

# A complete $4f^n$ energy level diagram for all trivalent lanthanide ions

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## Abstract

We describe the calculations of the  $4f^n$  energy levels, reduced matrix elements for  $4f^n$ - $4f^n$  transitions and the simulation of absorption and emission spectra. A complete  $4f^n$  energy level diagram is calculated for all trivalent lanthanide ions in  $\text{LaF}_3$ . The calculated energy levels are compared with experimentally obtained energies. For Ce, Pr, Nd, Eu, Gd, Ho, Er, Tm and Yb many, and in some cases all, energy levels have been observed. This work provides a starting point for future investigation of as yet unobserved VUV energy levels.

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## 1. Introduction

Extensive measurements of energy levels of the  $4f^n$  configurations of lanthanide ions in various host lattices were carried out in the 1950s and 1960s. Much of this work was carried out by Dieke and co-workers and the data summarized in his 1968 book [1] (published posthumously). The energy-level diagram for trivalent lanthanide ions presented in that book is commonly referred to as a “Dieke diagram”. These diagrams are useful because the energies of the  $J$  multiplets vary by only a small amount in different host crystals. The diagram allows rapid identification of the energy levels in new hosts, and has been a crucial tool in the design of materials suitable for phosphors or lasers.

As this diagram developed in the 1960s there was a fruitful interplay between measurements, theoretical models, and computational modeling of energy levels. Two- and three-body operators representing configura-

tion interaction corrections to the Coulomb interaction were found to be necessary to accurately reproduce the observed spectra [2–4]. Anomalies in the crystal-field splitting were also noted, but the modeling of correlation effects on the crystal-field levels were not performed until the late 1970s [5,6].

Dieke’s experimental data were largely gathered using the  $\text{LaCl}_3$  host. The high-symmetry ( $C_{3h}$ ) sites in this crystal mean that only a small number of crystal-field parameters (four) are required to fit the spectra, which made it attractive for early studies. However, other hosts with better optical properties, especially in the UV region, were sought. The  $\text{LaF}_3$  host-lattice has the advantage of being optically transparent up into the VUV, and the chemical stability in air makes it easy to handle.

An important legacy of the work by Bill Carnall and his co-workers was a detailed study of the spectra of trivalent lanthanide ions in  $\text{LaF}_3$ . They compared the absorption spectra of all lanthanides in  $\text{LaF}_3$  with calculated energies for  $C_{2v}$  site symmetry, which is a good approximation of the actual  $C_2$  site [7]. For configurations with an odd number of  $4f$ -electrons each multiplet with quantum number  $J$  splits into  $J + 1/2$

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crystal field levels in any symmetry lower than cubic. In the absence of a magnetic field the energy levels are doubly degenerate due to Kramers' degeneracy. For configurations with an even number of  $4f$ -electrons, the symmetry must be lower than  $D_3$  in order to split up into the maximum number of  $2J + 1$  crystal field levels. The  $\text{LaF}_3$  host-lattice is very suitable for comparison of calculations and measurements of energy levels as the  $C_2$  site symmetry in  $\text{LaF}_3$  [8] causes all multiplets to split up completely for lanthanide ions with an even number of  $4f$ -electrons.

In 1977 Carnall, Crosswhite, and Crosswhite published the "Blue Report" [9], which, curiously, contains no date and no report number. This was an important guide to workers in the late 1970s and 1980s for the analysis of spectra in other hosts, and the matrix elements were used by many workers in their analysis of transition intensities.

A decade later the report by Carnall et al. [10] and the subsequent paper [11] provided what is arguably still the most thorough study of the energy levels of the entire series of lanthanide ions in a host crystal. An important feature of this work was the detailed comparison between the computational modeling and the experimental data, with the analysis directed by the requirement for the Hamiltonian parameters to vary smoothly across the series. The parameters derived in that work have been widely used as starting points for analysis of other systems, and the data have been used to test extensions to the models, such as the inclusion of correlation crystal field effects, see, for example, Li and Reid [12].

The experimental data used by Carnall and coworkers rarely extended above  $40\,000\text{ cm}^{-1}$ . Parameter values were optimized by least squares fitting of energy level calculations to experimentally obtained energies. Since the absorption spectra recorded concern the energy region up to about  $40\,000\text{ cm}^{-1}$ , calculations are expected to be less accurate in the VUV region, especially for gadolinium which has 1716 (doubly degenerate) energy levels, where the parameters were obtained by fitting to only the lowest 70 levels measured by Carnall [11]. While there was some work in the 1970 and 1980s using synchrotron radiation [13,14], and multi-photon spectra have been used to probe a few levels, it is only relatively recently that extensive, detailed, high-resolution spectra have become available. We are now in the process of extending Carnall's energy-level diagram for trivalent lanthanide ions in  $\text{LaF}_3$  by assembling and analyzing data from synchrotron-radiation measurements [15–17], and laser techniques, including two-photon absorption and excited-state absorption [18]. This paper reports preliminary results of comparisons between calculations based on Carnall's parameters and the new experimental data. We show that the model is capable of providing a good

description of the new experimental measurements, and comment on some of the technical issues involved in the calculations.

## 2. Description of the calculations

This section describes the energy level calculations using programs written by Reid and coworkers [19,20], based on the model of Carnall [10] and Crosswhite and Crosswhite [21]. Besides energy level calculations the program also offers the possibility to calculate transition intensities and reduced matrix elements for transitions between multiplets and it is possible to simulate absorption and emission spectra. Recently, Edvardsson and Åberg [22] reported the complete energy level diagram of all actinides, using a similar calculation program.

The free-ion energy level calculation uses a matrix containing all allowed electronic states for a certain  $4f^n$  configuration. The matrix elements are

$$\langle \Psi_{[\tau SL]J} | \mathcal{H} | \Psi_{[\tau' S' L']J'} \rangle, \quad (1)$$

where  $\Psi_{[\tau SL]J}$  and  $\Psi_{[\tau' S' L']J'}$  are basis functions for the  $4f^n$  configuration and  $\mathcal{H}$  is the parameterized Hamiltonian. This expression is valid only for free-ion calculations, where  $J$  is a good quantum number.  $[\tau SL]$  are "nominal" identifiers for states, as  $\tau$ ,  $S$  and  $L$  are not good quantum numbers, where  $\tau$  (sometimes designated as  $\alpha$ ) is seniority, and  $S$  and  $L$  are spin and angular momentum quantum numbers, respectively. In a crystalline lattice, the non-spherical elements of the crystal field intermix states of different  $J$  and  $M_J$ , and the only good quantum number is the group theoretical irreducible representation ("irrep") of the site symmetry,  $\Gamma$  and the corresponding basis functions are  $\Psi_{[\tau SLJM_J]\Gamma}$ .

Calculation of the angular part of the matrix elements can be done exactly following the methods of Crosswhite and Crosswhite [21]. The radial parts of the matrix elements are included in the calculation parameters.

The full Hamiltonian  $\mathcal{H}_{\text{full}}$  has separable contributions from the "free-ion" terms and from the crystal field.

$$\mathcal{H}_{\text{full}} = \mathcal{H}_{\text{free-ion}} + \mathcal{H}_{\text{CF}}. \quad (2)$$

The expression for  $\mathcal{H}_{\text{free-ion}}$  is

$$\begin{aligned} \mathcal{H}_{\text{free-ion}} = & E_{\text{AVG}} + \sum_{k=2,4,6} F^k f_k + \zeta(4f) A_{\text{So}} \\ & + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) \\ & + \sum_{i=2,3,4,6,7,8} T^i t_i + \sum_{k=2,4,6} P^k p_k \\ & + \sum_{j=0,2,4} M^j m_j. \end{aligned} \quad (3)$$

and is given using the notation of standard practice [11,23].

The spherically symmetric part of the perturbations of the free ion and the crystal field are represented together by  $E_{\text{AVG}}$ . The value of  $E_{\text{AVG}}$  shifts the energy of the entire  $4f^n$  configuration, and represents the energy difference between the ground state energy and the configuration center of gravity (barycenter).

Diagonalization of the energy matrix yields eigenvectors describing the free ion levels, and eigenvalues of the matrix are the multiplet energies. At this point, reduced matrix elements for transition intensities between  $J$ -multiplets can be calculated. These  $(U^{(\lambda)})^2$  reduced matrix elements can be used in Judd–Ofelt calculations [24] for transition intensities and branching ratios.

The crystal field Hamiltonian is parameterized by  $\mathcal{H}_{\text{CF}}$  and is expressed in Wybourne notation as [25]

$$\mathcal{H}_{\text{CF}} = \sum_{k,q} B_q^k C_q^{(k)}, \quad (4)$$

where  $B_q^k$  parameters define the radially dependent part of the one-electron crystal field interaction, and  $C_q^{(k)}$  are the many-electron spherical tensor operators for the  $4f^n$  configuration. For  $4f$ -electron configurations the values of  $k$  are restricted to 2, 4 and 6. The applicable values of  $q$  depend on the site-symmetry of the lanthanide ion in the host-lattice. For the  $C_{2v}$  effective site symmetry used for  $\text{LaF}_3$  the restrictions are:  $q = \text{even}$  and  $0 \leq q \leq k$ .

The crystal field splits each multiplet into individual Stark components. Eigen-vectors obtained from diagonalization of the full Hamiltonian are used to obtain dipole strengths for transitions between individual crystal field levels.

Diagonalization of the matrix containing the complete Hamiltonian yields all states of the  $4f^n$  configuration. The gadolinium wavefunction matrix has a size of  $3432 \times 3432$  (which can be block-diagonalized into smaller submatrices), all other energy matrices are smaller. In Table 1 the number of electrons,  $SL$  states,  $SLJ$  multiplets and  $SLJM$  energy levels are listed for the trivalent lanthanide ions. The number of energy levels in the table does not take Kramers' degeneracy into account, as in the absence of a magnetic field all energy levels of configurations with an odd number of  $4f$ -electrons are doubly degenerate.

With the current computer systems it is no longer necessary to perform “truncated” calculations, where only energy levels up to a certain energy are included in the calculation and the complete set of wavefunctions are not used. In order to keep the calculations manageable, Carnall et al. [11] used truncation for configurations where the Hamiltonian matrices were greater than  $200 \times 200$ . This truncation may not only have a significant impact upon reported wavefunctions, but also may produce shifts in the calculated energies when compared to a full energy level calculation. We

performed energy level calculations for the  $4f^7$  energy levels of  $\text{Gd}^{3+}$  in  $\text{LaF}_3$  up to  $51\,000\text{ cm}^{-1}$ , which is the energy range studied by Carnall et al. [10] using truncation at different energies. Fig. 1 shows the energy shift for each level caused by truncation of the calculation as a function of the difference in energy between the calculated level and the truncation energy. From this figure it can be concluded that in order to have no significant effect on the calculated energies the truncation should be at least  $30\,000\text{ cm}^{-1}$  above the highest energy level of interest. For modern computers with a high clock speed and a large amount of memory there is no longer a need for truncation when calculating the  $4f^n$  levels of lanthanides. Another speed improving factor is the use of a “relatively robust” tridiagonalization routine [26], which for large matrices can result in a factor of 20 increase in speed. Especially in calculations where multiple diagonalizations are used this 20-fold increase in speed is important.

If a sufficient number of experimentally obtained values for energy levels is known, a least squares fitting routine can be used to adjust some or all of the parameters to give a better agreement between calculation and experiment. Care has to be taken using this

Table 1  
Number of electrons,  $SL$  states,  $SLJ$  multiplets and  $SLJM$  energy levels for all trivalent lanthanide ions

	Ce (Yb)	Pr (Tm)	Nd (Er)	Pm (Ho)	Sm (Dy)	Eu (Tb)	Gd
$n$	1	2	3	4	5	6	7
$SL$	1	7	17	47	73	119	119
$SLJ$	2	13	41	107	198	295	327
$SLJM$	14	91	364	1001	2002	3003	3432

Note. Configurations with  $14-n$  electrons (listed in parentheses) have the same number of states as configurations with  $n$  electrons.

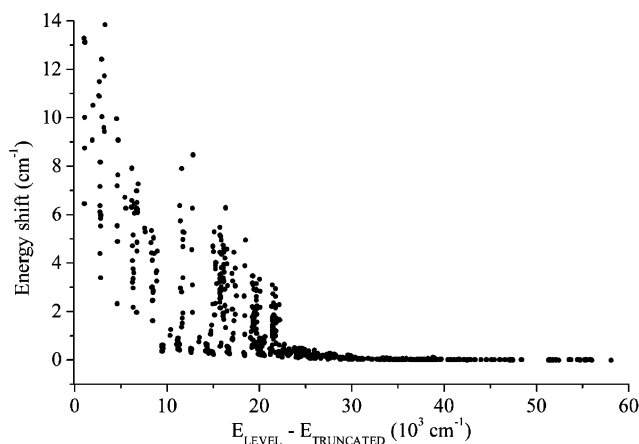


Fig. 1. Energy shifts for energy levels of  $\text{Gd}^{3+}$  up to  $51\,000\text{ cm}^{-1}$  due to truncation of the wavefunctions at different energies.

procedure to ensure that the set of parameters giving the best agreement yields physically reasonable parameter values. The standard deviation  $\sigma$  is used as a measure for the quality of this fit.

$$\sigma = \sqrt{\frac{\sum(E_{\text{exp}} - E_{\text{calc}})^2}{N - P}} \quad (5)$$

In this formula  $E_{\text{exp}}$  and  $E_{\text{calc}}$  are the experimental and calculated energies for the energy levels.  $N$  is the number of experimental levels and  $P$  is the number of parameters being varied. A parameter set giving a value of  $\sigma$  smaller than  $20 \text{ cm}^{-1}$  is considered to be a good fit [27].

After calculation of the crystal field levels a simulated absorption or emission spectrum may be plotted that is based on the calculated transition energies and intensities that takes into consideration the temperature and spectral linewidths. This simulated spectrum may be directly compared with experimental traces, and may help to facilitate interpretation of the experimental results.

### 3. Results and discussion

Using the parameter values published by Carnall et al. [11] we calculate the complete  $4f^n$  energy level diagram for all lanthanide ions in  $\text{LaF}_3$  and compare the calculations with the recent extension of the Dieke diagram with experimentally observed energy levels up to  $70\,000 \text{ cm}^{-1}$ . The highest level calculated was the  $^1S(1)_0$  level of terbium at approximately  $193\,000 \text{ cm}^{-1}$ . The complete  $4f^n$  energy level diagram is depicted in Fig. 2.

Fig. 3 shows the energy levels calculated in the region  $39\,000$  up to  $75\,000 \text{ cm}^{-1}$ . This is the region that is experimentally accessible using VUV spectroscopy. In this figure the calculated absorption energies of the lowest  $4f^n-4f^{n-1}5d$  transitions in  $\text{LaF}_3$  (based upon Ref. [29]) are indicated.

It is now well understood that for configurations with more than 7  $4f$ -electrons there exist so-called low-spin and high-spin  $4f^{n-1}5d$  states [28]. For example, the trivalent terbium ion has 8  $4f$ -electrons. When one of the  $4f$ -electrons is promoted to a  $5d$ -orbital, the remaining  $4f^7$  core has all spins parallel and the spin multiplicity is 8. There are two possibilities for the orientation of the spin of the  $d$ -electron with this  $4f^7$  core. In the case of a parallel spin of the  $d$ -electron, a high-spin configuration is formed, with a spin-multiplicity of 9 which is lower in energy than the low-spin configuration with the spin of the  $d$ -electron opposite to the parallel  $4f$ -electrons giving a spin multiplicity of 7. Transitions from the ground state to the low-spin state do not change the spin of the electrons, and are thus

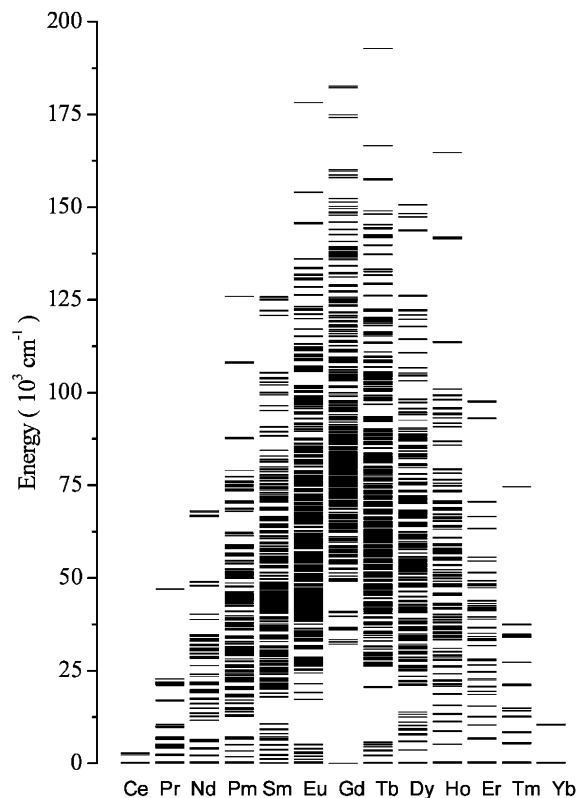


Fig. 2. Complete  $4f^n$  energy level diagram for the trivalent lanthanides in  $\text{LaF}_3$  calculated using parameters reported by Carnall [10].

“spin-allowed” and therefore more intense than the “spin-forbidden” transitions to the high-spin states. Dorenbos [29] reviewed the position of the  $4f^{n-1}5d$  states in many host-lattices and showed that the position of the first  $4f^{n-1}5d$  absorption band in a host-lattice could be estimated if the position is known for one of the lanthanide ions. In Fig. 3 the calculated positions of spin-allowed and spin-forbidden  $4f^{n-1}5d$  absorptions for  $\text{Ln}^{3+}$  in  $\text{LaF}_3$  are indicated with circles and squares, respectively.

Not all  $4f^n$ -levels in Fig. 3 are expected to be observed. The first reason for this is that the relatively weak  $4f^n-4f^n$  transitions are obscured by intense  $4f^n-4f^{n-1}5d$  absorptions that occur in this energy region. Another reason for the fact that not all energy levels can be observed is the occurrence of transitions to energy levels with a change in  $J$  of more than six with respect to the ground state. Transitions to these states are “forbidden” and tend not to be seen. A large number of energy levels in this region have been observed using excitation with synchrotron radiation [15,16], an overview of these energy levels is given in Fig. 4. If emission has been observed from this level this is indicated with a semicircle. Emission originating from a certain energy level can occur when the energy gap to the next lower level is more than four or five times the maximum

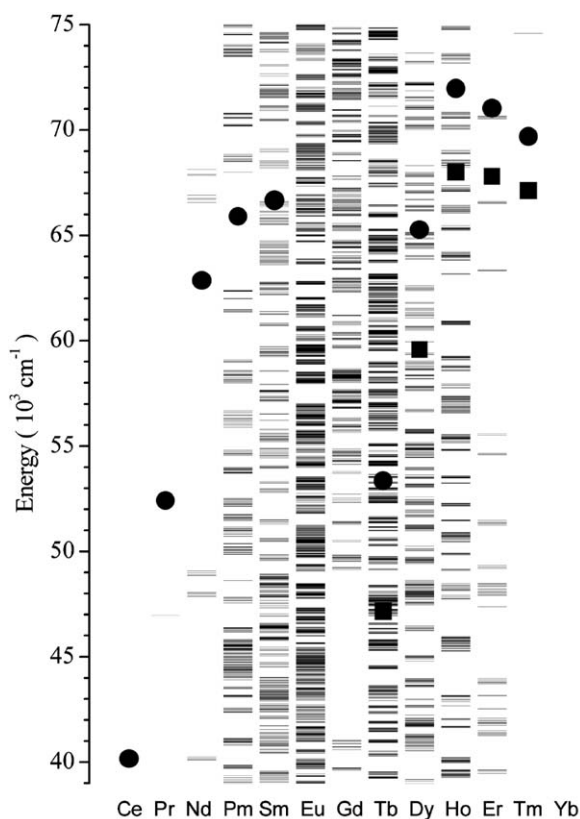


Fig. 3. Energy level diagram for the lanthanides in  $\text{LaF}_3$  in the region  $39\,000\text{--}75\,000\text{ cm}^{-1}$  calculated using parameters reported by Carnall [10]. The calculated lowest positions of the low-spin and high-spin  $4f^{n-1}5d$  states in  $\text{LaF}_3$  (based upon Ref. [29]) are indicated with filled circles and squares, respectively.

phonon energy of the host-lattice. If the energy gap is smaller, then multi-phonon relaxation dominates and emission is no longer seen. In  $\text{LaF}_3$  the maximum phonon energy is about  $350\text{ cm}^{-1}$  and emission can be expected from energy levels with an energy gap of  $1800\text{ cm}^{-1}$  or more to the next lowest level.

For  $\text{Ce}^{3+}$  [30,31] and  $\text{Pr}^{3+}$  [32,33] all  $4f^n$  levels have been observed. As can be seen when comparing Fig. 3 with Fig. 4 there are a few levels of  $\text{Nd}^{3+}$  around  $68\,000\text{ cm}^{-1}$  that have not been measured as they are situated within the  $4f^25d$  absorption band. Downer et al. [34] successfully applied two-photon excitation to investigate the  $4f^7$  energy levels of  $\text{Eu}^{2+}$  in  $\text{CaF}_2$  that are situated within the  $4f^65d$  absorption band. Since  $\text{Nd}^{3+}$  shows resonant one-photon absorption at approximately  $34\,000\text{ cm}^{-1}$ , two-photon excitation from the ground state is not probable. Two-photon absorption from an excited state of  $\text{Nd}^{3+}$  may be used to measure the position of the VUV levels.  $\text{Pm}^{3+}$  is a radioactive ion, with a lifetime of about 2.5 years. As far as we know there are no reports on the VUV energy levels of  $\text{Pm}^{3+}$ . Below the energy level calculated at  $61\,000\text{ cm}^{-1}$  there is an energy gap of more than  $2000\text{ cm}^{-1}$  and this indicates

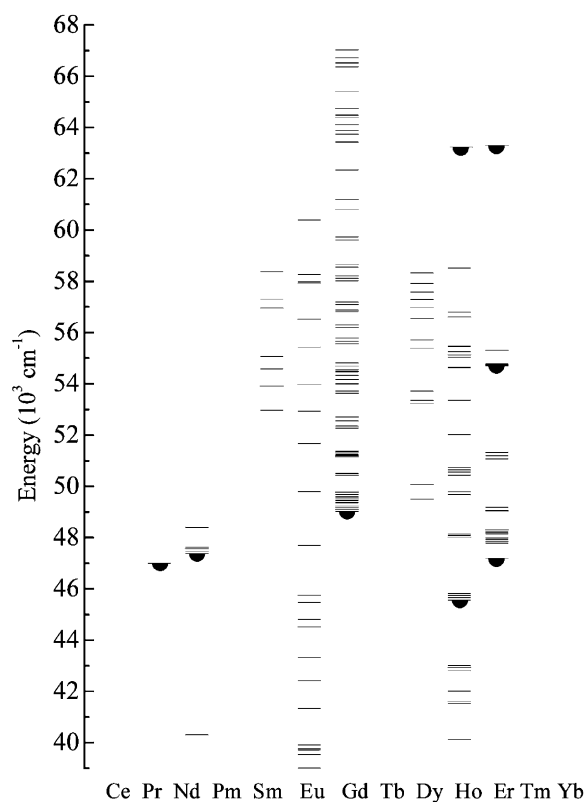


Fig. 4. Energy level diagram showing all experimentally observed  $4f^n$  energy levels for the trivalent lanthanides in the range  $39\,000\text{--}70\,000\text{ cm}^{-1}$ . Levels from which emission is observed are marked with a semicircle.

the possibility for emission from this level in  $\text{LaF}_3$ . However, as  $\text{Pm}^{3+}$  decays to  $\text{Sm}^{3+}$  ( $\beta$  decay), the  $\text{Sm}^{3+}$  eventually becomes a dopant in the crystal, and we expect efficient  $\text{Pm}^{3+} \rightarrow \text{Sm}^{3+}$  energy transfer to occur, quenching the  $\text{Pm}^{3+}$  emission. For  $\text{Sm}^{3+}$  some energy levels have been measured between  $52\,000$  and  $58\,000\text{ cm}^{-1}$ , and there are many levels that still have to be measured [15]. Many of the  $\text{Eu}^{3+}$  levels in the VUV have been identified, but above  $60\,000\text{ cm}^{-1}$  a charge transfer transition hampers the observation of  $\text{Eu}^{3+}$  excitation lines.

The VUV levels of  $\text{Gd}^{3+}$  have been measured up to  $68\,000\text{ cm}^{-1}$  and most of the calculated multiplets have been observed. Recently, high-resolution excited state absorption measurements showed differences between calculated and experimental energies of up to  $150\text{ cm}^{-1}$  for the levels probed [18]. This is not unexpected as the parameter values calculated by Carnall et al. [10] are based on 70 levels in the UV region of the spectrum with only a few VUV levels included in the fit. Moreover, the crystal field parameter values used for the calculation of the  $\text{Gd}^{3+}$  energy levels were set to the values for  $\text{Tb}^{3+}$  by Carnall. Upon inclusion of the VUV levels of  $\text{Gd}^{3+}$  the parameter values changed to some extent, but not more than a few percents.

The observation of the  $4f^8$  levels of  $Tb^{3+}$  in the VUV region of the spectrum is not possible using one photon techniques as the  $4f^7 5d$  bands start absorbing in the UV. We expect that two-photon excitation can be used to probe these levels, in analogy with the  $Eu^{2+}$  experiments described by Downer et al. [34]. Not all  $4f^9$  levels of  $Dy^{3+}$  have been observed yet and for this ion the  $4f^8 5d$  bands start to absorb at  $58\,000\text{ cm}^{-1}$ . Many of the  $4f^{10}$  levels of  $Ho^{3+}$  have been measured and recently emission from the  $^3P(1)_2$  level of  $Ho^{3+}$  situated at  $63\,000\text{ cm}^{-1}$  has been observed in  $YF_3$  [17].

Nearly all energy levels of  $Er^{3+}$  have been measured. The  $^2F(2)_{5/2}$  level situated at  $63\,000\text{ cm}^{-1}$  is the highest emitting level observed for  $Er^{3+}$  in  $LaF_3$  [16]. In Fig. 3 the  $^2G(2)_{7/2}$  level is situated around  $66\,500\text{ cm}^{-1}$ , just below the calculated position of the high-spin  $4f-5d$  absorption. This position is, however, the maximum of the  $f-d$  absorption band so the onset will be at lower energy and therefore the  $^2G(2)_{7/2}$  cannot be observed. Three multiplets situated at even higher energies, the  $^2G(2)_{9/2}$ ,  $^2F(1)_{5/2}$  and  $^2F(1)_{7/2}$  are calculated at  $70\,000$ ,  $93\,000$  and  $97\,800\text{ cm}^{-1}$ , respectively. For  $Tm^{3+}$  the  $^1S_0$  level is the only energy level that has not been observed yet. It is calculated at approximately  $73\,000\text{ cm}^{-1}$  and is situated above the onset of the  $4f^{11} 5d$  absorption bands. Finally,  $Yb^{3+}$  has no  $4f$  levels in the VUV.

#### 4. Conclusions

The Hamiltonian parameters for trivalent lanthanide ions derived by Carnall and co-workers for the  $LaF_3$  host are a valuable starting point for the analysis of the VUV levels of the  $4f^n$  configurations. Advances in computer technology now allow routine calculations for complete  $4f^n$  configurations. We have generated a complete  $4f^n$  energy level diagram and begun the process of analyzing the available experimental data in the VUV region. Comparison of the calculated energy level scheme with experimentally obtained energies allows identification of many  $4f^n$  levels that have been measured using synchrotron radiation, and predicts regions where high energy levels of various lanthanides that have not been observed yet may be probed by one- or two-photon spectroscopy. Using the extensive VUV data it should now be possible to further refine the parameter values.

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