Journal of Alloys and Compounds 323–324 (2001) 783–787

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Optical spectrum, crystal field analysis of Pr^{3+} in YPO_4

O.K. Moune[a,*], M.D. Faucher[a], N. Edelstein[b]

[a]Laboratoire « Structures, Propriétes et Modélisation des Solides », UMR 8580 du CNRS, Ecole Centrale Paris, 92295 Châtenay-Malabry Cedex, France

[b]Lawrence Berkeley Laboratory, Chemical Sciences Division, University of California, Berkeley, CA 94720, USA

Abstract

An optical investigation of Pr^{3+} (1 at.%) in YPO_4 single crystal is reported. The aim is an improvement of the crystal field analysis by the means of direct configuration interaction between the ground $4f^2$ configuration and the nearest excited configurations. The crystal field is analyzed in the theoretical D_{2d} site symmetry with and without configuration interaction. The results for the associations $4f^2$, $4f^2+4f5d$, $4f^2+4f6p$ and $4f^2+4f5d+4f6p$ are compared. The $4f^2+4f5d+4f6p$ configuration interaction gives the smallest r.m.s. deviation between experimental and calculated energy levels, lowering it from 23.9 cm^{-1} on the basis of the 91 $4f^2$ levels only, down to 5.8 cm^{-1}, when calculated on the basis of the 315 $4f^2+4f5d+4f6p$ levels. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: YPO_4:Pr^{3+}; Crystal field analysis; Configuration interaction; Optical spectrocopy

1. Introduction

The present work is focussed upon a theoretical method aiming to improve the crystal field analysis in rare earth compounds. It relies on a new spectroscopic investigation of YPO_4: Pr^{3+}, a compound which was examined earlier by one of us [1].

In the standard method for determining the electronic structure of $4f^n$ configurations, the free-ion effects are taken into account by one-, two- and three-electron operators, whereas the effect of the environment is exclusively described by a one-electron development. It is therefore not surprising that the agreement between calculated and experimental energy levels is sometimes deficient. A model based on the simulation of correlation effects by two-electron operators acting on the *f* shell has been developed to supplement the existing theory [2,3].

Some time ago, we showed that the performance of the standard model is improved if the interaction with the nearest excited configurations is explicitely taken into account [4–6]. Most demonstrations were made on trivalent praseodymium, and the excited configuration added in priority was $4f^{n-1}6p$. In the present work, it is firstly confirmed that: (a) as stated previously, the crystal field analysis is improved by the means of direct configuration interaction between the ground $4f^2$ and $4f6p$; and (b) in the particular case of YPO_4: Pr^{3+}, it is shown that a less efficient $4f^2/4f5d$ interaction still improves the agreement and lowers the mean deviation between experimental and calculated levels.

The choice of trivalent praseodymium for testing alternative procedures is dictated by two reasons: (a) the crystal field analysis in $4f^2$ often results in large experimental/calculated discrepancies (of the order of 15–30 cm^{-1}, depending on the crystal field strength) when correct assignments are made, clearly indicating that something is missing; and (b) the simple electronic structure of Pr^{3+} facilitates the inclusion of excited configurations into the basis set for the calculation of the electronic structures. Further, if a statement is verified for all Pr^{3+} compounds, it should be possible to generalize it for the other lanthanide ions.

One essential problem encountered in the analysis of configuration interaction-assisted crystal field concerns the reliability of the experimental datasets under examination. The experimental energy levels belong exclusively to the $4f^2$ set and the parameters acting between the ground and the excited configurations are fitted indirectly via their action on the $4f^2$ levels. Configuration interaction can therefore be analyzed correctly only if a large number of levels is accurately measured and assigned. For Pr^{3+} for instance, two mis-assignments in sensitive multiplets such as $^1D_2$ or $^1G_4$ can alter the performances of the configuration interaction-assisted crystal field analysis. Correct

---

*Corresponding author.

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01093-3

assignments are easier in case of single crystals of a material with a simple crystallographic structure. In the former study on this compound [1], 35 energy levels were measured. This number did not seem sufficient for a crystal field analysis in which additional parameters had to be introduced. Further experiments were therefore undertaken: optical absorption, excitation, and emission by selective excitation into $^1D_2$, $^3P_0$ and $^3P_1$, and at different temperatures between 20 K and 295 K. As a result, 50 levels among a total of 70 were measured and unambiguously assigned. Three more were detected but classified as uncertain.

2. Optical investigation and energy levels determination

The $4f^2$ configuration of the Pr^{3+} ion gives rise to thirteen $^{2S+1}L_J$ levels: i.e. $^3H_{4,5,6}$, $^3F_{2,3,4,}$, $^1G_4$, $^1D_2$, $^3P_{0,1,2}$, $^1I_6$ and $^1S_0$. In the D_{2d} symmetry of the rare earth site in YPO_4, the $J=0$, 1, 2, 3, 4, 5, 6 levels split into 1, 2, 4, 5, 7, 8, 10 irreducible representations. Only lines which are allowed by the selection rules for electric dipole transitions appear in the σ and π absorption spectra. All the observed polarized absorption lines are in complete agreement with analysis based on the unpolarized fluorescence data.

The complete set of $^3F_{2,3,4}$ sub-levels as well as the complete $^1D_2$ set were determined from absorption and emission spectra at various temperatures between 20 and 295 K. The identification of the $^3P_{0,1,2}$ sublevels is straightforward in the absorption and excitation spectra. The 17 missing levels are located in: $^3H_4$ (three), $^3H_5$ (one), $^1G_4$ (two), $^1I_6$ (eight), $^3P_2$ (two) and $^1S_0$ (one). There are three uncertain levels in $^3H_5$ (one) and $^3H_6$ (two). Concerning the $^1I_6$ sublevels, only two of them are determined unequivocally as $^3H_4(1)\rightarrow{}^1I_6(1,2)$ in the absorption and excitation spectra. The three other allowed transitions are probably weak and cannot be determined because of the background vibronic structure in this region of the spectrum.

3. Crystal field calculation

The calculations are performed on a |SLJM>basis. The interaction matrix may include at will, one or several of the complete $4f^2$, $4f6p$, and $4f5d$ configurations ($91+84+140=315$ levels). The $4f^2$, $4f6p$, and $4f5d$ configurations comprise seven, six and ten terms respectively, which are listed in Table 1.

The parametric hamiltonian [7–9] taking into account free-ion and one-electron crystal field interactions is written as:

$$\begin{aligned} H = {} & \sum F^k.f_k + \zeta(f).A_{so}(f) \\ & + \alpha\, L(L+1) + \beta\, G(G_2) + \gamma G(R_7) \\ & + \sum M^k.m_k + \sum P^k.p_k + \sum B^k_q(f,f).C^k_q(f,f) \\ & + \sum R^k(l_1,l_2,l'_1,l'_2).\; g\,(l_1,l_2,l'_1,l'_2,k) \\ & + \zeta\,(l).A_{so}(l) + \sum B^k_q(f,l).C^k_q(f,l) \end{aligned}$$

Table 1
The spectroscopic terms of the $4f^2$, $4f6p$, and $4f5d$ configurations

$4f^2$	^3P	^3F	^3H	^1S	^1D	^1G	^1I			
$4f6p$	^3D	^3F	^3G	^1D	^1F	^1G				
$4f5d$	^3P	^3D	^3F	^3G	^3H	^1P	^1D	^1F	^1G	^1H

The first eight terms represent the usually considered interactions in $4f^2$, which are: (a) free-ion interactions: the electrostatic (parameters$=F^k$), spin–orbit (ζ), free-ion interconfiguration (α, β, γ), orbit–orbit (M^k) and electrostatically correlated spin–orbit(P^k) interactions respectively, and (b) the crystal field approximated as a one-electron interaction ($B^k_q(f,f)$). The five CFP (f,f) relevant in the D_{2d} site symmetry are B^2_0, B^4_0, B^4_4, B^6_0 and B^6_4.

The following terms in the formula are absent in the standard expression, and are necessary for calculating the matrix elements of configuration interaction. The expressions for their calculation are given in Ref. [10]. The $R^k(l_1,l_2,l'_1,l'_2)$ are radial integrals linking the $n_1l_1\ n_2l_2$ and $n'_1l'_1\ n'_2l'_2$ configurations. The $g()$ are the associated operators. The R^k which have the largest effect are those linking $4f^2$ and $4f6p$, that is $R^k(f,\ f,\ f,\ p)$ ($k=2$ and 4). $\zeta(l)$ is the spin–orbit coupling constant of electron nl. $B^k_q(f,l)$ is a crystal field parameter (CFP) linking an f electron in $4f^2$ and an l electron in $4f\,nl$ and $C^{\boldsymbol{k}}_{\boldsymbol{q}}(f,l)$ is the associated operator.

Cowan's program RCN31 [12] was utilized to calculate the theoretical values of the atomic parameters: the gap between the configurations, the coulombic and exchange integrals, the radial wave functions for the evaluation of the two-electron hybrid integrals $R^k(f,\ f,\ f,\ p)$, and the spin–orbit coupling constants. Theoretical values were ascribed to all the atomic parameters within the $4f\ nl$ configurations. The hybrid integrals $R^k(f,\ f,\ f,\ p)$ are multiplied by two variable parameters X^k ($k=2$ and 4) adjusted to the experiment. The spin–orbit coupling constants for the p and d electrons are not varied. In addition, there are three (fp) CFP's B^2_0, B^4_0, B^4_4, and two (fd) CFP's B^3_2 and B^5_2. The values determined in Ref. [1] are introduced as starting values of the $4f^2$ parameters. Starting values of the (fp) and (fd) CFP's are calculated by the covalo–electrostatic model. It is assumed that $B^4_0/B^4_4(fp)=B^4_0/B^4_4(ff)$. The model predicts a small B^3_2 value and it becomes indeed vanishingly small in the course of the fitting process. Four refinements are carried out: in $4f^2$, $4f^2+4f5d$, $4f^2+4f6p$ and $4f^2+4f6p+4f5d$. The corresponding final standard deviations (Table 2) are equal to 24, 22.3, 9.8, and 5.8 cm^{-1} respectively. The fit in $4f^2+4f5d$ leads to a very slight improvement whereas the fit in $4f^2+4f6p$ results in a reduction of the standard deviation by a factor 2.4. The complete fit in $4f^2+4f6p+4f5d$ reduces further the deviation by 1.7. On a whole, between

Table 2
Free ion and crystal field parameters (cm^{-1}) of Pr^{3+} in YPO_4 without and with configuration interaction. (a)From Ref. [1]. In (b) (c) (d) (e), the following values were held constant: $\gamma = 1515\ cm^{-1}$, $F^0(f,d) - F^0(f,f) = 40\,000\ cm^{-1}$, $F^0(f,p) - F^0(f,f) = 124\,343\ cm^{-1}$, $\zeta(d) = 1148\ cm^{-1}$, $\zeta(p) = 3800\ cm^{-1}$. The standard deviations are between parentheses

Parameters	$4f^2$ (a)	$4f^2$ (b)	$4f^2 + 4f5d$ (c)	$4f^2 + 4f6p$ (d)	$4f^2 + 4f5d + 4f6p$ (e)
$F^0(f,f,f,f)$		12 183(10)	12 372(73)	12 674(1)	12 522(15)
$F^2(f,f,f,f)$	67 778(675)	67 824(55)	68 076(54)	67 929(36)	68 135(22)
$F^4(f,f,f,f)$	49 603(1780)	49 661(135)	49 830(116)	51 483(244)	50 209(88)
$F^6(f,f,f,f)$	32 413(64)	32 473(96)	32 363(87)	35 565(41)	33 058(112)
α	21.2(1)	22.53(0.49)	22.64(0.44)	9.59(0.44)	19.97(0.42)
β	−665(17)	−660(25)	−648(22)	−476(64)	−652(16)
γ	1534(632)	[1515]	[1515]	[1515]	[1515]
$M^{0(A)}$	[1.76]	1.63(0.45)	1.58(0.37)	1.61(0.18)	1.60(0.11)
P^2	[275]	162(89)	192(73)	87(36)	123(23)
$\zeta(f)$	739.0(14)	745.8(3.3)	746.6(2.0)	746.6(1.3)	747.6(0.8)
$B^2_0(f,f)$	78(18)	100(32)	311(30)	116(17)	220(19)
$B^4_0(f,f)$	321(51)	321(61)	246(57)	301(5)	303(4)
$B^4_4(f,f)$	849(43)	1064(39)	1309(38)	[1139]	[1332]
$B^6_0(f,f)$	−1376(67)	−1329(74)	−1469(73)	−1302(29)	−1443(22)
$B^6_4(f,f)$	−35(41)	0(22)	90(60)	0(4)	112(19)
$F^0(f,d) - F^0(f,f)$			[40 000]		[40 000]
$\zeta(d)$			[1148]		[1148]
$B^5_2(f,d)$			9720(217)		9431(351)
$F^0(f,p) - F^0(f,f)$				[124 343]	[124 343]
$X^2(f,f,f,p)$				4.91(0.19)	2.47(0.19)
$X^4(f,f,f,p)$				8.58(0.7)	3.20(0.37)
$\zeta(p)$				[3800]	[3800]
$B^2_0(f,p)$				806(145)	2145(265)
$B^4_0(f,p)$				1227(103)	2007(117)
$B^4_4(f,p)$				[4643]	[8815]
$B^4_4/B^4_0(f,f)$	2.64	3.31	5.32	3.78	4.40
$B^4_4/B^4_0(f,p)$				3.78	4.40
σ		20.4	18.7	7.8	4.6
n	13	14	15	18	19
N	35	50	50	50	50
Standard deviation	14.7	24.0	22.3	9.8	5.8

N: Number of the experimental levels introduced in the fit; n: Number of parameters which are allowed to vary freely. Standard deviation: $[\Sigma_{i=1,n}(Ei_{\mathrm{exp.}} - Ei_{\mathrm{calc.}})^2/(N-n)]^{1/2}$; σ: Un-barycentered mean deviation; (A): utilizing the relations: $M^2/M^0 = 0.56$; $M^4/M^0 = 0.38$; $P^4/P^2 = 0.75$; $P^6/P^2 = 0.5$ [11].

the calculation in $4f^2$ and in the largest set $4f^2 + 4f6p + 4f5d$, the deviation is divided by more than 4. The parameters values and their standard deviations are listed in Table 2. The X^k multipliers of the two-electron parameters $R^k(f,f,f,p)$ increase dramatically in the $4f^2 + 4f6p$ fit, five and eight times more than the theoretical values, respectively. This anomaly suggests that another interaction is missing, and it is more or less well mimicked by the $4f^2/4f6p$ interaction. The crystal field fit is globally improved, however not in the $^3P_1$ level where the deviation increases from 10 to 21 cm^{-1}. The introduction of the third configuration $4f5d$ removes the anomaly and the X^k multipliers decrease down to 2.5 and 3.2, for $k = 2$ and 4 respectively. These values are close to those stated previously for $LiYF_4$: Pr^{3+} [5], La_2O_3: Pr^{3+} and Pr_2O_3 [6]. Simultaneously, the deviation in $^3P_1$ falls down to 5.1 cm^{-1}, and nearly all the levels are improved. The final parameters as well as the mean and standard deviations of the fits are listed in Table 2. In Table 3 are listed the symmetry labels, the experimental and calculated energies (cm^{-1}), the differences between them (ΔE) and the un-barycentered mean deviations (σ) for the multiplets $^1G_4$, $^1D_2$ and $^3P_1$ in $4f^2 + 4f6p + 4f5d$, $4f^2 + 4f6p$, $4f^2 + 4f5d$ and $4f^2$ respectively.

4. Discussion

The total number of parameters introduced into the $4f^2$ fit is equal to 14, among which nine are utilized to adjust the levels barycenters and five the crystal field. In $4f^2 + 4f6p + 4f5d$, 19 parameters are utilized, hence five more, which can be considered as additional crystal field parameters. We are seeking rules that permit a decrease in the

Table 3
The symmetry labels, experimental and calculated energies (cm^{-1}) and the differences between experimental and calculated energy (ΔE) and un-barycentered mean deviations (σ) for the multiplets $^1G_4$, $^1D_2$ and $^3P_1$ in $4f^2+4f6p+4f5d$, $4f^2+4f6p$, $4f^2+4f5d$ and $4f^2$

Level	Label	Exp.	$4f^2+4f6p+4f5d$		$4f^2+4f6p$		$4f^2+4f5d$		$4f^2$	
			Calc.	ΔE	Calc.	ΔE	Calc.	ΔE	Calc.	ΔE
$^1G_4$	Γ_1	9643	9642	1	9641	2	9599	44	9597	46
	Γ_5	9684	9686	−2	9687	−3	9673	11	9669	15
	Γ_2	9850	9850	0	9860	−10	9876	−26	9881	−31
	Γ_1	/	9888	/	9901	/	9941	/	9960	/
	Γ_5	9934	9935	−1	9925	9	9996	−62	9995	−61
	Γ_4	9950	9950	0	9946	4	9915	35	9915	35
	Γ_3	/	10 163	/	10 182	/	10 259	/	10 291	/
σ				1.1		6.5		39.5		40.6
$^1D_2$	Γ_3	16 461	16 458	3	16 469	−8	16 513	−52	16 528	−67
	Γ_5	16 745	16 750	−5	16 740	5	16 724	21	16 720	25
	Γ_1	16 794	16 790	4	16 805	−11	16 767	27	16 776	18
	Γ_4	17 008	17 009	−1	16 995	13	17 004	4	16 983	25
σ				3.6		9.7		31.2		38.9
$^3P_1$	Γ_5	21 070	21 064	6	21 051	19	21 075	−5	21 062	8
	Γ_2	21 084	21 088	−4	21 106	−22	21 069	15	21 096	−12
σ				5.1		20.6		11.2		10.2

number of variable parameters. The relation $B_0^4/B_4^4(fp)=B_0^4/B_4^4(ff)$ has already been utilized and allowed to eliminate one variable parameter in $4f6p$. It might be a general rule, which was also verified for La_2O_3:Pr^{3+} and Pr_2O_3 [6], but not verified for $LiYF_4$: Pr^{3+} [5]. We are tempted, in the last case, to suspect a few mis-assignments in the experimental dataset, mis-assignments which do not affect much the CFP set but severely disturb the set of intra-configurational parameters striving to repair the discrepancy. In the previous work, 39 triplet states have been determined against 11 singlets only. The latter usually show the most discrepancies and are the most sensitive to the influence of inter-configurational parameters (fp). It is particularly frustrating that the highest $^1G_4$ level (probably one of the most discrepant of the set) is missing. However, even if only five energy levels over a total of seven for the $^1G_4$ level were determined in the course of the present work, their locations and symmetry labels were assigned without ambiguity.

It can be seen from Table 2 that $B_0^2(fp)/B_0^2(ff)=9.8$; and $B_0^4(fp)/B_0^4(ff)=6.6$ in the complete fit. The CFP's (fp) are 7 to 10 times larger than the CFP's (ff). Fixing this ratio to a unique value could be a means to reduce the number of parameters. Another feature can be noticed in Table 2: it is the amplitude of the shift in the CFP (ff) values in the different fits. B_4^4 increases by 40% between the fit in $4f^2$ and that in $4f^2+4f6p+4f5d$. B_0^2 increases by more than 100%. Another point needs to be underscored: the large X^k values which range between 2 and 3. Holding their values close to unity does not give good results and presently we see no means to make them fall to values close to 1 except by lowering the $4f6p$ configuration.

The beneficial influence of the $4f5d$ configuration becomes apparent when the complete set of $^3P_1$ levels is observed. In the previous work on La_2O_3: Pr^{3+} and Pr_2O_3 [6] the set was incomplete and there was no need for some additional correction. In the case of $YPO_{4:}$ Pr^{3+}, the introduction of the $4f5d$ configuration reduces the discrepancy from 20.6 to 5.1 cm^{-1} at the expense of one additional parameter. It can be argued that one additional parameter acting specifically on $^3P_1$ would accomplish the task. However, not only the $^3P_1$ multiplet is improved but also all the other levels, and a specific parameter could not do that. In another case, that of Pr^{3+} in $PrCl_3$, the deviations in $4f^2$, $4f^2+4f6p$ and $4f^2+4f6p+4f5d$ were equal to 7.2, 5.75 and 5.92 cm^{-1}. In that particular case, neither did it do much harm, nor did it improve the fit to add the $4f5d$ configuration. Further work on other reliable datasets are necessary to ascertain the influence of this configuration. Yet, we believe that at this stage, the procedure is reliable enough to allow the location of missing levels, within a few wavenumbers. Indeed, calculations performed before the last experiments on $^1G_4$ were done, revealed exactly where some missing transitions should show up, and they did so.

References

[1] T. Hayhurst, G. Shalimoff, J.G. Conway, N. Edelstein, J. Chem. Phys. 76 (8) (1982) 3960.

[2] T.S. Lo, M.F. Reid, J. Alloys Comp. 193 (1993) 180.

[3] G.W. Burdick, F.S. Richardson, Chem. Phys. 228 (1998) 81.

[4] M. Faucher, P. Tanner, Electronic structure and configuration interaction of Pr^{3+} in elpasolite lattices, in: International Conference on f Elements, ICFE3, Paris September 14–18, 1997.

[5] M. Faucher, O.K. Moune, Phys. Rev. A 55 (1997) 4150.
[6] O.K. Moune, M.D. Faucher, C.K. Jayasankar, A.M. Lejus, J. Lum. 85 (1999) 59.
[7] B.R. Judd, Phys. Rev. 141 (1966) 4.
[8] B.G. Wybourne, Spectroscopic Properties of Rare Earths, Interscience Publishers, John Wiley and Sons, Inc, New York. London. Sydney, 1965, Chapters 2 and 6.
[9] B.R. Judd, H.M. Crosswhite, H. Crosswhite, Phys. Rev. 169 (1968) 130.
[10] M. Faucher, D.J. Kooy, Sol. State Comm. 102 (1997) 663.
[11] H.M. Crosswhite, H. Crosswhite, J. Opt. Soc. Am. B 1 (1984) 246.
[12] R.D. Cowan, Computer Program RCN31, (September, 1981).