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Anisotropic shielding of the crystal field in Tm^{3+}

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Abstract. Whereas a sizeable configuration interaction has been detected earlier between the ground $4f^2$ configuration of $Pr^{3+}$and the excited $4f6p$ configuration, it is shown here that for $Tm^{3+}(4f^{12})$ at the other end of the rare earth series, there is evidence of a $4f^{12}5p^6/4f^{13}5p^5$ interaction.

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1 Introduction

The isotropic effects of configuration interaction on lanthanide $4f^n$ and actinide $5f^n$ energy levels have been considered for a long time. The introduction of corresponding effective free-ion operators [1] in the hamiltonian has largely contributed to improve the theoretical analysis of complex spectra [2–4]. However the anisotropic effects of configuration interaction on the energy level structure of $4f^2$, $4f^3$, and $5f^2$ have but recently been accounted for. It was shown on a few examples that prominent discrepancies which remain after standard crystal field analysis has been performed, can be assigned to configuration interaction (CI) with a nearbye equi-parity excited configuration [5–8].

The crystal field hamiltonian is written as the sum of products of one-electron operators $C_q^k(i)$ times their associated crystal field parameters $B_q^k(l_i,l'_i)$, *i.e.*:

$$H_{cf}=\sum_{kqi}B_q^k(l_i,l'_i)C_q^k(i) \tag{1}$$

where l and l' are the orbital moments of electron i. l,k,l' must satisfy the triangular condition, and $-k\leq q\leq k$. An excited configuration which differs from the ground configuration by more than one orbital has no crystal field interaction with the latter. Besides, large coulombic or exchange interactions within excited configurations generated by a double excitation, give rise to negligible anisotropic interaction inside Nf^n. These are the reasons why we only considered $Nf^n/Nf^{n-1}(N+2)p^1$ and $Nf^n(N+1)p^6/Nf^{n+1}(N+1)p^5$ interactions.

For $4f^2$, $4f^3$, and $5f^2$, the major interacting configurations are $4f6p$, $4f^26p$ and $5f7p$ respectively. Indeed, the crystal field analysis of the ground configuration levels is systematically and significantly improved when the states of the excited configuration are included in the interaction matrix. It was shown for:

- U^{4+} $(5f^2)$ in Cs_2UBr_6 and Cs_2ZrBr_6 [5]. All the levels are strongly displaced by CI.
- $Pr^{3+}(4f^2)$ in $LiYF_4$ and $Pr(La)Cl_3$ [6,7]. The triplet states are slightly affected but more severely the singlet $^1G_4$ and $^1D_2$ levels.
- $Nd^{3+}(4f^3)$. The $^2F_{5/2}$, $^2F_{7/2}$ and mainly the $^2\mathrm{H}(2)_{11/2}$ levels are affected [8].

The problem of anomalous multiplets has received attention for a long time and another solution based on correlation crystal field (CCF) has been proposed [9–12]. It succeeded in curing the anomalous $^2\mathrm{H}(2)_{11/2}$ of Nd^{3+} in a number of compounds [13–16]. A restricted form of the CCF is the δ-function model in which the interaction takes place between spin-paired electrons [17–19]. It was shown recently that this form of CCF eliminates the major "anomalies" of singlet states in Pr^{3+}compounds [20, 21].

By applying full configuration interaction, we are following a different track, yet it is interesting to note between the effects of the two methods, some similarities which have not been fully investigated yet.

After $Nd^{3+}$and Pr^{3+}, we shall show in this work that for trivalent thulium ($4f^{12}$), at the opposite end of the rare earth series, a *similar*, *although not symmetrical* effect occurs and that there exists a sizeable configuration interaction of $4f^{12}5p^6$ with $4f^{13}5p^5$. It unambiguously and significantly improves the crystal field analysis of Tm^{3+}compounds. Contrary to the $6p$ shell which is empty for trivalent rare earths, the $5p$ shell is full. Spatially, it extends beyond the $4f^{12}$shell and shields the crystal field exercised by the environment on the $4f$ electrons. The magnitude of the *spherical* part of this shielding was calculated by Sternheimer [22]. We shall deal here with the full $4f^{12}5p^6/4f^{13}5p^5$ configuration interaction which

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includes an *anisotropic* part of the shielding exercised by the perturbed $5p^6$ shell on the open $4f^{12}$shell. Experimental evidence is brought forward for three Tm^{3+}compounds: LuPO$_4$:Tm^{3+}, YPO$_4$:Tm^{3+}and LaOBr:Tm^{3+}.

2 Results

A crystal field analysis of LuPO$_4$and YPO$_4$:Tm^{3+}was performed earlier by Becker *et al.* [23]. The datasets comprised 33 and 37 energy levels respectively. The datafits resulted in σ values equal to 10.0 and 13.6 cm^{-1} respectively. 11 parameters were utilized. We performed a new crystal field analysis of these two datasets in $4f^{12}5p^6$ on one hand (the full $5p^6$ shell involves but one energy level) and in the larger matrix $4f^{12}5p^6$+$4f^{13}5p^5$ including the ground and the excited configurations on the other hand. Besides, 35 energy levels were measured recently for LaOBr:Tm^{3+} [24] and likewise, a crystal field datafit was performed with and without configuration interaction. The site symmetry of the Tm^{3+}ion is D_{2d} in YPO$_4$ and LuPO$_4$:Tm^{3+}and C_{4v} in LaOBr:Tm^{3+}. In all three cases the irreducible representations of the experimental levels have been determined and the same set of crystal field parameters (cfp): B^2_0, B^4_0, B^4_4, B^6_0 and B^6_4, is relevant. The datafits were performed by computer program $fffn$ described previously [7] which diagonalizes the complete interaction matrix comprising all the states of the $4f^{12}5p^6$ and $4f^{13}5p^5$ configurations (91+84 = 175 states).

The hamiltonian is therefore written as:

$$\begin{aligned} H = &\sum_{kij} R^k(l_i, l_j, l'_i, l'_j) g^k(i,j) \\ &+ \sum_i \zeta(l_i) A_{so} + \sum_{kqi} B^k_q(l_i, l'_i) C^k_q(i) \\ &+ \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) \\ &+ \sum_k M^k m_k + \sum_k P^k p_k \end{aligned} \tag{2}$$

i, j designates the electron (1 or 2), l and l' the orbital moments.

The R^k's ($k = 2, 4, 6$) are two-electron parameters which reduce to:

- the F^k's in $4f^{12}$ if l_i, l_j, l'_i, l'_j refer all four to two f electrons.
- the parameters of the electrostatic and exchange interaction in $4f^{13}/5p^5$ if the couples (l_i, l'_i) on one hand, (l_j, l'_j) on the other hand refer to p and f orbitals respectively.

The g^k's are the corresponding operators. $\zeta(l_i)$ is the coefficient of spin-orbit interaction. α, β and γ are inter-configuration free-ion parameters. G(G$_2$) and G(R$_7$) are Casimir's operators for groups G$_2$ and R$_7$. The M^k ($k = 0, 2, 4$) and the P^k ($k = 2, 4, 6$) are the orbit-orbit and electrostatically correlated spin-orbit interactions respectively. The $B^k_q(l_i, l'_i)$ are the coefficients of the one-electron crystal field interaction. The operators associated with α, β and γ, as well as the M^k's and P^k's are effective operators applied within the ground configuration only.

Table 1. Theoretical value of two-electron integrals involving the $4f^{12}5p^6$ configuration and its interaction with $4f^{13}5p^5$. The R^k's were evaluated from the wavefunctions given by RCN31 [25]. (1), (2), (3) are intra $4f^{12}5p^6$ direct and exchange integrals. (4) and (5) are $4f^{12}5p^6/4f^{13}5p^5$ interaction integrals.

	R^k	cm^{-1}
(1)	$R^2(f,p,f,p)$	55952
(2)	$R^2(f,f,p,p)$	27980
(3)	$R^4(f,f,p,p)$	21737
(4)	$R^2(f,f,f,p)$	−14616
(5)	$R^4(f,f,f,p)$	−6554

An additional parameter is the gap ($F^0(fffp)) - F^0(ffff)$) between the two configurations. It comes from the $k = 0$ terms of the electrostatic and crystal fields interactions. The gap and the spin-orbit coupling constant $\zeta(p)$ are both given by the Hartree-Fock program RCN31 [25] and maintained at their theoretical values (207403 and 32000 cm^{-1} respectively). The five relevant inter-configuration interaction parameters R^k: $R^2(fpfp)$, $R^2(ffpp)$, $R^4(ffpp)$, $R^2(fffp)$ and $R^4(fffp)$, listed in Table 1 are evaluated utilizing the wavefunctions given by RCN31. They are scaled by two variable parameters X^2 and X^4 while the crystal field parameters $B^k_q(fp)$ vary freely. The number of parameters is equal to 14 (13 for LaOBr:Tm^{3+}) without CI and 19 (18 for LaOBr) when CI is added. Table 2 lists the final parameters without and with CI, as well as their standard deviations. The cfp of LuPO$_4$ and YPO$_4$:Tm^{3+}are small and all the levels are uniformly improved. The final rms values are 8.8, 13.2 and 20.8 cm^{-1} without CI, 6.6, 10.9 and 12.5 cm^{-1} with CI. Therefore the improvement amounts to 25%, 17% and 39% for LuPO$_4$:Tm^{3+}, YPO$_4$:Tm^{3+}and LaOBr:Tm^{3+}respectively. We note that the strongest discrepancy occurs for LaOBr:Tm^{3+}where $B^2_0(ff)$ is strong (*ca.* −1800 cm^{-1}). The most discrepant levels are $^3F_2$,$^3F_3$. CI removes completely the discrepancy.

From Table 2 it can be seen that:

1. the $cfp(fp)$ display an opposite sign to those of the $cfp(ff)$. For LuPO$_4$:Tm^{3+}and YPO$_4$:Tm^{3+}, they are about ten times larger. For LaOBr:Tm^{3+}, $B^2_0(fp)$ is about twice larger than $B^2_0(ff)$, the fourth order (fp) parameters are about 15 times larger than the (ff) ones. For YPO$_4$:Tm^{3+}, it is visible from the standard deviations that the signs of $B^4_0(ff)$ and (fp) are not significant. It is however noteworthy that both fitted values are small.

2. For LaOBr:Tm^{3+}, the fit in the large matrix $4f^{12}5p^6/4f^{13}5p^5$ yields a ratio $B^4_0/B^4_4(ff) \approx B^4_0/B^4_4(fp) \approx \mp 0.8$ which is close to the point charge ratio ($\mp$ 1.0) whereas $B^4_0/B^4_4(ff)$ fitted in the f^{12} matrix is equal to $\mp$ 0.43.

Table 2. Free ion and crystal field parameters (in cm^{-1}) of Tm^{3+}in $LuPO_4$, YPO_4 and LaOBr, without and with configuration interaction respectively. n and n_p are the number of levels and of parameters respectively. γ is equal to 2200, $\zeta(p)$ to 32,000 and the gap $F^0(fffp)) - F^0(ffff)$ to 207403 cm^{-1}. $M^2/M^0 = 0.56$, $M^4/M^0 = 0.38$; $P^4/P^2 = 0.75$, $P^6/P^2 = 0.5$ [28]. In the last stages of the refinement, $B^6_0(ff)$ and $B^6_4(ff)$ were held constant. Standard deviations between parentheses.

	$LuPO_4$ $4f^{12}5p^6$	$LuPO_4$ $4f^{12}5p^6$ $+ 4f^{13}5p^5$	YPO_4 $4f^{12}5p^6$	YPO_4 $4f^{12}5p^6$ $+ 4f^{13}5p^5$	LaOBr $4f^{12}5p^6$	LaOBr $4f^{12}5p^6$ $+ 4f^{13}5p^5$
$F_0(ffff)$	21448(0)	21513(0)	21482(0)	21562(0)	21807(0)	22027(0)
$F^2(ffff)$	101273(0)	101301(0)	101144(0)	101203(0)	99964(0)	100056(0)
$F^4(ffff)$	70765(0)	70895(0)	70763(0)	70905(0)	70026(0)	70112(0)
$F^6(ffff)$	50126(0)	50463(0)	50077(0)	50499(0)	51170(1)	52497(0)
α	17.6(1.8)	16.25(1.1)	16.2(2.1)	14.8(1.8)	17.1(4.9)	13.6(3.6)
β	−642(2)	−651(1)	−599(2)	−595(2)	−844(5)	−833(3)
M_0	4.6(5.6)	4.7(3.7)	4.6(8.3)	4.8(6.0)	3.3(23.1)	3.8(10.0)
P_2	657(8)	674(4)	609(11)	636(8)	(600)	(600)
$\zeta(f)$	2629.1(0)	2629.5(0)	2629.3(0)	2629.6(0)	2628.4(0)	2628.6(0)
$B^2_0(ff)$	221(8)	**255**(8)	294(5)	**378**(7)	−1830(1)	**−1764**(2)
$B^4_0(ff)$	130(32)	**35**(71)	108(32)	**−5**(132)	−449(9)	**−702**(5)
$B^4_4(ff)$	−669(2)	**−656**(2)	−613(3)	**−588**(3)	1044(3)	**882**(3)
$B^6_0(ff)$	−718(3)	−710(2)	−693(4)	−673(3)	206(25)	(−4)
$B^6_4(ff)$	41(50)	18(87)	0	0	−60(64)	(4)
X^2		0.74		0.72		0.70
X^4		1.045		1.249		0.77
$B^2_0(fp)$		**−2838**(18)		**−2561**(23)		**5956**(9)
$B^4_0(fp)$		**−352**(105)		**−90**(134)		**10955**(9)
$B^4_4(fp)$		**5741**(15)		**7680**(12)		**−12423**(12)
δ [a]	6.7	4.3	10.4	7.6	16.5	8.7
σ [b]	8.8	6.6	13.2	10.9	20.8	12.5
n	33	33	37	37	35	35
n_p	14	19	14	19	13	18

[a] $(\sum_{i=1,n}(Ei_{exp} - Ei_{calc})^2/n)^{1/2}$

[b] $(\sum_{i=1,n}(Ei_{exp} - Ei_{calc})^2/(n - n_p))^{1/2}$

Point 1 hints at an interaction between a $4f$ electron and a hole in the $5p^6$ shell, hence an opposite sign for the two sets of cfp's: ff and fp. For the $Pr^{3+}$and U^{4+} compounds which were examined before, the contrary occurs: the corresponding (ff) and (fp) cfp's have the same sign and the major interaction occurs between a $4f$ (or $5f$) and a $6p$ (or $7p$) electron.

3 Conclusion

Following our previous investigations on the beginning of the rare earth series (Pr^{3+}, Nd^{3+}), we were expecting an anisotropic $4f^{12}/4f^{11}6p^1$ interaction in Tm^{3+}.

However, in the three cases examined here it did not improve the crystal field analysis whereas a $4f^{12}5p^6/4f^{13}5p^5$ interaction did improve it.

The valence states of the lanthanides in solid compounds are narrowly connected to the changes in the energies of the neutral atom configurations when the atoms condense into the solid state. As a consequence, the valency changes along the rare earth series are rather chaotic [26]. However, it is well known that $Pr^{3+}(4f^2)$ tends very easily towards Pr^{4+} $(4f^1)$ by losing an electron. On the other hand, $Tm^{3+}(4f^{12})$ is able to gain an extra $4f$ electron and become Tm^{2+} $(4f^{13})$: $TmCl_2$ exists and has been synthetized [27]. There seems to exist a relationship between the electron affinities of $Pr^{3+}$and $Tm^{3+}$and the mechanism we are describing here.

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