$4f^2/4f6p$ configuration interaction in LiYF$_4$:Pr^{3+}

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In two other papers [M. D. Faucher, O. K. Moune, D. Garcia, and P. Tanner, Phys. Rev. B **53**, 9501 (1996); M. D. Faucher and O. K. Moune, J. Alloys Compounds (to be published)], it was shown that the introduction of the $5f^n/5f^{n-1}7p$ (or $4f^n/4f^{n-1}6p$) configuration interaction eliminated large discrepancies in the crystal-field analysis of (i) U^{4+} ($5f^2$) in Cs$_2$UBr$_6$ and Cs$_2$ZrBr$_6$, for which the least root-mean-square deviation between experimental and calculated energy levels falls down from 241 to 56 cm^{-1}, and (ii) Nd^{3+} in Nd$_2$O$_2$S, for which the discrepancy of the ^{2}H(2)$_{11/2}$ level is eliminated by the configuration interaction with the excited $4f^26p$ configuration. The demonstration is now extended to Pr^{3+} and seems to be of general application. For LiYF$_4$:Pr^{3+} the mean deviation is divided by more than 2 by utilizing an interaction matrix including $4f6p$ in addition to the ground configuration $4f^2$. [S1050-2947(97)00406-X]

I. INTRODUCTION

The interpretation of complex spectra is the outcome of contributions spanning over more than 30 years [1–3]. The electronic structure of the ground $4f^n$ configuration of trivalent lanthanides and to a lesser extent actinides $5f^n$ is, on the whole, well simulated by a phenomenological rare-earth Hamiltonian consisting of effective operators with their associated parameters. The effectiveness of the Hamiltonian is estimated via the best match between experimental and calculated energy levels that can be obtained by varying the parameters. The check is restricted to the levels of the $4f^n$ configurations that can be experimentally determined, i.e., in the 0–40 000 cm^{-1} spectral range, at most.

The general adequacy of the Hamiltonian is well recognized. However, in the rare-earth and actinide series, a number of discrepancies downgrade the quality of the crystal-field analysis.

The urge for a more satisfying theoretical representation of crystal-field effects provoked in the 1970s the development of correlation (two-particle) crystal field [4,5], the practical application of which was hampered by the very large number of operators and associated parameters. Recent work [6,7] has shown that the utilization of a small number of correlation crystal-field operators generated by Judd's δ-function interaction [8] leads to promising results.

For a long time it has been recognized that interactions limited to the ground f^n configuration rendered an imperfect account of experimental results. Rajnak and Wybourne [9] worked out corrections to the free-ion electrostatic interaction with excited configurations. They mentioned, however, that ''in the case of low-energy perturbing configurations, it will still be necessary to take into account interactions explicitly.'' The closest excited configuration $4f^{n-1}5d$ seemed to be the best candidate.

However, in two recent papers [10,11], we have shown that the introduction of the $4f^n/4f^{n-1}6p$ (or $5f^n/5f^{n-1}7p$) configuration interaction alone resolved several flagrant discrepancies.

(i) The crystal-field analysis of U^{4+} ($5f^2$) in Cs$_2$UBr$_6$ and Cs$_2$ZrBr$_6$ (centrosymmetric sites forbidding $5f^2/5f6d$ interaction) becomes quite satisfactory if one includes in the interaction matrix the $5f7p$ excited configuration in addition to the ground configuration. The root-mean-square deviation of the experimental-calculated fit falls from 241 down to 56 cm^{-1}. The best fit occurs when the levels of the excited configuration lie between 50 000 and 73 000 cm^{-1} above the ground level [10].

(ii) The attempt to extend the demonstration to Nd^{3+} even in noncentrosymmetric sites was successful and the discrepancy that is always stated in the ^{2}H(2)$_{11/2}$ group at 15 000 cm^{-1} is completely eliminated by the configuration interaction with the excited $4f^26p$ configuration located at its theoretically calculated energy value [11].

What is proposed now is an extension of the proposition to Pr^{3+} and a tentative generalization.

II. EXPERIMENTAL DATA

The electronic spectra of praseodymium compounds are obscured more often than those of other lanthanides by spurious lines that are assigned either to impurities or to vibronic components. The crystal-field analysis is usually less satisfactory than analyses of other rare-earth compounds and the discrepancies affect all but the lowest electronic levels. It has been difficult to assert whether this arises from the quality of the experimental spectra or from some intrinsic theoretical reason.

For the present study, LiYF$_4$:Pr^{3+} is chosen as a test compound. Three spectroscopic investigations have been carried out on single crystals, leading to the determination of an extended energy-level scheme [12–14]. In Ref. [13], Esterovitz *et al.* reported 46 energy levels and their symmetry labels.

Esterovitz *et al.* [13] stated some large discrepancies in the crystal-field analysis of their data in $4f^2$. Some calculated levels were inverted with respect to experimental ones

in $^3F_2$, $^3F_4$, $^1G_4$, and $^1D_2$. Therefore, they withdrew four $^1G_4$ levels and one $^1D_2$ level from their dataset (the mean deviation of these five levels being 44 cm^{-1}) and obtained a least-rms value of 15.8 cm^{-1} for the remaining set of 41 experimental and calculated energy levels.

Malinowski *et al.* [14] measured by one-photon and two-photon (excited-state absorption) experiments the high-lying $^3P_1$ and some $^1I_6$ levels that were missing in the previous data. They also checked the previously examined $^1D_2$ and $^1G_4$ zones.

As a result, a total of 11 energy levels are reported in Refs. [13,14] for $^1G_4$, whereas only 7 are allowed. Therefore, we chose those lines that were observed in *both* series of experiments. The energy level at 10 112 cm^{-1} is reported in both papers, but as $\Gamma_{3,4}$ in one paper and as Γ_1 in the other. It was therefore cast aside and we were left with 9699 (Γ_1), 9832 ($\Gamma_{3,4}$), and 10 313 cm^{-1} (Γ_1). This last level is -156 cm^{-1} from its theoretical value in the normal calculation.

The two $^3P_1$ levels and two $^1I_6$ components measured by Malinowski *et al.* were included as well. The total number of observed energy levels introduced in the fit is therefore equal to 46 out of a total of 70 for the S_4 symmetry in $4f^2$.

III. THE $4f^2/4f6p$ CONFIGURATION INTERACTION IN LiYF$_4$:Pr^{3+}

The crystal-field analysis was performed by the means of program $fffn$, which works on the basis of $SLJM_J$ states and solves the complete $4f^2/4f6p/[4f5d]$ interaction matrix [15]. The terms of the excited $4f6p$ configuration are ^3D, ^3F, ^3G, ^1D, ^1F, and ^1G and the number of states equals 84. Added to the 91 states of the ground configuration makes a total of 175 states.

The system is defined by the following parameters. (i) Thirteen parameters act within the ground $4f^2$ configuration: the Slater parameters F^2, F^4, and F^6; α, β, and γ (γ is held constant); M_k and P_k ($M_2/M_0=0.56$, $M_4/M_0=0.38$, $P_4/P_2=0.75$, and $p_6/P_2=0.5$ [16]); the spin-orbit coupling constant $\zeta(f)$; the S_4 site symmetry of Pr^{3+} gives rise to six crystal-field parameters B_0^2, B_0^4, B_4^4, B_0^6, B_4^6, and S_4^6. Since the site symmetry is close to D_{2d}, S_4^6 is tiny and is neglected. (ii) Six parameters act between the $4f^2$ and $4f6p$ configuration: the intraconfigurational free-ion parameters $R^2(f,p,f,p)$, $R^2(f,f,p,p)$, $R^4(f,f,p,p)$, $R^2(f,f,f,p)$, and $R^4(f,f,f,p)$, which are evaluated by numerical integrations and only the multipliers of the R^k's are varied (two values): the Coulombic and exchange integrals $R^2(f,p,f,p)$, $R^2(f,f,p,p)$, and $R^4(f,f,p,p)$ act within the $4f6p$ configuration, while $R^2(f,f,f,p)$ and $R^4(f,f,f,p)$ intervene between $4f^2$ and $4f6p$; $\zeta(p)$, a theoretical value of which is given by a Hartree-Fock calculation [17] and held constant; the distance between the two configurations' barycenters $F^0(fp)-F^0(ff)$ is held constant and equal to 124 343 cm^{-1} (the Hartree-Fock value); the crystal-field parameters $B_0^2(fp)$, $B_0^4(fp)$, and $B_4^4(fp)$; $B_0^2(pp)$ is not considered in the variable set. Its influence is very small: a 5000 cm^{-1} variation of $B_0^2(pp)$ causes a 0.01 cm^{-1} variation of the mean deviation. The total number of variable parameters is therefore equal to 18, 5 more than in the $4f^2$ calculation.

TABLE I. Slater parameters, interconfiguration-interaction integrals, spin-orbit coupling constants, and crystal-field parameters: (1) theoretical Hartree-Fock free-ion values, (2) $4f^2$ ground configuration of Pr^{3+} only, and (3) the full configuration interaction $4f^2/4f6p$ with a gap of 124 000 cm^{-1}. Fixed values are in square brackets.

Parameters (cm^{-1})	(1)	(2)	(3)
$F^2(ff)$	79326	68871	69159
$F^4(ff)$	52199	50243	50573
$F^6(ff)$	38454	32910	33420
α		21.37	21.70
β		-660	-672
γ		[1370]	[1370]
M_0		0.36	1.39
P_2		268	215
ζ	799	745.2	748.4
$B_0^2(ff)$		407	314
$B_0^4(ff)$		-864	-272
$B_4^4(ff)$		1223	790
$B_0^6(ff)$		-150	-102
$B_4^6(ff)$		974	1596
$R^2(f,p,f,p)$	11576		16137
$R^2(f,f,p,p)$	3249		4529
$R^4(f,f,p,p)$	2973		6576
$R^2(f,f,f,p)$	-4886		-6811
$R^4(f,f,f,p)$	-2968		-6565
$\zeta(p)$	3800		[3800]
$B_0^2(fp)$			2172
$B_0^4(fp)$			-23425
$B_4^4(fp)$			15493
$F^0(fp)-F^0(ff)$	124000		[124000]
experimental levels		46	46
parameters		13	19
mean deviation [a]		33.0	14.8
rms [b]		39.0	19.3

[a]$[\Sigma_{i=1,n}(Ei_{\text{expt}}-Ei_{\text{calc}})^2/n]^{1/2}$.
[b]$[\Sigma_{i=1,n}(Ei_{\text{expt}}-Ei_{\text{calc}})^2/(n-n_p)]^{1/2}$.

IV. RESULTS AND DISCUSSION

Table I lists the fitted parameters and the deviations in two calculations: $4f^2$ and $4f^2/4f6p$. The mean deviations are equal to 33.0 and 14.8 cm^{-1}, respectively. The deviation in $4f^2/4f6p$ is divided by more than 2 with respect to the calculation in $4f^2$. It is a significant decrease. Let us compare it with the influence of the M_k and P_k parameters. Without these two sets of parameters the smallest deviation increases to 20.9 cm^{-1} (instead of 14.8 cm^{-1}). The improvement due to M_k and P_k is less than the gain obtained by the configuration interaction with $4f6p$.

The multipliers of the interconfiguration integrals are 1.4 and 2.2 times the theoretical values for $k=2$ and 4, respectively, and the crystal-field parameters $B_q^4(fp)$ are about 15 times larger than the $B_q^4(ff)$ parameters, which is an order of magnitude larger than might be expected from the ratio of the radial integrals $r^4(fp)/r^4(ff)=(5.7/3.5)$.

It is worth mentioning that slightly better fits can be obtained by lowering the gap from 124 000 (the theoretical

TABLE II. Experimental-calculated deviations in the $4f^2$ and $4f^2/4f6p$ calculations for LiYF$_4$:Pr^{3+}. All the levels are barycentered. Values are in cm^{-1}.

Level	Interaction matrix	
	$4f^2$	$4f^2/4f6p$
$^3H_4$	17.3	9.0
$^3H_5$	10.2	11.5
$^3H_6$	35.4	19.1
$^3F_2$	18.0	9.0
$^3F_3$	18.9	9.3
$^3F_4$	16.5	8.9
$^1G_4$	66.4	21.4
$^1D_2$	47.8	13.1
$^3P_1$	27.8	31.6

Hartree-Fock value) down to 33 000 cm^{-1}. When the gap is smaller, the multipliers of the interconfiguration integrals come closer to 1 (1.05 and 1.64, instead of 1.39 and 2.21). In addition, the fp crystal-field parameters decrease by a factor 4. They are still 3 times larger than what would be expected from the ratio of radial integrals $r^4(fp)/r^4(ff)$. The fact that the fitted R^k multipliers are larger than 1 is surprising since the Slater parameters are lower than their theoretical values in the $4f^n$ configurations.

Utilizing the theoretical values of the R^k with the theoretical gap yields a lowest mean deviation equal to 18.6 cm^{-1}. There are 16 parameters left, which gives a rms equal to 22.6 cm^{-1}. For Nd$_2$O$_2$S [11], the best lowest square deviation was obtained for a gap equal to its theoretical value.

The barycentered deviations in the eight levels $^3H_4$, $^3H_5$, $^3H_6$, $^3F_2$, $^3F_3$, $^3F_4$, $^1G_4$, and $^1D_2$ are indicated in Table II. All the deviations decrease in the $4f^2/4f6p$ calculation and the largest discrepancies are the best corrected ones. The 84 levels of the $4f6p$ configuration are grouped between 130 000 and 143 000 cm^{-1}. The total spreading of the excited configuration is about 13 000 cm^{-1}. The lowest levels of $4f6p$ are $^3G_3$ and $^3F_3$, the highest are $^1G_4$ and $^1D_2$.

Table III reports the values of experimental and calculated energy levels with their irreducible representations in both calculations. The levels Γ_2 and $\Gamma_{3,4}$ at 5201 and 5221 cm^{-1} and Γ_1 and Γ_2 at 16 740 and 16 810 cm^{-1}, which are inverted in the $4f^2$ calculation, are in the correct order in the complete calculation. Only two close levels remain inverted: Γ_2 and $\Gamma_{3,4}$ at 6686 and 6671 cm^{-1}.

The Γ_1 level at 10 313 cm^{-1}, initially at -156 cm^{-1} from the calculated value in the $4f^2$ calculation, is much closer (-47 cm^{-1}) in the $4f^2/4f6p$ calculation. No correspondence could be found in the calculation for two $^1I_6$ levels measured by Malinowski et al.: a $\Gamma_{3,4}$ level at 21 082 cm^{-1} corresponding to a rather weak yet distinct feature in the excited-state absorption spectrum and a Γ_1 level at 21 772 cm^{-1} measured by one photon absorption. However, a $\Gamma_{3,4}$ component is found at 21 786 cm^{-1}.

In the σ-polarized excitation spectrum of the blue emission $^3P_0 \rightarrow {}^3H_4$, the most prominent feature is a strong structured peak, from which Malinowski et al. [14] deduced, in addition to the $\Gamma_{3,4}$ level at 21 477 cm^{-1}, another line of

TABLE III. Crystal-field analysis of Pr^{3+} in LiYF$_4$. Listed are the symmetry labels, the experimental energies, the calculated levels in $4f^2/4f6p$, the difference of experimental minus calculated levels, the calculated levels in $4f^2$, and the difference of experimental minus calculated levels (energies in cm^{-1}).

No.	Level	Label	Expt.	Calc. $4f^2/4f6p$	Expt. − Calc.	Calc. $4f^2$	Expt. − Calc
1	$^3H_4$	Γ_2	0	0	0	0	0
2		$\Gamma_{3,4}$	79	78	1	85	−6
3		Γ_1	220	233	−13	215	5
4		Γ_1		235		214	
5		Γ_1		480		459	
6		$\Gamma_{3,4}$	496	489	7	462	34
7		Γ_2		509		475	
8	$^3H_5$	Γ_1	2253	2251	2	2261	−8
9		$\Gamma_{3,4}$	2272	2273	−1	2269	3
10		Γ_2	2280	2278	2	2275	5
11		Γ_1	2297	2304	−7	2307	−10
12		$\Gamma_{3,4}$	2341	2334	7	2322	19
13		Γ_2	2549	2574	−25	2551	−2
14		Γ_1		2590		2564	
15		$\Gamma_{3,4}$		2604		2582	
16	$^3H_6$	Γ_2	4314	4338	−24	4345	−31
17		Γ_1		4391		4425	
18		$\Gamma_{3,4}$	4394	4412	−18	4426	−32
19		$\Gamma_{3,4}$	4454	4458	−4	4487	−33
20		Γ_2		4482		4471	
21		Γ_1	4486	4502	−16	4516	−30
22		Γ_2	4557	4537	20	4537	20
23		Γ_1		4879		4857	
24		$\Gamma_{3,4}$	4907	4887	20	4867	40
25		Γ_2	4945	4922	23	4891	54
26	$^3F_2$	Γ_2	5201	5197	4	5224	−23
27		$\Gamma_{3,4}$	5221	5207	14	5212	9
28		Γ_1		5234		5181	
29		Γ_2	5342	5350	−8	5315	27
30	$^3F_3$	$\Gamma_{3,4}$	6481	6486	−5	6511	−30
31		Γ_2	6521	6526	−5	6547	−26
32		Γ_1	6586	6593	−7	6566	20
33		Γ_2	6686	6664	22	6682	4
34		$\Gamma_{3,4}$	6671	6684	−13	6667	4
35	$^3F_4$	Γ_1	6920	6905	15	6925	−5
36		$\Gamma_{3,4}$	6942	6944	−2	6922	20
37		Γ_2	6983	6983	0	6957	26
38		Γ_1	7105	7096	9	7122	−17
39		Γ_2	7116	7131	−15	7137	−21
40		$\Gamma_{3,4}$	7142	7144	−2	7144	−2
41		Γ_1	7220	7220	0	7234	−14
42	$^1G_4$	Γ_1	9699	9677	22	9684	15
43		$\Gamma_{3,4}$	9832	9827	5	9763	69
44		Γ_2	9930[a]	9933	−3	9875	55
45		Γ_1	10217[a]	10014		10072	
46		Γ_2	10011[a]	10018	−7	10020	−9
47		$\Gamma_{3,4}$	10112[a]	10091	21	10118	−6
48		Γ_1	10313	10363	−50	10463	−150
49	$^1D_2$	Γ_2	16740	16745	−5	16822	−82
50		Γ_1	16810	16788	22	16821	−11

TABLE III. (*Continued*).

51		$\Gamma_{3,4}$	17083	17098	-15	17050	33
52		Γ_2	17406	17378	28	17356	50
53	$^3P_0$	Γ_1	20860	20868	-8	20854	6
54	$^1I_6$	Γ_2	21241	21244	-3	21245	-4
55		Γ_2	21241	21248	-7	21247	-6
56	$^3P_1$	$\Gamma_{3,4}$	21416	21395	21	21402	14
57	$^1I_6$	Γ_2		21452		21487	
58		$\Gamma_{3,4}$	21477	21467	10	21463	14
59		Γ_1		21494		21471	
60	$^3P_1$	Γ_1	21494	21535	-41	21539	-45
61	$^1I_6$	$\Gamma_{3,4}$		21787		21683	
62		Γ_1	21772^a	21942		21804	
63		Γ_2		22200		22092	
64		$\Gamma_{3,4}$		22228		22085	
65		Γ_1		22274		22076	
66	$^3P_2$	Γ_1	22498	22499	-1	22537	-39
67		Γ_2		22631		22677	
68		$\Gamma_{3,4}$	22645	22647	-2	22640	5
69		Γ_2		22774		22768	
70		Γ_1		46258		46927	

^{a}Not introduced into the fit.

undetermined symmetry at about 21 470 cm^{-1}. This is interesting because the ''complete'' calculation displays, close to the $\Gamma_{3,4}$ level at 21 466 cm^{-1}, two other levels at 21 460 (Γ_2) and 21 487 (Γ_1) cm^{-1}.

One point needs to be discussed: it is the large change in the $B_q^k(ff)$ parameters when the excited configuration is added. The $k=4$ crystal-field parameters shrink, especially B_0^4, which is divided by more than 3. On the contrary, B_6^6 is multiplied by 2. Table IV compares the B_4^4/B_0^4 and B_4^6/B_0^6 ratios given by the two calculations with point charge values. The value of B_4^4/B_0^4 in $4f^2$ seems physically more realistic. This problem did not arise for U^{4+} [10] since the B_4^4/B_0^4 and B_4^6/B_0^6 ratios were imposed by the cubic symmetry. There exists a strong correlation between the $B_q^k(ff)$ and $B_q^k(fp)$ parameters. Clearly, an additional relation is necessary to stabilize the whole parameter set. For instance, if we assign to the B_4^4/B_0^4 ratio its value in $4f^2$ (-1.42), then the mean deviation increases slightly from its lowest value 14.8 up to 15.9 cm^{-1}. It would probably be advisable to transform the

TABLE IV. Crystal-field parameters of LiYF$_4$:Pr^{3+}. Values of the B_4^4/B_0^4 and B_4^6/B_0^6 ratios calculated in $4f^2$ and $4f^2/4f6p$, compared with point charge values

Ratio	Point charge value	$4f^2$ (ff)	$4f^2/4f6p$ (ff)	(fp)
B_4^4/B_0^4	-1.33	-1.42	-2.90	-0.66
B_4^6/B_0^6	-10.05	-6.49	-15.65	

whole set of crystal-field parameters into a new orthogonal set as stressed by Newman [18] or Judd and Crosswhite [19] in such a way that none of the parameters in the set be either purely ff or purely fp.

The effect of the excited $4f5d$ configuration on the calculation was also investigated. When it is added to $4f^2$ alone, the lowest mean deviation is 31.8 cm^{-1}, which is slightly better than for $4f^2$ alone. When the three configurations $4f^2$, $4f5d$, and $4f6p$ are involved, the lowest mean deviation is 15.7 cm^{-1}, which is slightly worse than for the $4f^2/4f6p$ calculation. The $4f5d$ configuration has but a small effect. This can perhaps be assigned to the fact that there is no electrostatic interaction between $4f^2$ and $4f5d$, but only an odd crystal-field interaction due to parameters B_2^3 and B_2^5. When a new configuration is added, a number of unknown R^k values have to be introduced, which explains why the $4f^2/4f6p/4f5d$ calculation is worse than that of $4f^2/4f6p$.

V. CONCLUSION

We endeavored to show that the utilization of a larger interaction matrix $4f^2/4f6p$ is an efficient way to improve the crystal-field analysis in LiYF$_4$:Pr^{3+}. After U^{4+} and Nd^{3+}, the demonstration therefore has been extended to Pr^{3+}. The root-mean-square deviation of the energy level fit in $4f^2/4f6p$ is divided by more than 2 with respect to the calculation in $4f^2$. With this additional example, we suggest a generalization, following which the most prominent process rendering ''normal'' the ''abnormal'' levels of the $4f^n$ (or $5f^n$) configurations is the $4f^n/4f^{n-1}6p$ (or $5f^n/5f^{n-1}7p$) configuration interaction.

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