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Crystal-field analyses for trivalent lanthanide ions in $LiYF_4$

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Abstract: Based on the completely parametric crystal-field model, the energy level parameters, including free-ion parameters and crystal-field parameters, obtained by fitting the experimental energy level data sets of Ln^{3+} in $LiYF_4$ were systematically analyzed. The results revealed that the regular variation trends of the major parameters at relatively low site symmetry still existed. The *g* factors of ground states were calculated using the parameters obtained from least-squares fitting. The results for Ce^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+} and Yb^{3+} were in good agreement with experiment, while those of Er^{3+} deviated from experiment dramatically. Further study showed that the *g* factors depended strongly on B_4^6, and a slightly different B_4^6 value of −580 cm^{-1} led to *g* factors agreeing well with the experimental values.

Keywords: crystal-field interactions; $LiYF_4$; lanthanide ions; variation trends; *g* factors; rare earths

The energy level parameters of trivalent lanthanide (Ln^{3+}) ions in hosts can be determined by least-squares fitting to the experimental energy level data sets[1–3]. Previous results on the energy level parameters of all Ln^{3+} in $Cs_2NaLnCl_6$[4] with high site symmetry show that the major parameters vary smoothly across the Ln^{3+} series. If the trend holds for Ln^{3+} in all hosts, especially for those with low site symmetry, then it can be used to predict the crystal-field parameters (CFPs) for all Ln^{3+} from those for one particular Ln^{3+} ion in the same host. In particular, the CFPs of Ce^{3+} in crystals can be calculated from *ab-initio* calculations[5–7].

Ln^{3+} doped luminescent materials are widely applied as phosphors, scintillators, laser materials and temperature sensors[8–13]. Among these, Ln^{3+} doped $LiYF_4$ crystal has been deeply investigated with many spectroscopic and theoretical studies in the last several decades[14–17]. Hence, we chose Ln^{3+} in $LiYF_4$ to study the variation trends of energy level parameters, especially for crystal-field (CF) interactions, for a low site symmetry case.

The $LiYF_4$ crystal has the scheelite structure. Ln^{3+} ion occupies Y^{3+} site at S_4 point symmetry, surrounded by a slightly distorted dodecahedron of eight F^- ions. As the distortion is very small, D_{2d} symmetry is chosen as a realistic approximation to the actual S_4 site symmetry[18–20]. In D_{2d} symmetry, all the CFPs are real. Firstly, the energy level parameters of Ln^{3+} series in $LiYF_4$ were calculated from least-squares fitting to the experimental energy level data sets. Based on the fitted parameters, the *g* factors of the ground states of Ln^{3+} were analyzed. The results for Ce^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+} and Yb^{3+} were in good agreement with the experimental data, while those of Er^{3+} deviated from the experimental data. Further study showed that the *g* factors of Er^{3+} were sensitive to B_6^4 value in a particular range, and a slightly different value of $B_4^6 = -580$ cm^{-1} could predict correct *g* factors.

1 Theoretical calculations

The energy levels of $4f^N$ configuration of Ln^{3+} in $LiYF_4$ were analyzed in terms of a completely parametric effective operator Hamiltonian:

$$H = E_{\mathrm{av}} + \sum_k F^k f_k + \sum_i \zeta_f s_i \cdot l_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_h T^h t_h + \sum_s M^s m_s + \sum_k P^k p_k + H_{\mathrm{CF}} \quad (1)$$

where all the parameters and operators have the same meaning as those in Ref. [21]. Specifically, E_{av} adjusts the configuration barycenter energy of the entire 4f*N* configuration. F^k (k=2, 4, 6) are the Slater parameters and f_k represent the angular operator parts of the electrostatic interaction. ζ_f is the spin-orbit parameters and $s_i \cdot l_i$ represent the spin-orbit interactions. α, β, and γ are the parameters describing the two-body interactions. L is the total orbital angular momentum, and $G(G_2)$ and $G(R_7)$ are Casimir operators for the groups G_2 and R_7. For $4f_N$ and 4f14-*N* configurations of $N \geq 3$, the three-body parameters T^h (h=2, 3, 4, 6, 7, 8) and corresponding operators t_h are employed. M^s (s=0, 2, 4) are the Marvin inte-

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grals which describe the spin-spin and spin-other-orbit relativistic interactions between electrons. P^k (k=2, 4, 6) describe the two-body magnetic interactions. HCF is the CF Hamiltonian comprising the non-spherically symmetric crystal field.

In order to minimize the number of parameters in fitting the experimental data sets, M^2 and M^4 were constrained by the ratios M^2=0.56M^0, M^4=0.38M^0, and P^4 and P^6 were constrained by the ratios P^4=0.75P^2, P^6= 0.5P^2 [22,23].

The CF Hamiltonian H_{CF} for D_{2d} symmetry can be written (in the formalism of Wybourne) as[24]

$$H_{CF} = \sum_{k,q} B_q^k C_q^k = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 \left(C_4^4 + C_{-4}^4\right) + B_0^6 C_0^6 + B_4^6 \left(C_4^6 + C_{-4}^6\right) \quad (2)$$

where C_q^k is a spherical tensor of rank k, with components q; B_q^k are the CFPs.

Based on the effective Hamiltonian, least-squares fitting to the experimental energy levels available was performed to obtain the energy level parameters across the Ln^{3+} series in $LiYF_4$ using the f-shell program package[25]. Moreover, the magnetic properties were investigated. In the presence of an external magnetic field B, the Zeeman term can be written as[26]

$$\hat{H}_Z = \mu_B \left(g_s s + l\right) \cdot B \quad (3)$$

where μ_B is the Bohr magneton, g_s=2.00232 is the electron spin g factor, s and l are the spin and orbital angular momentum, respectively.

2 Results and discussion

The experimental energy level data sets of Ln^{3+} series in $LiYF_4$[20,24,27–35] except Pm^{3+} and Gd^{3+} were systematically analyzed by least-squares fitting using the parametric effective Hamiltonian. The Gd^{3+} in $LiYF_4$ was not included due to lack of energy level data at low excited states[36]. A summary of the calculated energy level parameters are presented in Table 1. Because of the limited amount of experimental data, some free-ion parameters were fixed using the values in Ref. [23]. The number of parameters (N_p) employed to fit the N_e energy levels is given in each case.

As can been seen, the Slater parameters F^k and the spin-orbit parameters ζ_{4f} have a regular increase across the Ln^{3+} series, which can be described by linear or second-order polynomial relation. The variation equations are as follows:

$$F^2=(63453\pm1016)+(3137.7\pm126.1)N \quad (4)$$

$$F^4=(46898\pm757)+(1993.4\pm94.0)N \quad (5)$$

$$F^6=(29965\pm1099)+(1960.0\pm136.4)N \quad (6)$$

$$\zeta_{4f}=(558.6\pm13.4)+(83.03\pm4.40)N+(7.443\pm0.310)N^2 \quad (7)$$

The variation trends of CFPs of Ln^{3+} in $LiYF_4$ were not as regular as those in Cs_2NaLnF_6, but smooth variations were presented by linear fitting to CFPs across the Ln^{3+} series, as shown in Fig. 1(a). The CF strength parameter S is a quantitative measure of the overall CF interaction of Ln^{3+} within a particular host and is defined as[37]

Table 1 Energy level parameters (in cm^{-1}) from fitting the $4f^N$ energy levels of Ln^{3+} series in $LiYF_4$[a,b]

Ln^{3+}	Ce	Pr	Nd	Sm	Eu	Tb	Dy	Ho	Er	Tm	Yb
E_{avg}	1513	10202	24412	47597	63642	69519	55344	48159	35753	18004	4632
F^2		68955	72952	79515	82573	90972	90421	93512	97326	101938	
F^4		50505	52681	56766	59646	(64499)	(63928)	66084	67987	71553	
F^6		33098	35476	40078	43203	(45759)	(46657)	49765	53651	51359	
ζ_{4f}	630	748	877	1168	1329	1702	1895	2126	2377	2632	2916
α		23.3	21.0	[20.5]	21.6	[17.6]	[17.9]	[17.2]	18.1	[17.3]	
β		[−644]	−579	[−616]	−482	[−581]	[−628]	[−596]	−599	[−665]	
γ		[1413]	1446	[1565]	1140	[1792]	[1790]	[1839]	1870	[1936]	
T^2			210	[282]	[370]	[330]	[326]	[365]	380		
T^3			41	[26]	[40]	[40]	[23]	[37]	41		
T^4			74	[71]	[40]	[45]	[83]	[95]	69		
T^6			−293	[−257]	[−300]	[−365]	[−294]	[−274]	−356		
T^7			321	[314]	[380]	[320]	[403]	[331]	239		
T^8			205	[328]	[370]	[349]	[340]	[343]	390		
M^0		[1.88]	[1.85]	[2.38]	2.41	[2.70]	[4.46]	3.92	4.41	[4.93]	
P^2		[244]	304	[336]	332	[482]	[610]	[582]	795	[730]	
B_0^2(ff)	354	512	391	370	339	413	360	386	325	339	446
B_0^4(ff)	[−1043]	−1127	−1031	−757	−733	−867	−737	−629	−749	−627	−560
B_4^4(ff)	[−1249]	−1239	−1271	−941	−1067	−1114	−943	−841	−1014	−913	−843
B_0^6(ff)	[−65]	−85	−28	−67	−36	−41	−35	−33	−19	−39	[−23]
B_4^6(ff)	[−1069]	−1205	−1046	−895	−764	−736	[−700]	−687	−635	−584	[−512]
σ	21.9	21.7	23.5	11.2	20.1	16.4	9.3	4.3	12.0	13.8	48.8
N_e	5	44	149	55	103	28	21	69	108	41	7
N_p	3	11	20	10	15	8	7	11	21	10	5

[a] Values in brackets were fixed according to Ref. [23]; for Ce^{3+} and Yb^{3+}, values were fixed according to variation trends; [b] Values in parentheses were constrained according to Ref. [23]: for Tb^{3+}, F^4/F^2=0.709, F^6/F^2=0.503; for Dy^{3+}, F^4/F^2=0.707, F^6/F^2=0.516