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Energy Levels of Pr^{3+} in the Modulated Incommensurate Structure of $ThCl_4$

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Abstract

The matrix β-$ThCl_4$ which presents an incommensurate modulated structure at low temperature is doped with the lanthanide ion Pr^{3+}. The strong features in the absorption and the laser-excited fluorescence spectra have been interpreted as arising from levels of Pr^{3+} in the site of D_{2d} symmetry. In a least-squares fit calculation, the best parameters are determined.

Introduction and Review of some Results Obtained on the Matrix $ThCl_4$

Recently there has been great interest in studying the optical spectra of U^{4+} ($5f^2$) in the $ThBr_4$ [1–3] and $ThCl_4$ [4] matrices. β-$ThBr_4$ and β-$ThCl_4$ both undergo a second order structural phase transition at 95 and 70 K respectively. At low temperature, Raman [5], nuclear quadrupolar resonance [6], and neutron diffraction experiments [7, 8] reveal that the tetragonal structure is incommensurate, resulting in a loss of periodicity along the *c* axis. At room temperature, the matrix β-$ThCl_4$ has a tetragonal structure ($I4_1/amd$) [9] and is isostructural with β-$ThBr_4$. The thorium ion is at a site of relatively high symmetry D_{2d}. At low temperature the site symmetry of the thorium ion or of its substitute is reduced. For β-$ThCl_4$ that is presently being studied by neutron diffraction experiments, those symmetries are C_2, D_2 and S_4 [8] as a consequence of the continuous modulation of the distance halogen–metal. Then the crystal field perceived by the optically active ion varies continuously. It was shown that in this case the crystal field transitions give rise to absorption and emission lines which can be quite broad and are characterized by edge singularities [3] reflecting the effect of the crystal field changes on the energy levels of U^{4+}. Given those interesting characteristics in the U^{4+} spectra in ThX_4, it seemed of particular interest to study the spectra of the Pr^{3+} ion ($4f^2$) isoelectronic with the actinide ion U^{4+} ($5f^2$), to see whether the existence of the incommensurate structure can be seen with a lanthanide probe. Indeed the optical spectra of Pr^{3+} in β-$ThBr_4$ [10] were analyzed at a time when the low temperature structure of the β-$ThBr_4$ matrix was not yet known. This article reports a tentative assignment of the energy levels of Pr^{3+} in β-$ThCl_4$.

Symmetry Considerations

The Th^{4+} ions in the crystal are assumed to be substituted for by the Pr^{3+} ions. Pr^{3+} is a tripositive 3+ impurity in the tetravalent matrix. The missing charge distorts the site and brings up new symmetries due to charge compensation. Thus additional lines appear in the spectra. Following the work on $ThBr_4$: Pr^{3+} [10] and as was proved by a careful study on the line and satellites of the $^3H_4 \rightarrow {}^3P_0$ transition [11], we assumed that the strongest lines in the spectra are the signature of the Pr^{3+} ions in the high temperature D_{2d} site symmetry which transforms into S_4–C_2–D_2 symmetries at low temperature.

Because of the weak effect of the modulation which suggests that the environment of the actinide ions in the different symmetries are close together, it was not possible to distinguish between the D_2, C_2 and S_4 sites inside the bands of absorption and emission spectra. Moreover, a contribution from the S_4 symmetry is expected in the intense lines of the spectra, as will be seen later.

It can be noticed that the selection rules for the electronic dipole transitions in the D_{2d} and S_4 (subgroup of D_{2d}) groups are different only for the transitions (Tables I and II) $\Gamma_3 \rightarrow \Gamma_1$ and $\Gamma_2 \rightarrow \Gamma_4$ that are forbidden in the D_{2d} symmetry and allowed with a π polarization in the S_4 symmetry. The other selection rules are the same.

In the S_4 symmetry, the loss of symmetry elements results in the introduction of imaginary terms in the Hamiltonian: $im\ B_4{}^4$ and $im\ B_4{}^6$, whereas all the crystal field parameters in the D_{2d} symmetry are real. Interpreting the data in the D_{2d} symmetry instead of the S_4 symmetry amounts to neglecting those imaginary terms in the even rank crystal field components that are used for the calculations of the energy levels of the optically active ions. Nevertheless, the use of the D_{2d} symmetry instead of the S_4 symmetry should give the

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TABLE I. Spectroscopic Best Fit Parameters from Fitting Pr^{3+} in β-$ThCl_4$. Set 1 Corresponds to a Γ_5 Ground State and Set 2 to a Γ_4 Ground State

	Set 1	Set 2
F^2	67947(112)	67866(180)
F^4	50576(304)	50219(574)
F^6	33468(161)	33322(311)
	742(3)	742(6)
α[a]	21(1)	19(2)
$\beta/12$[a]	–39(4)	–43(6)
γ[a]	1343	1343
B^2_0	545(37)	20(76)
B^4_0	–657(90)	292(155)
B^4_4	876(58)	–964(95)
B^6_0	1398(115)	–1525(199)
B^6_4	508(97)	52(188)
Number of levels	52	52
r.m.s.: σ[b]	34	66

[a] γ is fixed at the value for aqueous solution [14]; α and β were varied and then fixed. [b] r.m.s.: $\sigma = (\Sigma\,(E_{calc} - E_{obs})^2/(n_{obs} - n_{par}))^{1/2}$, where E_{calc} and E_{obs} are the calculated and observed energy respectively; n_{obs} and n_{par} are the number of observed energy levels and the number of varying parameters.

main features of the spectra. Esterowitz *et al.* [12] had already noticed with Pr^{3+} doped in $LiYF_4$ at a site of S_4 symmetry that the D_{2d} selection rules have been useful in identifying the energy levels of Pr^{3+}.

Thus we shall interpret the spectra of Pr^{3+} in β-$ThCl_4$ in the D_{2d} symmetry. The crystal field eigenstates are the Γ_1, Γ_2, Γ_3, Γ_4 and Γ_5 point group representations associated with the D_{2d} symmetry. Only the Γ_5 representation is doubly degenerate, the other ones being non-degenerate.

Analysis of the Spectra

β-$ThCl_4$:Pr^{3+} single crystals were grown by the Bridgeman method [13]. The doping material was Pr_6O_{11} or $PrCl_3$ using approximately 1% by weight. The absorption and fluorescence spectra were recorded with a one-meter monochromator Jobin Yvon 'HR 1000' equipped for the visible region with a 1200 lines/mm grating and a photomultiplier, and with a 600 lines/mm grating and a PbS photocell for the IR region. Fluorescence of the crystal was excited with a Sopra nitrogen pumped dye laser tuned in the $^3P_0$ region (around 20 500 cm^{-1}) with a minimal bandwidth of 0.75 Å (3 cm^{-1}).

Because of the charge compensation, many more lines appeared and we could not get polarized spectra.

TABLE II. Energy Levels of Pr^{3+} in $ThCl_4$ (52 observed energies). Set 1 corresponds to a Γ_5 ground state. Set 2 corresponds to a Γ_4 ground state

L-S state	Observed (cm^{-1})	Set 1		Set 2	
		Calculated (cm^{-1})	Irreducible representation in D_{2d} symmetry	Calculated (cm^{-1})	Irreducible representation in D_{2d} symmetry
$^3H_4$	0	33	Γ_5	43	Γ_4
	172[a]	198	Γ_1	185	Γ_1
		206	Γ_2	196	Γ_5
	317[a]	255	Γ_3	244	Γ_2
	318[a]	357	Γ_1	312	Γ_3
	497[a]	434	Γ_5	446	Γ_1
	557[a]	572	Γ_4	486	Γ_5
$^3H_5$	2123[a]	2159	Γ_2	2225	Γ_3
	2153[a]	2180	Γ_1	2252	Γ_5
	2288[a]	2265	Γ_5	2322	Γ_5
	2307[a]	2332	Γ_5	2343	Γ_2
	2340[a]	2353	Γ_4	2405	Γ_4
	2423[a]	2476	Γ_2	2474	Γ_5
	2475[a]	2514	Γ_5	2476	Γ_1
	2612[a]	2616	Γ_3	2578	Γ_2
$^3H_6$	4250	4215	Γ_5	4286	Γ_4
	4422	4400	Γ_1	4325	Γ_5
	4445	4459	Γ_3	4412	Γ_3
	4477	4494	Γ_5	4435	Γ_4

(continued on facing page)

TABLE II. *(continued)*

L-S state	Observed (cm^{-1})	Set 1		Set 2	
		Calculated (cm^{-1})	Irreducible representation in D_{2d} symmetry	Calculated (cm^{-1})	Irreducible representation in D_{2d} symmetry
	4504	4497	Γ_4	4455	Γ_1
	4522	4500	Γ_3	4561	Γ_3
	4539	4530	Γ_2	4580	Γ_2
	4629	4638	Γ_1	4640	Γ_5
	4784	4756	Γ_5	4730	Γ_1
	4833	4789	Γ_4	4812	Γ_5
$^3F_2$	4976	5042	Γ_1	5051	Γ_4
	5039	5048	Γ_5	5076	Γ_5
	5100	5106	Γ_3	5103	Γ_1
	5160	5153	Γ_4	5119	Γ_3
$^3F_3$	6377	6328	Γ_5	6338	Γ_2
	6405	6412	Γ_3	6392	Γ_3
	6444	6458	Γ_2	6446	Γ_5
	6486	6486	Γ_5	6449	Γ_4
	6533	6498	Γ_4	6538	Γ_5
$^3F_4$	6818	6819	Γ_3	6843	Γ_1
	6894	6886	Γ_5	6890	Γ_5
	6929	6912	Γ_1	6929	Γ_4
	6967	6995	Γ_2	6947	Γ_2
	7023	7010	Γ_4	7018	Γ_1
	7044	7057	Γ_5	7040	Γ_5
	7066	7070	Γ_1	7099	Γ_3
$^1G_4$		9634	Γ_3	9654	Γ_1
		9800	Γ_4	9721	Γ_5
		9825	Γ_1	9947	Γ_2
		9885	Γ_5	10001	Γ_1
		9969	Γ_2	10012	Γ_4
		10142	Γ_5	10035	Γ_5
		10378	Γ_1	10372	Γ_3
$^1D_2$	16710	16679	Γ_1	16656	Γ_3
	16734	16781	Γ_4	16861	Γ_5
	16921	16899	Γ_5	16911	Γ_1
	17122	17120	Γ_3	17063	Γ_4
$^3P_0$	20517	20459	Γ_1	20457	Γ_1
$^3P_1$	20994	21026	Γ_5	21082	Γ_5
	21235 (Set 1)	21204	Γ_2	21090	Γ_2
$^1I_6$	21235 (Set 2)	20934	Γ_4	21161	Γ_1
		20935	Γ_3	21168	Γ_5
		21348	Γ_5	21265	Γ_3
		21371	Γ_4	21339	Γ_5
	21406	21392	Γ_1	21376	Γ_2
		21457	Γ_5	21463	Γ_4
	21522	21535	Γ_2	21506	Γ_3
		21787	Γ_5	21634	Γ_1

(continued overleaf)

TABLE II. *(continued)*

L-S state	Observed (cm^{-1})	Set 1		Set 2	
		Calculated (cm^{-1})	Irreducible representation in D_{2d} symmetry	Calculated (cm^{-1})	Irreducible representation in D_{2d} symmetry
		21799	Γ_1	21653	Γ_5
		21800	Γ_3	21693	Γ_4
$^3P_2$	22179	22226	Γ_1	22310	Γ_3
	22427 (Set 2)	22312	Γ_5	22313	Γ_5
	22427 (Set 1)	22415	Γ_4	22333	Γ_1
	22483	22517	Γ_3	22402	Γ_4
$^1S_0$		46660	Γ_1	46570	Γ_1

[a] Corresponds to the lines observed in fluorescence spectra.

We overcame the difficulty by comparing the spectra of Pr^{3+} in $ThCl_4$ with those of Pr^{3+} in $ThBr_4$ that were polarized [10]. The similarity of those two sets of spectra encouraged us to follow their analysis. In $ThBr_4$:Pr^{3+}, the ($^3P_0$) Γ_1 line clearly showed a σ polarization, thus leading to a ($^3H_4$) Γ_5 ground state in the D_{2d} symmetry.

The selection rules for the zero phonon electric dipole transitions in the D_{2d} symmetry are the following (notation of Koster *et al.* [14]):

$\Gamma_5 \longrightarrow \Gamma_5$ polarization π

$\Gamma_5 \longrightarrow \Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4 polarization σ

In the most intense lines, a contribution due to Pr^{3+} ions in the D_{2d} symmetry is expected. Indeed, the intensity of electric dipole transition in the same configuration and regardless of the symmetry of the ion site is proportional to a matrix element involving the crystal field parameters of odd rank (B^{k*}_q). The D_2 symmetry is close to the D_{2d} symmetry at low temperature. Thus the additional parameter B^{5*}_4 to be added to the odd rank parameters for the D_2 symmetry B^{3*}_2 and B^{5*}_2 – common with the D_{2d} symmetry – can be supposed to be weak. Therefore the intensity of the lines corresponding to ions in the D_{2d} and D_2 symmetries will follow the same trend as was observed on ThBr:U^{4+} [1] and $ThCl_4$:U^{4+} [4].

Another argument is in favour of this hypothesis: the most intense lines of the spectrum at 4.2 K still exist at 80 K, above the phase transition temperature where the symmetry to be considered is the initial D_{2d} symmetry. The weak lines were systematically excluded from our analysis whether they are due to charge compensation and thus correspond to other sites of symmetry or whether they come from transitions with weak intensity in D_{2d} (e.g., some transitions towards the $^1I_6$ Stark levels) or transitions allowed in D_2 symmetry. So we tried to sort out the lines that correspond to Pr^{3+} in D_{2d} symmetry, though the selection rules seem to be somewhat relaxed because more transitions can be seen than are expected.

The absorption and fluorescence data obtained by exciting the $^3P_0$ were used in the fitting program which adjusted the various spectroscopic parameters of [15]: (i) interelectronic repulstion F^k, with $k =$ 0.2,4,6. (ii) spin–orbit coupling ξ. (iii) crystal field characteristic of the D_{2d} symmetry: $B_0{}^2$, $B_0{}^4$, $B_4{}^4$, $B_0{}^6$, $B_4{}^6$. In addition to these major contributions the configuration interaction parameters α, β and γ were used.

The starting values were those of Pr^{3+} in $ThBr_4$ [10], and in the first step only the absorption data were fitted. Once reasonable values for $B_q{}^k$ were obtained, the calculated values were compared to the lines determined from fluorescence experiments. These fluorescence lines were assigned in the order derived from the fit, and the calculation was continued. The final set of best fit parameters values is listed in Table I. In the last step, the configuration interaction parameters α and β were varied, but not γ, whose value depends on the position of both the $^3P_0$ and $^1S_0$ levels. The starting values of α and β and γ were fixed at the values in aqueous solution [16].

The values of the experimental and calculated energies with their irreducible representations and the *L-S* states from which they are derived are given in Table II.

Conclusion

We already stressed the similarity between β-$ThCl_4$:Pr^{3+} and β-$ThBr_4$:Pr^{3+} [10]. Assuming that the ground state is Γ_5 as in β-$ThBr_4$:Pr^{3+}, the fitting (set 1, Tables I and II) results in a calculated set of energy and parameters very close to those of $ThBr_4$:Pr^{3+},

TABLE III. Spectroscopic Parameters of Pr^{3+} in the D_{2d} symmetry and of U^{4+} for comparison

	$ThCl_4:Pr^{3+}$		$ThBr_4:Pr^{3+}$ [10]	$LuPO_4:Pr^{3+}$ [17]	$YPO_4:Pr^{3+}$ [17]	$ThBr_4:U^{4+}$ [1]	$ThCl_4:U^{4+}$ [4]
	Set 1	Set 2					
F^2	67947	67866	68354	67688	677779	42253	42752
F^4	50576	50219	50310	48633	49603	40458	39925
F^6	33468	33322	33799	32151	32413	25881	24519
ξ	742	742	739	744	739	1783	1808
α	21	19	21	21	21	31	30
$\beta/12$	−39	−43	−67	−55	−55	−54	−41
γ	1343	1343	1343	1534	1534	1200	1200
B_0^2	545	20	260	21	78	−1096	−1054
B_0^4	−657	292	−644	280	321	1316	1146
B_4^4	876	−964	929	−808	−849	−2230	−2767
B_0^6	1398	−1525	1089	−1658	−1377	−3170	−2135
B_4^6	508	52	241	291	35	686	−(312)
Number of levels	52	52	42	18	35	26	25
σ (cm^{-1})	34	66	61	27	15	36	46

but with crystal field parameters $B^k{}_q$ different in sign from those found in $LuPO_4:Pr^{3+}$ [17] and ThX_4: U^{4+} (X = Br [1]; X = Cl [4]) [Table III]. This difference seemed somewhat surprising in view of the similar coordination polyhedron of U^{4+} or Pr^{3+} in the D_{2d} symmetry in all those compounds.

Following the calculation of the energy levels of Pr^{3+} in $LUPO_4$ and YPO_4 [17] and of U^{4+} in ThX_4 [1, 4], we repeated the calculation with a Γ_4 ground state (set 2 in Tables I and III). The starting values for the $B^k{}_q$ were taken with the same sign as in those compounds. We concluded upon a fitting with a somewhat larger discrepancy between calculated and experimental levels but whose consistency according to the other studies is more satisfactory.

In the crystal that was studied, the effects of the structure modulation of the matrix are not clear in absorption. In fluorescence, the emission spectra showed some differences when the $^3P_0$ line was scanned. Unfortunately the laser used in our experiments did not have a bandwidth small enough to permit us to clearly relate the effect of the modulation on the emission spectra. Moreover, the crystals were too concentrated for that type of study. But the effect of the modulation with Pr^{3+} in $ThCl_4$ has been observed when studying the fluorescence of the $^3P_0$ line in less concentrated crystals (0.01%) and using a laser with a better definition [11].

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