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1992 J. Phys.: Condens. Matter 4 3453

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## Energy levels and crystal field parameters of $\text{Nd}^{3+}$ and $\text{Er}^{3+}$ in $\text{LiRP}_4\text{O}_{12}$ single crystals

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Received 10 December 1991

**Abstract.** The experimental Stark energy levels for the  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in  $\text{LiRP}_4\text{O}_{12}$  crystals were presented in our previous paper [13]. A crystal field analysis of these data is based on a Hamiltonian of  $C_{2/c}$  point group symmetry, including  $J$ -mixing effects. We find that the twinned  $C_{2/c}$  ( $C_2$ ) structure is consistent with all available experimental results. A Hamiltonian parametrized in monoclinic symmetry was used to describe the observed crystal-field splittings of  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in  $\text{LiRP}_4\text{O}_{12}$ . Resulting RMS deviations between calculated and experimental levels range from 6.8 to 7.4  $\text{cm}^{-1}$ .

### 1. Introduction

Luminescence and laser properties of the stoichiometric neodymium compounds  $\text{LiNdP}_4\text{O}_{12}$  and  $\text{KNdP}_4\text{O}_{12}$ , which show exceptionally low concentration quenching of neodymium luminescence, are well documented in numerous papers [1–5]. Considerably less progress has been achieved in the spectroscopy of the other rare-earth ions in stoichiometric rare-earth compounds. However, works on the spectroscopic behaviour of  $\text{LiLa}_{1-x}\text{Pr}_x\text{P}_4\text{O}_{12}$  [6–8], or  $\text{LiGd}_{1-x}\text{Er}_x\text{P}_4\text{O}_{12}$  [9, 10] have recently been published. In our paper, we present some data and analysis concerning the optical spectra of  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in lithium tetrphosphate single crystals. Our interest is focused at the calculation of the Stark energy levels and crystal field parameters (CFP) for the  $f^n(f^{14-n})$  configuration.

### 2. Experimental details

#### 2.1. Absorption spectra

The low-temperature absorption spectra of  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  were recorded on a Cary-17 spectrophotometer equipped with a liquid helium cryostat operating between 4.2 and 10 K. The absorption measurements reported for both  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in  $\text{LiRP}_4\text{O}_{12}$  were carried out by S Maia-Melo at the Laboratory of Transition Elements of CNRS (Meudon-Bellevue, France).

### 3. Analysis of experimental data

We determined the Stark energy levels of  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$  in  $\text{LiRP}_4\text{O}_{12}$  from the low-temperature absorption and luminescence spectra which were presented in our previous works [6–10, 13].

#### 3.1. Crystal field parameters for the rare earth tetrphosphates

The point group symmetry of the rare-earth tetrphosphate is  $C_{2/C}$  [7, 10]. In our crystal-field analysis, we assume a crystal-field Hamiltonian of  $C_2$  symmetry, which we take in the irreducible tensor form:

$$H_x = \sum_{km} B_{km}^\dagger \sum_i C_{km}(r_i) \quad (1)$$

where the  $B_{km}^\dagger$  are crystal-field parameters ( $\dagger$  = complex conjugate) satisfying:

$$B_{km}^\dagger = (-1)^m B_{k,-m} \quad (2)$$

and where  $C_{km}$  are spherical tensors, related to ordinary spherical harmonics  $Y(\theta_i, \varphi_i)$  by:

$$C_{km}(r_i) = [4\pi/(2k+1)]^{1/2} Y_{km}(\theta_i, \varphi_i) \quad (3)$$

where  $\theta_i$  and  $\varphi_i$  are polar coordinates of the  $i$ th electron. In (1), the sums for  $k$  and  $m$  run over  $k = 2, 4, 6$  and  $m = 0, \pm 2, \dots, \pm k$ , as is appropriate for the  $C_2$  symmetry (with the  $C_2$  axis chosen as the quantization axis), and the sum for  $i$  runs over the electrons in the  $4f^n$  configuration. In general the  $B_{km}$  are complex, except for  $B_{k0}$  which are real. In addition, we assume that the coordinate system has been rotated about the  $C_2$  axis so that  $B_{22}$  is real. The resulting Hamiltonian given by (1), together with the added restrictions, results in 14 independent parameters.

The crystal-field Hamiltonian is diagonalized together with an effective free-ion Hamiltonian of the form:

$$H_{\text{free}} = \sum_{[S,L]J} \Delta_{[S,L]J} |[S,L]J\rangle \langle [S,L]J| \quad (4)$$

where the sum for  $[S,L]J$ , in general, runs over several of the lowest states of the  $4f^n$  configuration. The quantities  $\Delta_{[S,L]J}$  are centroid parameters, which would be equal to the experimental centres of gravity of the crystal-field split levels if effects of  $J$  mixing by the crystal field were neglected. By diagonalizing the sum of equations (1) and (4), we include the major effect of  $J$  mixing. We include the lowest ten  $[S,L]J$  states in our calculations for  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$ .

Matrix elements of the crystal-field Hamiltonian are obtained from wavefunctions associated with the intermediate-coupling diagonalization of a free-ion Hamiltonian consisting of Coulomb, spin-orbit and configuration interactions. Parameter values for this free-ion Hamiltonian are those appropriate for rare-earth ions in aqueous solutions [11]. The procedure used in calculations has been described previously by Morrison *et al* [12].

Table 1. Crystal-field parameters  $B_{km}$  in  $\text{cm}^{-1}$  for  $\text{LiNdP}_4\text{O}_{12}$  and  $\text{LiErP}_4\text{O}_{12}$ . Assume space group  $C_{2/c}$ ;  $m = 0, \mp 2, \dots, k$  results in 14 independent  $B_{km}$  parameters of  $C_2$  symmetry.

	$B_{20}$	$B_{22}$	$B_{40}$	$B_{42}$		$B_{44}$		$B_{62}$		$B_{64}$		$B_{66}$		energy RMS ( $\text{cm}^{-1}$ )	
				real	imag.	real	imag.	real	imag.	real	imag.	real	imag.		
Nd	-560	103	-170	-628	160	-528	60	248	-250	-290	250	-340	40	-300	7.4
Er	-415	85	-108	-85	420	102	-260	140	-388	180	300	-63	435	210	6.8

Table 2. Calculated and experimental energy levels for Nd<sup>3+</sup> in LiNdP<sub>4</sub>O<sub>12</sub>. Total of 29 experimental levels; RMS deviation = 7.4 cm<sup>-1</sup>.

State [S, L]J	Label	Energy		State [S, L]J	Label	Energy		State [S, L]J	Label	Energy	
		Calc.	Exp.			Calc.	Exp.			Calc.	Exp.
<sup>4</sup> I <sub>9/2</sub>	Z <sub>1</sub>	0	0	<sup>4</sup> F <sub>9/2</sub>	Q <sub>1</sub>	14708	14708	<sup>4</sup> F <sub>7/2</sub>	T <sub>1</sub>	13370	13358
	Z <sub>2</sub>	95	106		Q <sub>2</sub>	14765	14771		T <sub>2</sub>	13476	13470
	Z <sub>3</sub>	204	197		Q <sub>3</sub>	14867	14863	<sup>4</sup> S <sub>3/2</sub>	T <sub>3</sub>	13494	13495
	Z <sub>4</sub>	267	263		Q <sub>4</sub>	14891	14899		T <sub>4</sub>	13579	13582
	Z <sub>5</sub>	338	320		Q <sub>5</sub>	14903	14910		T <sub>5</sub>	13590	13600
						T <sub>6</sub>	13593		...		
<sup>4</sup> I <sub>11/2</sub>	Y <sub>1</sub>	1935	1940								
	Y <sub>2</sub>	1948	...								
	Y <sub>3</sub>	2007	1998								
	Y <sub>4</sub>	2059	2050								
	Y <sub>5</sub>	2076	2075								
	Y <sub>6</sub>	2137	2132								
<sup>4</sup> F <sub>3/2</sub>	R <sub>1</sub>	11470	11479								
	R <sub>2</sub>	11590	11585								
<sup>4</sup> F <sub>5/2</sub>	S <sub>1</sub>	12390	12390								
	S <sub>2</sub>	12454	12445								
<sup>2</sup> H <sub>9/2</sub>	S <sub>3</sub>	12516	12500								
	S <sub>4</sub>	12578	12573								
	S <sub>5</sub>	12603	12600								
	S <sub>6</sub>	12678	12687								
	S <sub>7</sub>	12754	12762								
	S <sub>8</sub>	12756	...								

The first step in our analysis of lanthanide ions in tetraphosphate crystals was to obtain starting values for  $B_{km}$  by means of point-charge lattice sums  $A_{km}$ . These are related to the  $B_{km}$  by:

$$B_{km} = \rho_k A_{km} \quad (5)$$

where

$$\rho_k = \tau^{-k} \langle r^k \rangle_{\text{HF}} (1 - \sigma_k) \quad (6)$$

and where  $\tau$  is a host-independent, ion-dependent radial expansion parameter,  $\langle r^k \rangle_{\text{HF}}$  are Hartree-Fock expansion values and  $\sigma^k$  are shielding factors.

Crystal-field parameters for Nd<sup>3+</sup> and Er<sup>3+</sup> were determined by starting with  $B_{km}$  given by (5) and varying the  $B_{km}$  and the  $\Delta_{[S, L]J}$  simultaneously until a minimum RMS deviation between calculated and experimental energy levels was found. The best-fit  $B_{km}$  are presented in table 1, together with the corresponding RMS deviations.

Values of the RMS deviations in table 1, ranging from 6.8 cm<sup>-1</sup> for Er<sup>3+</sup> to 7.4 cm<sup>-1</sup> (for Nd<sup>3+</sup>), are somewhat larger than values obtained for the same ions in LaF<sub>3</sub> [14] (LaF<sub>3</sub> also has R<sup>3+</sup> ions in C<sub>2</sub> symmetry). The reason for this is as follows. Consider the strength parameter, which is a quantitative measure of the strength of the crystal-field interaction of the particular rare-earth ion with a particular host crystal. As an illustration, for Nd<sup>3+</sup> in LiRP<sub>4</sub>O<sub>12</sub>, from values of table 1, we obtain  $S = 548$  cm<sup>-1</sup>. The

**Table 3.** Calculated and experimental energy levels of  $Er^{3+}$  in  $LiErP_4O_{12}$ . Total of 35 experimental levels; RMS deviation =  $6.8\text{ cm}^{-1}$ .

State [S, L]J	Label	Energy		State [S, L]J	Label	Energy		State [S, L]J	Label	Energy	
		Calc.	Exp.			Calc.	Exp.			Calc.	Exp.
$^4I_{15/2}$	Z <sub>1</sub>	0	0	$^2H_{11/2}$	F <sub>1</sub>	19145	19140	$^4F_{9/2}$	D <sub>1</sub>	15244	15243
	Z <sub>2</sub>	31	36		F <sub>2</sub>	19164	19156		D <sub>2</sub>	15300	15295
	Z <sub>3</sub>	112	130		F <sub>3</sub>	19168	19171		D <sub>3</sub>	15317	15318
	Z <sub>4</sub>	164	170		F <sub>4</sub>	19199	19204		D <sub>4</sub>	15362	15372
	Z <sub>5</sub>	219	215		F <sub>5</sub>	19223	19215		D <sub>5</sub>	15383	...
	Z <sub>6</sub>	250	245		F <sub>6</sub>	19250	19252				
	Z <sub>7</sub>	282	280	$^4F_{9/2}$	G <sub>1</sub>	20450	20450	$^4S_{3/2}$	E <sub>1</sub>	18414	18422
	Z <sub>8</sub>	326	...		G <sub>2</sub>	20498	20483		E <sub>2</sub>	18473	18467
$^4I_{13/2}$	Y <sub>1</sub>	6545	6550	G <sub>3</sub>	20533	20533					
	Y <sub>2</sub>	6581	6581	G <sub>4</sub>	20599	20579					
	Y <sub>3</sub>	6630	6629								
	Y <sub>4</sub>	6646	6644								
	Y <sub>5</sub>	6694	6676								
	Y <sub>6</sub>	6707	...								
	Y <sub>7</sub>	6721	6717								
$^4I_{11/2}$	A <sub>1</sub>	10211	10211								
		10238	10230								
		10262	10256								
		10286	10288								
		10294	...								
	10311	10315									

corresponding strength parameter for  $Nd^{3+}$  in  $LaF_3$  is  $378\text{ cm}^{-1}$  [14]. The crystal field is stronger in  $LiRP_4O_{12}$  than in  $LaF_3$ .

Detailed comparisons of the calculated and experimental energy levels are given in tables 2 and 3. In these tables, states are identified by the maximum component in the free-ion wavefunctions. The theoretical energy levels are calculated by means of the crystal-field parameters of table 1.

The analysis of the  $Nd^{3+}$  spectrum (table 2) is straightforward. Our calculation spans 32 sublevels, and of these only 3 are not identified experimentally. In the case of  $Er^{3+}$  (table 3), we fit the lowest 35 levels: the largest deviation between theory and experiment for the individual crystal-field split level is  $20\text{ cm}^{-1}$  (for the level at  $20\,579\text{ cm}^{-1}$  in the  $^4F_{9/2}$  state).

#### 4. Conclusions

We have furthered our investigation of optical properties of rare-earth ions in  $LiRP_4O_{12}$  by considering the crystal-field parameters and calculated energy levels. We used a crystal-field Hamiltonian in the monoclinic site symmetry for our crystal-field analysis and obtained RMS deviation of  $6.8\text{--}7.4\text{ cm}^{-1}$ . Better fits for all values of  $B_{km}$  allowed by symmetry are obtained for Er.

## Acknowledgment

The Polish Academy of Sciences, CPBP 01.12 Program, has financially supported this work.

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