^2/(E-P) \right)^{1/2}$$

or the linear mean deviation

$$f = \sum_{i=1}^{E} \omega_i |\Delta_i|/E.$$

In the latter two relations ω_i is an assigned weight associated to the ith level, Δ_i the difference between the observed and computed values for the ith level, E the number of equations, and P the number of parameters varied. Clearly, σ and f are two acceptable (while inequivalent) measures of the discrepancy between theory and experiment. Which function f or σ is taken to be minimized is often a matter of rapid convergence. In this respect, it is more advantageous to use σ than f.

3. Results

We return now to Eu^{3+} in KLu_3F_{10} and KY_3F_{10}. In that case, $nl^N \equiv 4f^6$. Furthermore, the site symmetry of Eu^{3+} in both KLu_3F_{10} and KY_3F_{10} is C_{4v}, so that $G \equiv C_{4v}$. The branching multiplicity problem between O_3 and C_{4v} is readily overcome by introducing $G_a \equiv C_{\infty v}$. For classification purposes, it will prove useful to take $G_v \equiv C_{2v}$. We are thus led to the chain $O_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$. We shall use $\Gamma(n)$ to denote an IRC of C_{nv}, with $n \equiv \infty$, 4, or 2. The various IRC's of $C_{\infty v}$, C_{4v}, C_{2v} are, respectively, in Mulliken's nomenclature:

$$\begin{aligned}\Gamma(\infty) &= A_1, A_2, E_1, E_2, E_3, \ldots,\\ \Gamma(4) &= A_1, A_2, B_1, B_2, E,\\ \Gamma(2) &= A_1, A_2, B_1, B_2.\end{aligned}$$

It is an experimental fact that for both $KLu_3F_{10}{:}Eu^{3+}$ (*1*) and $KY_3F_{10}{:}Eu^{3+}$ (*2*) the Stark levels arising from the ground term ^7F of Eu^{3+} are well separated from the Stark levels arising from the excited terms ^5D, ^5L, $^5G, \ldots$ of Eu^{3+}. As a consequence, it is a reasonable approximation to restrict $\mathscr{H}_{\mathrm{fi}} + \mathscr{H}_{\mathrm{im}}$ to $\mathscr{H}_{\mathrm{so}} + \mathscr{H}_{\mathrm{im}}$ and to introduce $\mathscr{H}_{\mathrm{so}} + \mathscr{H}_{\mathrm{im}}$ onto the manifold $\varepsilon(^7F)$ generated by the 49 state vectors of the septuplet ^7F. This will allow the mixture through $\mathscr{H}_{\mathrm{im}}$ of state vectors of unequal J issued from ^7F to be determined.

The matrix of $\mathscr{H}_{\mathrm{so}} + \mathscr{H}_{\mathrm{im}}$ in an $O_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ symmetry-adapted weak-field basis is easily obtained by specializing Eqs. (1) and (3) to the case under consideration. We thus get

$$\begin{aligned}&\langle 4f^6\,{}^7FJ'\Gamma(\infty)'\Gamma(4)'\Gamma(2)'|\mathscr{H}_{\mathrm{so}}|\\ &\qquad 4f^6\,{}^7FJ\Gamma(\infty)\Gamma(4)\Gamma(2)\rangle\\ &= \delta(J'J)\delta(\Gamma(\infty)',\Gamma(\infty))\delta(\Gamma(4)',\Gamma(4))\delta(\Gamma(2)',\\ &\quad \cdot\Gamma(2))(-1)^J 2(21)^{1/2}\\ &\quad \cdot\begin{Bmatrix}3&3&1\\3&3&J\end{Bmatrix}(f^6\,{}^7F\|V^{11}\|f^6\,{}^7F)\,\zeta_{4f},\end{aligned} \tag{1'}$$

where V^{11} is a double Racah unit tensor (*13, 15, 16*), and

$$\begin{aligned}&\langle 4f^6\,{}^7FJ'\Gamma(\infty)'\Gamma(4)'\Gamma(2)'|\mathscr{H}_{\mathrm{im}}|\\ &\qquad 4f^6\,{}^7FJ\Gamma(\infty)\Gamma(4)\Gamma(2)\rangle\\ &= \delta(\Gamma(4)',\Gamma(4))\delta(\Gamma(2)',\Gamma(2))\\ &\quad\cdot(-1)^{J'}((2J'+1)(2J+1))^{1/2}\\ &\quad\cdot\sum_{\substack{k=2,4,6\\ a_0=A_1,E_4}}\begin{Bmatrix}3&k&3\\J&3&J'\end{Bmatrix}(f^6\,{}^7F\|U^k\|f^6\,{}^7F)\\ &\quad\cdot f\begin{pmatrix}J'&J&k\\ \Gamma(\infty)'\Gamma(4)&\Gamma(\infty)\Gamma(4)&a_0A_1\end{pmatrix}D[ka_0],\end{aligned} \tag{3'}$$

where the crystal-field parameters $D[ka_0]$, with $a_0 \equiv \Gamma(\infty)$, are adapted to the chain $O_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$. It can be seen from Eq. (2) that these parameters are related to the B^k_q's of (*11*, *12*) via

$$D[2A_1] = -2\left(\frac{7}{15}\right)^{1/2} B^2_0,$$

$$D[4A_1] = \left(\frac{14}{11}\right)^{1/2} B^4_0,$$

$$D[6A_1] = -10\left(\frac{7}{429}\right)^{1/2} B^6_0,$$

$$D[4E_4] = 2\left(\frac{7}{11}\right)^{1/2} B^4_{\pm 4},$$

$$D[6E_4] = -10\left(\frac{14}{429}\right)^{1/2} B^6_{\pm 4}. \qquad (2')$$

The connection between our $D[k\Gamma(\infty)]$'s and the more common $B^q_k \equiv A^q_k \langle r^k \rangle$ parameters (*10*) is obtainable by combining Eq. (2′) with the formulas[7]

$$B^2_0 = 2B^0_2, \qquad B^4_0 = 8B^0_4, \qquad B^6_0 = 16B^0_6,$$

$$B^4_{\pm 4} = 4(2/35)^{1/2} B^4_4, \quad B^6_{\pm 4} = (8/3)(2/7)^{1/2} B^4_6.$$

The 49 × 49 matrix of $\mathscr{V}_{so} + \mathscr{V}_{im}$ in an $O_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ symmetry-adapted weak-field basis may be arranged into the direct sum of six submatrices, each submatrix being associated to an IRC of C_{4v}. In the detail, we have six submatrices of dimensions: 7 × 7 (A_1), 6 × 6 (A_2), 6 × 6 (B_1), 6 × 6 (B_2), 12 × 12 (E), and 12 × 12 (E). By using the abbreviation $|J\Gamma(\infty)\Gamma(4)\Gamma(2)\rangle$ for $|4f^6\ {}^7F\ J\Gamma(\infty)\Gamma(4)\Gamma(2)\rangle$, the state vectors for each of the six matrices turn out to be

7 × 7 (A_1) matrix : $|0A_1A_1A_1\rangle$, $|2A_1A_1A_1\rangle$, $|4A_1A_1A_1\rangle$, $|4E_4A_1A_1\rangle$, $|5E_4A_1A_1\rangle$, $|6A_1A_1A_1\rangle$, $|6E_4A_1A_1\rangle$,

6 × 6 (A_2) matrix : $|1A_2A_2A_2\rangle$, $|3A_2A_2A_2\rangle$, $|4E_4A_2A_2\rangle$, $|5A_2A_2A_2\rangle$, $|5E_4A_2A_2\rangle$, $|6E_4A_2A_2\rangle$,

6 × 6 (B_1) matrix : $|2E_2B_1A_1\rangle$, $|3E_2B_1A_1\rangle$, $|4E_2B_1A_1\rangle$, $|5E_2B_1A_1\rangle$, $|6E_2B_1A_1\rangle$, $|6E_6B_1A_1\rangle$,

6 × 6 (B_2) matrix : $|2E_2B_2A_2\rangle$, $|3E_2B_2A_2\rangle$, $|4E_2B_2A_2\rangle$, $|5E_2B_2A_2\rangle$, $|6E_2B_2A_2\rangle$, $|6E_6B_2A_2\rangle$,

12 × 12 (E) matrix : $|1E_1EB_1\rangle$, $|2E_1EB_1\rangle$, $|3E_1EB_1\rangle$, $|3E_3EB_1\rangle$, $|4E_1EB_1\rangle$, $|4E_3EB_1\rangle$, $|5E_1EB_1\rangle$, $|5E_3EB_1\rangle$, $|5E_5EB_1\rangle$, $|6E_1EB_1\rangle$, $|6E_3EB_1\rangle$, $|6E_5EB_1\rangle$,

12 × 12 (E) matrix : $|1E_1EB_2\rangle$, $|2E_1EB_2\rangle$, $|3E_1EB_2\rangle$, $|3E_3EB_2\rangle$, $|4E_1EB_2\rangle$, $|4E_3EB_2\rangle$, $|5E_1EB_2\rangle$, $|5E_3EB_2\rangle$, $|5E_5EB_2\rangle$, $|6E_1EB_2\rangle$, $|6E_3EB_2\rangle$, $|6E_5EB_2\rangle$.

The two 12 × 12 (E) matrices are responsible for the doublet levels of symmetry E; it is therefore possible to choose the basis of $\varepsilon({}^7F)$ in such a way that the two 12 × 12 (E) matrices be identical.

A general program has been realized in Fortran IV to obtain crystal-field and spin–orbit parameters for reproducing the Stark components of $(4f^6)\ {}^7F$ in tetragonal symmetry (*17*). The program computes the geometrical part of Eqs. (1′) and (3′) once for all: The reduced matrix elements are offered to the machine as input data whereas the 6-j symbols and f coefficients are computed by means of subroutines. The above-mentioned submatrices may then be coded and diagonalized (by use of a subroutine based on the Jacobi rotations method) for various trial values of the $D[ka_0]$ and ζ_{4f} parameters. These parameters are optimized from the experimental ${}^7F$ levels by minimizing a given function of the Δ_i's. The various minimizations are achieved by use of a subroutine based on the Simplex

[7] Formulas connecting B^k_q and $A^q_k \langle r^k \rangle$ parameters appear in (*12*). The reader using Table 6-1 of (*12*) is reminded that $B^4_4 = (8(70)^{1/2}/55)\ A^4_4\ \langle r^4 \rangle$ and $B^6_4 = ((14)^{1/2}/21)\ A^4_6 \langle r^6 \rangle$ should read $B^4_4 = 4(2/35)^{1/2} A^4_4 \langle r^4 \rangle$ and $B^6_4 = (8/3)(2/7)^{1/2} A^4_6 \langle r^6 \rangle$, respectively.

method. By conveniently modifying the coded submatrices, the program also allows the $D[ka_0]$ and ζ_{4f} parameters to be determined without mixing the J's issued from ^7F.

At this point it should be noted that our approach for determining the crystal-field and spin–orbit parameters differs from the one developed by various authors (*18*) and employed by Porcher and Caro (*2*) in the KY_3F_{10}:Eu^{3+} case. As a matter of fact, it is well known that a minimization of the quadratic (or linear) mean deviation by freely varying both the crystal-field and spin–orbit parameters does not correctly reproduce the centers of gravity of the Stark levels arising from the ^7F_J multiplets. This difficulty is generally overcome by adjusting the observed and calculated centers of gravity (*18*), a procedure which amounts, in a last analysis, to associate a (fictitious) spin–orbit parameter to each ^7F_J. In our approach we retain only one (freely varying) spin–orbit parameter and proceed as follows. The Stark levels are computed for a given set of $D[ka_0]$ and ζ_{4f} parameters. We then compare the observed and calculated distances between Stark levels issued from each of the ^7F_J multiplets. The optimization of the parameters is performed by minimizing either the quadratic mean deviation

$$\bar{\sigma} = \sum_J \sum_{i=1}^{E_J} \delta_i(J)^2/E_J$$

or the linear mean deviation

$$\bar{f} = \sum_J \sum_{i=1}^{E_J} |\delta_i(J)|/E_J,$$

where $\delta_i(j)$ is the difference between the ith observed and calculated distance between two Stark levels arising from ^7F_J and E_J the number of experimental Stark levels arising from ^7F_J.

The program ran on the CDC 6600 system of the IN_2P_3 for Eu^{3+} in phosphates, vanadates, and arsenates with tetragonal zircon (D_{2d}) structure (*19*) and for Eu^{3+} in various fluorides with tetragonal (C_{4v}) structure. In particular, we have determined the parameters $D[k\Gamma(\infty)]$ and ζ_{4f} for KLu_3F_{10}:Eu^{3+} from the $E = 16$ experimental ^7F levels of (*1*). The parameters obtained with and without J-mixing from $\bar{\sigma}$- and $\bar{f}$-minimization are reported in Table I.[8] (For the sake of comparison, the crystal-field parameters are listed in the B_q^k notation.) The corresponding values for

$$\sigma = \left(\sum_{i=1}^{E} \Delta_i^2/E \right)^{1/2}$$

and

$$f = \sum_{i=1}^{E} |\Delta_i|/E$$

are included in Table I too. We have reported in Table II, in the cases where J-mixing is taken into account, the calculated (from $\bar{\sigma}$- and $\bar{f}$- minimization) and observed Stark levels expressed with respect to the centers of gravity of the ^7F_J multiplets.

The results of Tables I and II for KLu_3F_{10}:Eu^{3+} compare with the corresponding ones for KY_3F_{10}:Eu^{3+} (*2*).[9] For the purpose of comparison, we have redetermined, in the same vein as the one followed for

TABLE I

CRYSTAL-FIELD AND SPIN–ORBIT PARAMETERS FOR KLu_3F_{10}:Eu^{3+}

	From $\bar{\sigma}$-minimization		From $\bar{f}$-minimization	
	Without J-mixing	With J-mixing	Without J-mixing	With J-mixing
B_0^2	−409	−541	−433	−551
B_0^4	−1551	−1323	−1504	−1326
B_0^6	280	512	305	508
B_4^4	404	357	422	356
B_4^6	−100	−45	−32	−39
ζ_{4f}	1474	1551	1619	1497
σ	16.13	2.44	16.63	2.46
f	11.88	1.68	11.73	1.45

[8] All quantities in this paper have units of cm^{-1}.

[9] Note that, in (*2*) $B_4^6 = 243$ should read $B_4^6 = -243$ (*20*). Additionally, Porcher and Caro have recently obtained (*20*) a best-fit parameters set for KY_3F_{10}:Eu^{3+}, viz., $B_0^2 = -528$, $B_0^4 = -1356$, $B_0^6 = 479$, $B_4^4 = 367$, and $B_4^6 = -41$.

TABLE II

OBSERVED AND CALCULATED STARK SPLITTINGS (FROM THE CENTER OF GRAVITY) OF ^7F_J MULTIPLETS FOR $KLu_3F_{10}:Eu^{3+}$

Labeling of the levels	Observed splittings	Calculated splittings with J-mixing ($\bar{\sigma}$-minimization)	Calculated splittings with J-mixing ($\bar{f}$-minimization)
$^7F_1$ A_2	−86.67	−86.07	−86.67
E	43.33	43.03	43.33
$^7F_2$ A_1	107.00	105.96	107.00
B_1	−8.00	−7.04	−8.00
B_2	119.00	118.76	119.00
E	−109.00	−108.84	−109.00
$^7F_3$ A_2	−63.71	−69.86	−71.43
B_1	89.29	88.14	90.57
B_2	75.29	77.14	78.57
E	−33.71	−30.86	−32.43
E	−16.71	−16.86	−16.43
$^7F_4$ A_1		−157.43	−158.14
A_1	−108.57	−108.43	−108.14
A_2	−127.57	−123.43	−125.14
B_1	140.43	143.57	141.86
B_2		61.57	60.86
E	−54.57	−58.43	−58.14
E	102.43	102.57	103.86

$KLu_3F_{10}:Eu^{3+}$, the crystal-field and spin–orbit parameters for $KY_3F_{10}:Eu^{3+}$ from the $E = 17$ experimental ^7F levels of (*2*). The results appear in Tables III and IV.

A few remarks about the results of Tables I to IV are in order.

Our crystal-field parameters for $KY_3F_{10}:Eu^{3+}$, cf. Table III, agree for the most part with the corresponding ones of Porcher and Caro (*2*).[10]

Both for $KY_3F_{10}:Eu^{3+}$ and $KLu_3F_{10}:Eu^{3+}$, the crystal-field parameters determined without J-mixing change more than admissible when going from $\bar{\sigma}$- to $\bar{f}$-minimization. On the contrary, there is consistency between crystal-field parameters obtained from $\bar{\sigma}$- and $\bar{f}$-minimization in the J-mixing case. In that case, it is only the distribution of the deviation between observed and calculated levels that changes when going from $\bar{\sigma}$- to $\bar{f}$-minimization.

The quadratic (σ) and linear (f) mean deviations, cf. Tables I and III, significantly decrease when J-mixing is taken into account. This clearly shows the importance of J-mixing for the fluorides under consideration [see also (*2*)].

The values for ζ_{4f} obtained in the J-mixing case both for $KLu_3F_{10}:Eu^{3+}$ and

[10] See Footnote 9.

TABLE III

CRYSTAL-FIELD AND SPIN–ORBIT PARAMETERS FOR $KY_3F_{10}:Eu^{3+}$

	From $\bar{\sigma}$-minimization		From $\bar{f}$-minimization	
	Without J-mixing	With J-mixing	Without J-mixing	With J-mixing
B^2_0	−413	−552	−443	−552
B^4_0	−1552	−1332	−1501	−1334
B^6_0	250	512	238	502
B^4_4	414	366	407	368
B^6_4	−102	−41	−78	−41
ζ_{4f}	1432	1574	1503	1636
σ	15.56	2.47	16.18	2.47
f	11.72	2.06	10.91	2.03

TABLE IV

OBSERVED AND CALCULATED STARK SPLITTINGS (FROM THE CENTER OF GRAVITY) OF ^7F_J MULTIPLETS FOR $KY_3F_{10}:Eu^{3+}$

Labeling of the levels	Observed splittings	Calculated splittings with J-mixing ($\bar{\sigma}$-minimization)	Calculated splittings with J-mixing ($\bar{f}$-minimization)
$^7F_1$ A_2	−88.67	−87.87	−88.67
E	44.33	43.93	44.33
$^7F_2$ A_1	107.40	106.08	105.08
B_1	−10.60	−7.92	−7.12
B_2	118.40	121.28	121.88
E	−107.60	−109.72	−109.92
$^7F_3$ A_2	−66.00	−70.14	−67.71
B_1	88.00	88.86	87.29
B_2	78.00	77.86	77.29
E	−29.00	−31.14	−30.71
E	−21.00	−17.14	−16.71
$^7F_4$ A_1	−139.00	−139.88	−139.38
A_1	−87.00	−87.88	−88.38
A_2	−109.00	−104.88	−104.38
B_1	165.00	164.13	163.63
B_2		81.13	79.63
E	−42.00	−38.88	−39.38
E	127.00	123.13	123.63

$KY_3F_{10}:Eu^{3+}$ are higher than the generally accepted value $\zeta_{4f} \sim 1300$ (*21*). The reason for this apparent discrepancy is clear: The interaction via $\mathscr{H}_{so}$ of the ground term ^7F with the excited terms ^5D and ^5G has been neglected. This is an evidence of the necessity of enlarging the $\varepsilon(^7F)$ subspace for producing more realistic spin–orbit parameters (*21*). However, such an enlargement would not lead to crystal-field parameters which would substantially differ from the ones reported in this work [see also (*2*)].

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