

Trends in parameters for the $4f^N \leftrightarrow 4f^{N-1}5d$ spectra of lanthanide ions in crystals

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Abstract

Transitions between the $4f^N$ and $4f^{N-1}5d$ configurations of trivalent lanthanide ions in various host crystals may be modeled by using extensions to the standard crystal-field model for the $4f^N$ configuration. In this work we discuss the trends in calculated and experimental parameters across the lanthanide series.

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1. Introduction

There has been considerable interest in the spectroscopy of the $4f^{N-1}5d$ configuration of lanthanide compounds as part of the effort to develop technological applications, such as new phosphors for lamps and displays [1]. Though a lot of data exist [2] it is only recently that sufficiently detailed and extensive spectra have become available to allow meaningful comparisons between theory and experiment for the entire lanthanide series. It has now been demonstrated [3,4] that $4f^N \leftrightarrow 4f^{N-1}5d$ transitions for lanthanide ions in crystals may be modeled using straightforward extensions to the standard calculations for $4f^N$ to include the $4f^{N-1}5d$ states. In our work [4] atomic and crystal-field parameters derived from $4f^N$ spectra for interactions involving only $4f$ electrons were used for both the $4f^N$ and $4f^{N-1}5d$ configurations, other atomic parameters for the $4f^{N-1}5d$ configuration were estimated from standard atomic calculations [5] and crystal-field parameters for the $5d$ electrons were fitted to the Ce^{3+} spectrum. We have now extended these investigations to excitation spectra of most ions of the lanthanide series doped into LiYF_4 , YPO_4 and CaF_2 [6,7]. $4f^{N-1}5d \rightarrow 4f^N$ emission

spectra have also been measured and calculated for several ions [8].

In this recent work we have refined our knowledge of the relationship between the theoretical calculations and the experimental data. Here we discuss some of the issues raised and possibilities for the future.

2. Hamiltonian for the $4f^{N-1}5d$ configuration

Standard ‘crystal-field’ calculations for lanthanide ions in crystals [9–11] make use of an ‘effective Hamiltonian’ that acts only within the $4f^N$ configuration. In these calculations the Hamiltonian parameters are determined by least-squares fitting of calculated energies to experimental data. Good estimates of the atomic parameters may be obtained from atomic physics calculations [9,12], but quantitative values for crystal-field parameters cannot be obtained from an atomic calculation since crystal-field splittings arise from complex mixing and interactions between ion and ligand orbitals [13–15].

Our approach to calculating the $4f^{N-1}5d$ energy levels [4] is to extend the crystal-field calculations for the $4f^N$ configuration. For the $4f^N$ configuration the Coulomb interaction between the $4f$ electrons is parameterized by the F^k parameters, with $k=2, 4$ and 6 and two and three-electron Coulomb correlation effects by α, β, γ and T^k , with $k=2, 3, 4, 6, 7, 8$. Spin-orbit coupling is parameterized by ζ and higher-order magnetic interactions

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by M^k , with $k=0, 2, 4$ and P^k , with $k=2, 4, 6$. The crystal-field interaction of the $4f$ electrons with the lattice is parameterized by the crystal-field parameters B_q^k , with $k=2, 4, 6$. Furthermore, there are symmetry restrictions on q . For example, in D_{2d} symmetry, which is the exact symmetry for Y^{3+} sites in YPO_4 and a good approximation for the Y^{3+} sites in $LiYF_4$, the allowed values of q are limited to 0 and 4.

For the excited $4f^{N-1}5d$ configuration the $4f^{N-1}$ ‘core’ experiences the same interactions as the $4f^N$ configuration. We distinguish these parameters from the $4f^N$ parameters by appending ‘(ff)’. These parameters can be expected to be similar, but not necessarily identical, to the $4f^N$ parameters. Depending on the value of N , some operators will not exist in $4f^{N-1}5d$. For example, if $N=1$ the excited configuration is $5d$ and there are no $4f$ operators at all and if $N=2$ there are no Coulomb operators.

The parameters for the $4f^{N-1}$ core ($F^k(ff)$, $\zeta(ff)$, $B_q^k(ff)$, etc.) must be supplemented by the Coulomb interaction of the $5d$ electron with the $4f$ electrons, parameterized by $F^k(fd)$, with $k=2, 4$ and $G^k(fd)$, with $k=1, 3, 5$, the spin-orbit interaction for the $5d$ electron, parameterized by $\zeta(dd)$, and the crystal-field interaction of the $5d$ electron with the lattice, parameterized by $B_q^k(dd)$, with $k=2$ and 4 , and the same restrictions on q as for the $B_q^k(ff)$. In contrast to the $4f^N$ configuration, where the crystal-field is small, the $5d$ crystal-field interactions dominate the splitting of the $4f^{N-1}5d$ configuration. The relative energies of the $4f^N$ and $4f^{N-1}5d$ configurations are adjusted by a parameter $\Delta_E(fd)$ that absorbs contributions from both atomic and lattice effects. We do not include the odd-rank crystal-field operators, with $k=1, 3$ and 5 , that mix the $4f^N$ and $4f^{N-1}5d$ configurations. This mixing is important for electric dipole transitions within $4f^N$ [16,17], but our calculations indicate that it has only a small effect on the energy levels of either configuration.

3. Determination of Hamiltonian parameters

Transitions within the $4f^N$ configuration consist predominantly of sharp zero-phonon lines, allowing the measurement of a large number of energy levels and hence the accurate determination of the Hamiltonian parameters. In contrast, transitions to the $4f^{N-1}5d$ configuration are dominated by broad vibronic bands, with a limited number of observable zero-phonon lines. Fitting all of the atomic and crystal-field parameters for $4f^{N-1}5d$ is therefore not currently possible and it is crucial to begin with good estimates of the parameters and then use spectroscopic information from as many ions as possible to refine the calculation, since the effect of some parameters is more apparent in particular ions. For example, the $4f^{N-1}5d$ configuration for Ce^{3+} is simply $5d$, for which the only parameters are $\zeta(dd)$, and the $B_q^k(dd)$, making this ion particularly suitable for determining the $5d$ crystal-field

parameters. As another example, the energy difference between the first spin-forbidden and spin-allowed $4f^N \rightarrow 4f^{N-1}5d$ transitions for the heavy lanthanides, particularly Tb^{3+} , is dominated by the exchange operators $G^k(fd)$.

Our approach has been to make initial estimates for the parameters and then to determine overall scalings of groups of parameters. The initial estimates have three sources:

1. Parameters for the $4f^{N-1}$ core from parameters for the $4f^N$ configuration of the same ion.
2. $5d$ crystal-field parameters $B_q^k(dd)$ from the Ce^{3+} spectrum.
3. Atomic parameters involving the $5d$ electron from ab initio calculations.

The atomic calculation methods are described by Cowan [5]. The calculations are Hartree–Fock, with relativistic corrections. In Table 1 we give a summary of Hamiltonian parameters and radial integrals. In Fig. 1 we show radial functions P_{nl} for the outer orbitals of Pr^{3+} . The filled $5s$ and $5p$ orbitals define the ionic radius of approximately 1 Å. From the figure we see that only a small fraction of the $4f$ orbitals, but a large proportion of the $5d$ orbitals, extend beyond 1 Å. These observations suggest that, since the $4f$ orbitals are ‘shielded’ from the environment by the $5s$ and $5p$ orbitals, the atomic parameters involving $4f$ electrons for the ions in crystals are likely to be quite similar to the parameters determined for gaseous ions and from ab initio calculations. This is, in fact, what is observed for the $4f^N$ configuration [9]. Though the $5d$ orbitals will be perturbed much more by the host lattice than the $4f$ orbitals, the $F^k(fd)$ and $G^k(fd)$ parameters are largely determined by the part of the $5d$ orbitals close to the nucleus where they interact with the $4f$ orbitals and the $\zeta(dd)$ parameters also have their largest contribution from close to the nucleus. Therefore, we expect that these parameters will also not be very different from the free-ion values.

As we proceed across the lanthanide series, the calculations indicate that the $4f$ orbitals contract substantially, as the nuclear charge increases. The $5d$ orbitals also contract, but not so much. With these contractions in mind, we can understand the trends in the parameters across the series, as we shall explain below.

3.1. Crystal-field parameters

The crystal-field parameters associated with the $5d$ electron of the $4f^{N-1}5d$ configuration are large, typically 10 to 20 times the parameters for the $4f$ electrons. For the hosts that we have studied in detail, $LiYF_4$, CaF_2 , and YPO_4 , the crystal-field splitting of the $5d$ orbitals is approximately $20\,000\text{ cm}^{-1}$. Crystal-field parameters for Pr^{3+} and Tm^{3+} are shown in Table 2. Parameters for other

Table 1

Calculated parameters for the $4f^N$ and $4f^{N-1}5d$ configurations of trivalent lanthanide ions

Ion	Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Tb ³⁺	Dy ³⁺	Ho ³⁺	Er ³⁺	Tm ³⁺	Yb ³⁺	Lu ³⁺
<i>N</i>	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>4f^N</i> parameters and radial integrals														
<i>F</i> ²	–	96 682	100 643	104 391	107 970	111 413	114 744	117 979	121 133	124 216	127 237	130 203	133 120	135 993
<i>F</i> ⁴	–	60 534	63 029	65 384	67 629	69 785	71 866	73 885	75 850	77 769	79 648	81 490	83 301	85 082
<i>F</i> ⁶	–	43 509	45 307	47 003	48 618	50 168	51 663	53 112	54 523	55 899	57 246	58 567	59 864	61 140
<i>ζ</i>	681	798	926	1064	1213	1373	1546	1732	1932	2146	2376	2621	2882	3161
<i>r</i> ²	0.3726	0.3472	0.3216	0.2999	0.2812	0.2648	0.2504	0.2374	0.2258	0.2153	0.2057	0.1969	0.1888	0.1814
<i>r</i> ⁴	0.3155	0.2785	0.2409	0.2113	0.1874	0.1678	0.1514	0.1375	0.1256	0.1153	0.1064	0.0985	0.0916	0.0855
<i>r</i> ⁶	0.5069	0.4297	0.3504	0.2918	0.2472	0.2123	0.1845	0.1620	0.1435	0.1281	0.1151	0.1041	0.0947	0.0866
<i>4f^{N-1}5d</i> parameters and radial integrals														
$\Delta_E(fd)$	57 812	65 413	71 773	77 635	82 813	87 401	91 584	95 256	98 526	101 535	104 024	106 306	108 203	109 809
<i>F</i> ² (<i>ff</i>)	–	–	108 416	111 922	115 304	118 585	121 778	124 897	127 951	130 948	133 894	136 794	139 653	142 474
<i>F</i> ⁴ (<i>ff</i>)	–	–	68 283	70 479	72 594	74 642	76 632	78 573	80 471	82 332	84 159	85 956	87 726	89 472
<i>F</i> ⁶ (<i>ff</i>)	–	–	49 197	50 776	52 295	53 765	55 193	56 585	57 945	59 278	60 587	61 873	63 140	64 389
<i>ζ</i> (<i>ff</i>)	–	873	1025	1167	1321	1487	1665	1858	2064	2284	2520	2773	3041	3328
<i>F</i> ² (<i>fd</i>)	–	30 271	30 300	30 207	30 111	30 010	29 905	29 795	29 681	29 562	29 439	29 312	29 180	29 044
<i>F</i> ⁴ (<i>fd</i>)	–	15 094	15 038	14 890	14 748	14 611	14 477	14 347	14 219	14 092	13 967	13 843	13 720	13 598
<i>G</i> ¹ (<i>fd</i>)	–	12 903	12 914	12 739	12 590	12 461	12 348	12 247	12 156	12 073	11 997	11 927	11 861	11 799
<i>G</i> ³ (<i>fd</i>)	–	11 160	11 135	10 985	10 851	10 728	10 614	10 508	10 408	10 313	10 221	10 133	10 047	9963
<i>G</i> ⁵ (<i>fd</i>)	–	8691	8659	8540	8431	8330	8235	8146	8060	7978	7898	7821	7746	7672
<i>ζ</i> (<i>dd</i>)	1082	1149	1216	1283	1351	1419	1488	1557	1627	1697	1768	1839	1910	1982
<i>r</i> ² (<i>ff</i>)	–	0.2945	0.2788	0.2621	0.2474	0.2343	0.2225	0.2119	0.2022	0.1933	0.1852	0.1777	0.1708	0.1644
<i>r</i> ⁴ (<i>ff</i>)	–	0.1875	0.1705	0.1520	0.1366	0.1235	0.1124	0.1029	0.0946	0.0873	0.0809	0.0752	0.0701	0.0656
<i>r</i> ⁶ (<i>ff</i>)	–	0.2221	0.1965	0.1674	0.1444	0.1258	0.1107	0.0981	0.0876	0.0787	0.0711	0.0646	0.0590	0.0541
<i>r</i> ² (<i>dd</i>)	1.6592	1.6113	1.5676	1.5286	1.4932	1.4609	1.4313	1.4040	1.3788	1.3555	1.3339	1.3138	1.2951	1.2777
<i>r</i> ⁴ (<i>dd</i>)	4.2618	4.0380	3.8396	3.6679	3.5160	3.3807	3.2594	3.1502	3.0515	2.9620	2.8805	2.8063	2.7384	2.6764
<i>4f^N/4f^{N-1}5d</i> radial integrals														
<i>r</i> ¹ (<i>fd</i>)	0.4350	0.4168	0.3953	0.3771	0.3614	0.3477	0.3356	0.3247	0.3150	0.3062	0.2982	0.2908	0.2841	0.2778
<i>r</i> ³ (<i>fd</i>)	2.3338	2.1529	1.9562	1.7941	1.6579	1.5417	1.4414	1.3538	1.2768	1.2085	1.1475	1.0929	1.0436	0.9990
<i>r</i> ⁵ (<i>fd</i>)	17.8557	15.9657	13.9501	12.3567	11.0658	10.0010	9.1098	8.3548	7.7085	7.1504	6.6649	6.2397	5.8652	5.5337

Parameters have units cm⁻¹ and radial integrals have units Å^k.

ions and crystals may be found in Refs. [6,7]. In our calculations we used literature values for the $4f$ parameters and scaled the $5d$ parameters linearly across the lanthanide

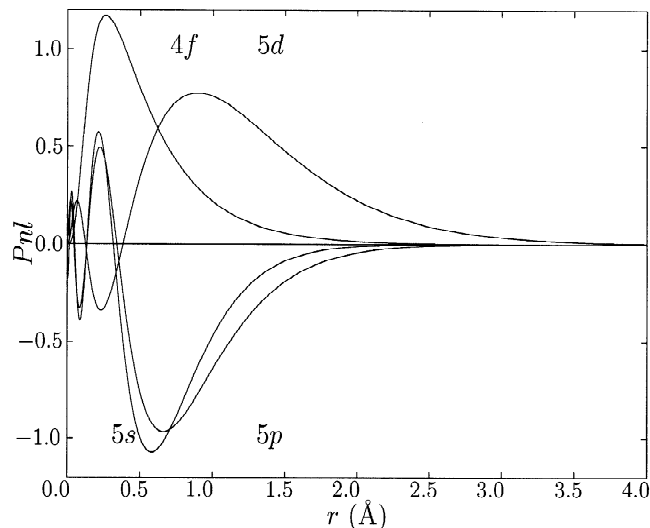


Fig. 1. Radial functions P_{nl} calculated for Pr^{3+} . The function for $5s$ has been multiplied by -1 .

series to give good agreement with experiment. The $4f$ parameters decrease dramatically across the lanthanide series, whereas the $5d$ parameters decrease by a relatively small amount. In our calculations we have used $4f$ crystal-field parameters deduced from $4f^N$ spectra. Since the $4f$ orbitals contract somewhat in the $4f^{N-1}5d$ configuration, as indicated by the differences between the r^k radial integrals in Table 1, it may be useful to reduce their value somewhat. However, our current data are not detailed enough to test this possibility.

Table 2

Crystal-field parameters used in calculations for the $4f^{N-1}5d$ configuration of lanthanide ions in LiYF_4 [6,7]

	Pr ³⁺	Tm ³⁺
$B_0^2(ff)$	481	348
$B_0^4(ff)$	– 1150	– 639
$B_4^4(ff)$	– 1228	– 864
$B_0^6(ff)$	– 89	– 182
$B_4^6(ff)$	– 1213	– 641
$B_0^2(dd)$	4673	4206
$B_0^4(dd)$	– 18 649	– 16 784
$B_4^4(dd)$	– 23 871	– 21 484

Units are cm⁻¹.

For ions near the beginning or end of the lanthanide series the $5d$ crystal-field splitting dominates the spectra, with the splitting caused by atomic interactions giving a fine-structure built on top of the crystal-field splitting. Towards the center of the series the atomic splitting of the $4f^{N-1}$ core is quite large and the $5d$ crystal-field splitting is more difficult to definitively identify. A notable exception is Tb^{3+} , where the large splitting between the lowest states of the $4f^7$ core makes the identification of the $5d$ crystal-field splitting straightforward [7].

We note that the fit to the Ce^{3+} $5d$ energy levels in LiYF_4 is rather poor [8]. This problem is well known and is thought to be a result of distortions of the lattice in the excited states [14,15].

If the crystal-field splitting was merely the result of an electrostatic potential then the parameters would be proportional to the expectation values of the r^k . From Table 1 the ratios of r^2 and r^4 for $5d$ orbitals of the $4f^{N-1}5d$ configuration and $4f$ orbitals of the $4f^N$ configuration are 4.6 and 14 for Pr^{3+} , whereas from Table 2 the crystal-field parameter ratios for LiYF_4 are 10 and 18. For Tm^{3+} the expectation value ratios are 6.7 and 28, whereas the experimental parameter ratios are 12 and 26. The different r^k for $4f$ and $5d$ orbitals reflect the larger radial extent of the $5d$ orbitals, which clearly gives rise to larger parameters, but accurate calculations of crystal-field splitting require the consideration of more than merely electrostatic effects [13–15].

3.2. Atomic interaction parameters

A detailed discussion of experimental and calculated atomic parameters for the $4f^N$ configuration may be found in Carnall et al. [9]. The atomic calculations overestimate the F^k and ζ parameters for $4f^N$, particularly F^2 . More elaborate perturbation-theory calculations [12] reduce this discrepancy.

Atomic parameters predicted by Cowan's computer code [5] for the $4f^N$ and $4f^{N-1}5d$ configurations are given in Table 1. The $F^k(ff)$ and $\zeta(ff)$ parameters are predicted to be slightly larger for the $4f^{N-1}5d$ configuration than the $4f^N$ configuration. This is a result of contraction of the $4f$ orbitals in the $4f^{N-1}5d$ configuration. To take this contraction into account for the $4f^{N-1}5d$ configuration we have taken F^k , ζ and other parameters fitted to $4f^N$ energy levels of lanthanide ions in LaF_3 and increased them by 6% [7].

The calculated $F^k(ff)$ parameters increase dramatically across the series, as the $4f$ orbitals contract. The calculated $F^k(fd)$ and $G^k(fd)$ parameters decrease gradually, since the $5d$ orbitals do not contract as much as the $4f$ orbitals. Similarly, the $\zeta(ff)$ increase dramatically and the $\zeta(dd)$ somewhat less.

We found that the calculated $F^k(fd)$ and $G^k(fd)$ parameters were too large, particularly from examining the

splitting between the high-spin and low-spin states of the $4f^{N-1}5d$ configuration of the heavy lanthanides [7]. Better agreement was obtained when the fd parameters were reduced to about 67% of their calculated value. In Table 3 we show available atomic parameters for gaseous ('free') ions. These also show general reductions from the calculated values, so this reduction is not purely induced by the crystalline environment. The free-ion data indicate that the overestimation is mainly for the $F^2(fd)$ and $G^1(fd)$ parameters, so in future calculations, when more detailed spectra are available, it may be useful to experiment with different parameter ratios.

Some papers on the $4f^{N-1}5d$ configuration have tried to analyze the spectra by considering only the $5d$ crystal-field and the atomic splitting of the $4f^{N-1}$ core (e.g. [18]). However, this is not a very good approximation since the Coulomb interaction between the $4f$ and $5d$ electrons (parameterized by $F^k(fd)$ and $G^k(fd)$) has a significant effect. This is illustrated in Fig. 2 of Ref. [4] and Fig. 6 of Ref. [7].

3.3. Differences between the average energies of the configurations

The difference between average energies of the $4f^{N-1}5d$ and $4f^N$ configurations, parameterized by $\Delta_E(fd)$, may be calculated by comparing the total energies of the ion in different configurations. Note that this is not merely the energy difference between the $4f$ and $5d$ orbitals, which is much larger but is compensated by relaxation of the other orbitals of the ion.

Note that $\Delta_E(fd)$ should not be confused with the energy of the first $4f^N \rightarrow 4f^{N-1}5d$ transition (see, for example, Fig. 2 of [2]). This energy depends crucially on the relative energy of the lowest $4f^N$ and $4f^{N-1}5d$ states. For example, the $^8S_{7/2}$ states of the $4f^7$ ground configuration of Gd^{3+}

Table 3
Experimental parameters for the $4f^{N-1}5d$ configuration of gaseous lanthanide ions

	Ce^{3+}	Pr^{3+}	Tb^{3+}	Lu^{3+}
$\Delta_E(fd)$	49 943±72	57 033±74		104 474±61
$F^2(ff)$				
$F^4(ff)$				
$F^6(ff)$				
$\zeta(ff)$		926±42		3406±38
$F^2(fd)$		21 941±437		22 675±509
$F^4(fd)$		16 690±791		19 606±1323
$G^1(fd)$		10 374±189	7456	7064±178
$G^3(fd)$		12 369±702	8616	11 281±1427
$G^5(fd)$		8786±546	6003	7087±1687
$\zeta(dd)$	996±40	1014±71	1389	1939±56

Units are cm^{-1} . Experimental data are from Ce^{3+} [22], Pr^{3+} [23], Tb^{3+} [24], Lu^{3+} [25]. Data are also available from NIST [26]. We have refitted the data for Ce^{3+} , Pr^{3+} and Lu^{3+} in order to ensure consistency with our choices of Hamiltonian operators.

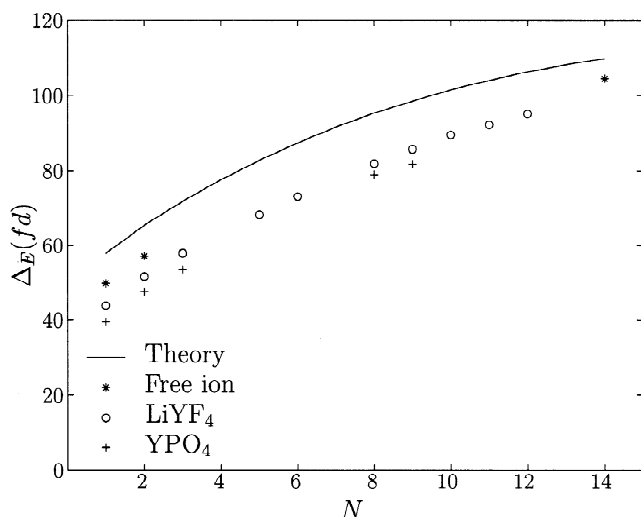


Fig. 2. Theoretical and experimental differences between the average energies of the $4f^{N-1}5d$ and $4f^N$ configurations. Units are 1000 cm^{-1} . Theoretical values are from Table 1. Experimental data for free ions are from Table 3. Experimental data for ions in LiYF_4 and YPO_4 are from Refs. [6,7].

and the $4f^7$ core of the $4f^75d$ excited configuration of Tb^{3+} have particularly low energies. Hence, the onset of the $4f^7 \rightarrow 4f^65d$ transitions in Gd^{3+} is particularly high and the onset of the $4f^8 \rightarrow 4f^75d$ transitions in Tb^{3+} is particularly low.

Calculated and experimental (free ion, LiYF_4 , and YPO_4) values of $\Delta E(fd)$ are shown in Fig. 2. The values for CaF_2 are very similar to LiYF_4 , which is to be expected, since both hosts have F^- ligands. Note that the difference between experiment and theory becomes smaller towards the end of the series. Possible mechanisms for the depression of the excited configuration energy are discussed by Dorenbos [19].

4. Transition intensities

Transitions between $4f^N$ and $4f^{N-1}5d$ are electric-dipole allowed and it is straightforward to calculate the matrix elements of the electric-dipole moment operator for the transitions. This is in contrast to transitions within the $4f^N$ configuration, for which a much more elaborate calculation is necessary [16]. However, since the $5d$ orbitals are more extended than the $4f$ orbitals, there is a displacement of the equilibrium positions of the ligands in the excited states and most of the intensity is in vibronic bands. Background on the modeling of such transitions may be found in the literature [20]. In our modeling we have approximated the vibronic bands by a single Gaussian and more accurate band-shape calculations are an obvious area for improvement.

Most of our data are from excitation spectra, and so absolute transition intensities are not measured. Moreover,

there is the possibility of saturation of the more intense transitions distorting even the relative intensities, causing the most intense transitions to lose some intensity. The best quantitative data related to transition intensities come from lifetime measurements.

The radial integrals of r between $4f$ orbitals of the $4f^N$ configuration and $5d$ orbitals of the $4f^{N-1}5d$ configuration are required for lifetime calculations. These integrals are given in Table 3. They reduce across the series, as the $4f$ orbitals contract. Calculations of radiative lifetimes of Ce^{3+} , Pr^{3+} , Nd^{3+} , Er^{3+} and Tm^{3+} in LiYF_4 using these calculated radial integrals give good agreement with experiment [8]. Lifetimes for the spin-allowed emission transitions for ions in the first half of the series (Ce^{3+} , Pr^{3+} , Nd^{3+}) are short (tens of nanoseconds). For ions in the second half of the series (i.e. Er^{3+} and Tm^{3+}) the lowest energy $4f^{N-1}5d$ states are ‘high-spin’ (HS), i.e. have a spin quantum number that is one unit higher than the spin of any of the $4f^N$ states, and so all emission is spin-forbidden. These spin-forbidden emissions have lifetimes in the μs range. In these cases, both long-lived emission from HS states and short-lived spin-allowed emission from higher-energy ‘low-spin’ (LS) states are observed [21]. The radiative and non-radiative lifetimes of the LS states may be deduced from lifetime and intensity measurements [8].

For Ce^{3+} and Pr^{3+} the calculated lifetimes agree with the experimental values within 20%. For ions later in the series the agreement is not so good, but in most cases the difference is less than 50%. This is an encouraging result considering that the lifetimes depend on the squares of matrix elements and the third power of the transition energies, as well as the refractive index [20].

5. Conclusions

Our comparisons between theory and experiment show that it is possible to understand the spectroscopy of the $4f^{N-1}5d$ configurations of lanthanide ions in several host crystals in terms of a relatively straightforward theoretical model. However, the exact values for many of the Hamiltonian parameters are not known. More detailed data (including polarization measurements) would give definitive identification of the electronic origins and allow the accurate determination of more of the parameters and hence better calculations of various spectroscopic properties.

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References

- [1] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink, *Science* 283 (1999) 663.
- [2] P. Dorenbos, *J. Lumin.* 91 (2000) 91.
- [3] M. Laroche, J.-L. Doualan, S. Girard, J. Margerie, R. Moncorgé, *J. Opt. Soc. Am. B* 17 (2000) 1291.
- [4] M.F. Reid, L. van Pieterse, R.T. Wegh, A. Meijerink, *Phys. Rev. B* 62 (2000) 14744.
- [5] R.D. Cowan, *The Theory of Atomic Structure and Spectra*, University of California, Berkeley, 1981.
- [6] L. van Pieterse, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, *Phys. Rev. B* 65 (2002) 045113.
- [7] L. van Pieterse, M.F. Reid, G.W. Burdick, A. Meijerink, *Phys. Rev. B* 65 (2002) 045114.
- [8] L. van Pieterse, M.F. Reid, R.T. Wegh, A. Meijerink, *J. Chem. Phys.* 115 (2001) 9382.
- [9] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana, *J. Chem. Phys.* 90 (1989) 3443.
- [10] C. Görller-Walrand, K. Binnemans, Rationalization of crystal–field parameterization, in: J.K.A. Gschneidner, L. Eyring (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 23, North-Holland, Amsterdam, 1996, pp. 121–283.
- [11] D.J. Newman, B. Ng (Eds.), *Crystal Field Handbook*, Cambridge University Press, Cambridge, 2000.
- [12] J. Morrison, K. Rajnak, *Phys. Rev. A* 4 (1971) 643.
- [13] B. Ng, D.J. Newman, *J. Chem. Phys.* 87 (1987) 7110.
- [14] J. Andriessen, H. Merenga, C.M. Combes, P. Dorenbos, C.W.E. van Eijk, in: *Proc. Int. Conf. on Inorganic Scintillators and their Applications, SCINT95*, Delft University Press, The Netherlands, 1996, pp. 142–143.
- [15] M. Marsman, J. Andriessen, C.W.E. van Eijk, *Phys. Rev. B* 61 (2000) 16477.
- [16] C. Görller-Walrand, K. Binnemans, in: K.A. Gschneidner Jr., L. Eyring (Eds.), *Handbook on the Physics and Chemistry of the Rare Earths*, Vol. 25, North Holland, Amsterdam, 1998, p. 101.
- [17] G.W. Burdick, F.S. Richardson, M.F. Reid, H.J. Kooy, *J. Alloys Comp.* 225 (1995) 115.
- [18] A. Meijerink, R.T. Wegh, L. van Pieterse, *Proc. Electrochem. Soc.* 99-40 (2000) 23.
- [19] P. Dorenbos, *Phys. Rev. B* 62 (2000) 15640.
- [20] B. Henderson, G.F. Imbusch, *Optical Spectroscopy of Inorganic Solids*, Clarendon Press, Oxford, 1989.
- [21] R.T. Wegh, A. Meijerink, *Phys. Rev. B* 60 (1999) 10820.
- [22] R.J. Lang, *Phys. Rev.* 49 (1936) 552.
- [23] J. Sugar, *J. Opt. Soc. Am.* 55 (1965) 1058.
- [24] N. Spector, J. Sugar, *J. Opt. Soc. Am.* 66 (1976) 436.
- [25] J. Sugar, V. Kaufman, *J. Opt. Soc. Am.* 62 (1972) 562.
- [26] National Institutes of Standards and Technology, Physical Reference Data, <http://physics.nist.gov/>.