Spectroscopy of high-energy states of lanthanide ions

February 15, 2010

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Abstract

We discuss recent progress and future prospects for the analysis of the 4f\textsuperscript{N−1}5d excited states of lanthanide ions in host materials. Ab-initio calculations for Ce\textsuperscript{3+} in LiYF\textsubscript{4} are used to estimate crystal-field and spin-orbit parameters for the 4f\textsuperscript{1} and 5d\textsuperscript{1} configurations. We discuss the possibility of using excited-state absorption to probe the electronic and geometric structure of the 4f\textsuperscript{N−1}5d excited states in more detail and we illustrate these ideas with calculations for Yb\textsuperscript{2+} ions in SrCl\textsubscript{2}. 
1 Introduction

The electronic structure of the $4f^N$ configuration of lanthanide ions in condensed matter environments has been a field of intense study since the 1960s. The parametric models that were developed in the 1960s [1, 2, 3] gained further sophistication through the 1970s and 1980s (see, for example, Ref [4]). For a recent review see Ref. [5].

Many applications of lanthanide materials, such as scintillators, lasers, and phosphors, involve the $4f^{N-1}5d$ excited configuration. An understanding of these states, and other high-energy states, such as charge-transfer, conduction-band, and exciton states [6, 7, 8, 9], is crucial to the development of better materials for such applications.

Transitions to the $4f^{N-1}5d$ excited states of lanthanide ions have been studied for a long time, particularly for divalent ions [10, 11] and for Ce$^{3+}$ [12], which have transitions in the UV region. The availability of VUV synchrotron radiation from the 1970s allowed systematic experimental studies and some limited calculations to be carried out for the trivalent ions [13, 14]. Good availability of VUV beamlines during the past two decades has led to renewed interest in these energy levels, and detailed analyses have been made over the past ten years [15, 16, 17, 18]. These analyses have been reviewed in Ref. [19].

Though the extension of the parametrized model is straightforward, its application to the $4f^{N-1}5d$ configuration is different from application to the $4f^N$ configuration. The $4f^N$ spectra consist of sharp lines, allowing detailed identification of energy levels and accurate fitting of parameters. In contrast, transitions between $4f^N$ and $4f^{N-1}5d$ configurations consist mainly of broad vibronic lines, so interpretation of the spectra is not so straightforward, and accurate determination of the parameters is difficult. The crystal-field splittings of the $4f^{N-1}5d$ configuration are large compared to the splittings caused by the Coulomb interaction. Whereas for the $4f^N$ configuration the crystal field can be considered as a minor perturbation to the free ion, this is not the case for the $4f^{N-1}5d$ configuration, where the crystal field dominates the structure of the spectra.

It is now possible to make reasonably accurate ab-initio calculations for the $4f^N$ and $4f^{N-1}5d$ configurations of lanthanide ions in crystals [20, 21, 22, 23, 24, 25]. This raises the possibility of determining crystal-field and other parameters from such calculations. A method for doing this was developed in Ref. [26], and here is applied to Ce$^{3+}$ ions in LiYF$_4$.

Ab-initio calculations can also give information about excited state bonding and geometry [21, 22, 23, 25]. We discuss how the predictions might be tested using excited-state absorption (ESA), and how ESA might be used to reveal detailed electronic structure of the $4f^{N-1}5d$ configuration by examining transitions where the 5d electron is in the same orbital. These transitions should give sharp-line spectra because there is no change in bond length. On the other hand, transitions between states where the 5d electron changes to a different orbital will again give broad bands, with the width of the band a measure of the change in excited-state
2 Analysis of the $4f^N$ and $4f^{N-1}5d$ configurations of lanthanide ions in crystals

Modelling of the $4f^N$ and $4f^{N-1}5d$ configurations by parametrized calculations has been reviewed in Ref. [19]. Such “crystal field” calculations make use of an “effective Hamiltonian” [27, 28, 29] that acts solely within the $4f^N$ and $4f^{N-1}5d$ configurations. Rather than solving for the eigenvalues and eigenstates of the full Hamiltonian, the effective Hamiltonian is diagonalized within the model space ($4f^N$ and $4f^{N-1}5d$ configurations), and the expectation values of the effective operators are evaluated between the model-space eigenvectors.

The effective Hamiltonian for the $4f^N$ configuration may be written as [4, 5]:

$$
H_f = E_{avg} + \sum_{k=2,4,6} F_k f_k + \zeta_f A_{so} + \alpha L(L + 1) + \beta G(G_2) + \gamma G(R_7)
+ \sum_{i=2,3,5,6,7,8} T^i t_i + \sum_{h=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k + \sum_{k=2,4,6} \sum_q B_k^q C_q^{(k)}. \tag{1}
$$

$E_{avg}$ is the energy difference between the ground-state energy and the configuration center of gravity and is included to allow the ground-state energy to be set to zero. The Coulomb interaction between the 4f electrons is parametrized by the radial electronic integrals $F_k$ and the spin-orbit interaction by $\zeta_f$. These parameters are multiplied by appropriate tensor operators. The $\alpha$, $\beta$, $\gamma$, $T^i$, $M^k$, and $P^k$ parameters represent higher-order Coulomb and magnetic interactions. The major features of the spectra are determined by the $F_k$ and $\zeta_f$ parameters, with the other parameters giving small, but crucial, adjustments.

The $B_k^q$ are “crystal-field” parameters, which represent the interaction of the 4f electrons with the surrounding ions. For 4f electrons the non-zero parameters have $k = 2, 4, 6$, and $q$ values determined by symmetry [1, 2, 5].

For lanthanide $4f^N$ configurations the Coulomb interaction gives splittings of tens of thousands of cm$^{-1}$, the spin-orbit interaction splittings of a few thousand cm$^{-1}$, and the crystal-field interaction splittings of a few hundred cm$^{-1}$. Thus, the positions of the electronic multiplets are quite similar in different crystals, leading to the useful concept of a “Dieke diagram”, which summarises the energy levels of the entire lanthanide series [2, 4, 5].

Transitions between $4f^N$ states are parity forbidden, so the transitions are rather weak, consisting of magnetic-dipole and “forced” electric-dipole transitions. The latter are parametrized according to the “Judd-Ofelt” approach [30, 31, 32].

To extend the model to the $4f^{N-1}5d$ configuration we must add more terms to our Hamil-
tonian. The extra terms are:

$$H_d = \Delta E(fd) + \sum_{k=2,4} F^k(fd) f_k + \sum_{k=1,3,5} G^k(fd) g_k + \zeta(dd) A_{so}(d)$$

$$+ \sum_{k=2,4} \sum_q B^k_q(d) C^{(k)}_q(d).$$

(2)

In this equation $\Delta E(fd)$ represents the energy difference between the $4f^N$ and $4f^{N-1}5d$ configurations, the $F^k(fd)$ and $G^k(fd)$ direct and exchange Coulomb interactions between the $4f$ and $5d$ electrons, and $B^k_q(d)$ the crystal-field interaction of the $5d$ electron with the surrounding ions. This interaction is generally about twenty times larger than the interaction for the $4f$ electrons, so the splittings due to this interaction are tens of thousands of cm$^{-1}$, the same magnitude as the Coulomb interaction.

This difference in interaction strength of the $4f$ and $5d$ electrons with the ligands results in a shift in the excited-state geometry, and hence the broad bands seen in transitions between the $4f^N$ and $4f^{N-1}5d$ configurations. Since transitions between the $4f^N$ and $4f^{N-1}5d$ configurations generally consist of broad bands, rather than sharp lines, analyses have made use of a variety of ways to reducing the number of parameters, such as by using atomic calculation for the “free ion” parameters. Examination of spectra for ions across the series is also helpful, since certain features may be used to calibrate the model. For example, the splitting between spin-allowed and spin-forbidden transitions in the second half of the series may be used to estimate the parameters for the Coulomb interaction between the $4f$ and $5d$ electrons [18].

Calculations based on the above Hamiltonians give a spectrum with hundreds or thousands of transitions. But since many of the details are obscured by the vibronic bands comparison with experiment is not straightforward. Therefore, it is helpful to think of some simple ways to catalog some of the experimental results. Dorenbos [33, 34, 6] has given simple formulae to relate the lowest-energy $f$-$d$ transition energies, and also charge transfer transition energies, across the lanthanide series. In another approach, Duan and co-workers [35, 36] have used a “simplified model”, where the Coulomb interaction is approximated by a simple exchange potential. Such models are helpful to rationalizing the important features of the spectra.

3 Ab-initio calculations

First-principles (ab-initio) calculations of the electronic structure of the $4f^N$ and $4f^{N-1}5d$ configurations of lanthanide ions in solids are now becoming common [21, 24, 20, 25]. Ishii, Ogasawara and co-workers [37, 38, 39, 20, 40] have applied the DV-Xα method for ions across the entire lanthanide series. Similar calculations have been performed by other workers [24, 41]. Seijo and co-workers [21, 22, 23] have concentrated on a smaller number of systems and have used a sophisticated quantum-mechanical embedding scheme to calculate realistic excited-state
3.1 Extracting parameters from ab-initio calculations

Though quite good agreement can now be obtained between ab-initio calculations and experimental energies, it is desirable to compare the ab-initio calculations with parametric models. Comparison with parametric models would provide more detailed tests of the ab-initio calculations because it would be easier to deduce which effects are being poorly represented in the ab-initio calculations. Also, parameters have the great advantage that they may be extrapolated to other ions. For example, crystal-field parameters may be calculated for Ce$^{3+}$, where there is only one valence electron, and the parameters extrapolated to ions with more complex electronic structure for which ab-inito calculations are much more time consuming.

In some cases, particularly in high symmetries, such as $O_h$, the parameters may be determined from ab-initio calculations by fitting them to the calculated energy levels [42]. However, this is not always possible in low symmetry, where, for Ce$^{3+}$ there are often more free parameters than energy levels. However, it is possible to determine the $4f^N$ or $4f^{N-1}5d$ “effective Hamiltonian” [27], and therefore the parameters, directly, if one has the eigenvectors, as well as the energies, for the relevant states. A straight-forward way of doing this has been discussed recently [26].

We now give an example by using the DV-Xα [43] method to calculate crystal-field and spin-orbit parameters for the $4f^1$ and $5d^1$ configurations of Ce$^{3+}$ in LiYF$_4$. Further details and calculations for other hosts will be presented elsewhere.

The DV-Xα technique was originally developed by Ellis and co-workers for quantum chemical calculations of electronic and structural properties of molecular systems [43]. It was further developed by Adachi and co-workers [44] and it has been used for various calculations on lanthanide systems [37, 38, 39, 40, 24, 41]. These calculations are fully relativistic and so automatically include the spin-orbit interaction. While more sophisticated programs exist, with this code it is relatively straightforward to extract the wavefunctions from the calculation, which is essential to our method.

The coordinates for LiYF$_4$ were taken from Ref. [45]. Two cluster sizes were used, a small (CeF$_8$)$_5^-$ cluster, as used in Refs. [38, 39, 40], and a large cluster, (CeLi$_8$Y$_4$F$_{12}$)$_{11+}$. In each case a Madelung embedding was included to take account of ions not explicitly included in the cluster.

The calculated energy levels are presented in Table 1. Also shown are the experimental $5d^1$ energies and the results of similar calculations by Ogasawara and co-workers [39, 40]. Since the main focus of this work is the crystal-field splitting of the $4f^1$ and $5d^1$ configurations the average energy of the $5d^1$ configuration has been shifted to match the experimental average. The average before this adjustment is given in the last line of the Table.
For Ce$^{3+}$ there is only one valence electron so the Hamiltonian only includes the crystal-field and spin-orbit interactions. In LiYF$_4$ the energy levels consist of seven and five Kramer’s doublets for 4f$^1$ and 5d$^1$ respectively. Taking into account the S$_4$ site symmetry, the Hamiltonian may be written as:

$$H_{\text{Ce}} = E_{\text{avg}} + \zeta(f) + \sum_{k=2,4,6} \sum_{q=0,4} B_{q}^{k}(f)C_{q}^{(k)} + \Delta_{E}(fd) + \zeta(d) + \sum_{k=2,4} \sum_{q=0,4} B_{q}^{k}(d)C_{q}^{(k)}. \quad (3)$$

In S$_4$ symmetry the $q = 4$ parameters are complex. However, we may rotate about the z axis to make one of our calculated parameters real (e.g. see [1, 46]). If we perform the rotation to make $B_{4}^{1}(f)$ real we find that in practise the imaginary parts of the other parameters are small. Since the experimental parameters are derived assuming a higher D$_{2d}$ symmetry, where all parameters are real, we report real $B_{k}^{q}$ parameters by calculating the magnitude and using the sign of the real part.

To use the approach of Ref. [26] we must identify 4f$^1$ and 5d$^1$ energy levels and eigenvectors. This is straightforward for the small cluster, but for the large cluster the mixing of 5d orbitals with Y$^{3+}$ orbitals make this difficult. In order to proceed we simply take the five states with the largest 5d fraction. It is possible that a more sophisticated approach to selecting states (such as combining some of the states) would give better results but such considerations are beyond the scope of this work. In Table 2 we list the crystal-field parameters for 4f$^1$ and 5d$^1$. We list experimental parameters for Pr$^{3+}$ and Nd$^{3+}$, as well as Ce$^{3+}$, since the crystal-field parameters for Ce$^{3+}$ are difficult to determine because there are the same number of parameters as energy levels.

For the small cluster the calculated crystal-field parameters and spin-orbit parameters agree quite well with experiment. For the larger cluster there is considerable interaction with next-nearest neighbor ions and the calculation is very sensitive to small changes, such as which orbitals the valence electron is distributed amongst. In this case $B_{0}^{2}(f)$, $B_{0}^{4}(f)$, $\zeta(d)$ have become rather unphysical.

Note that we could not have determined crystal-field parameters from only the calculated energies since there are as many parameters as energies. Thus, knowledge of the wave-functions are crucial to our calculation.

### 3.2 Mixing with conduction-band states

For the small cluster the 4f and 5d orbitals can only mix with F$^{-}$ orbitals and for 5d$^1$ 75% to 90% of the wavefunctions come from 5d orbitals. However, for the large cluster there is also considerable mixing of 5d orbitals with “conduction band” orbitals on the Y$^{3+}$ ions. This has been previously noted in Ref. [37]. In Figure 1 we show the percentage of 5d orbitals for the states in the 5d$^1$ region. In this case only the lowest state has more than 50% contribution from
5d orbitals. It is clear that it is not a good approximation to consider this region as having five 5d\(^1\) states. While a calculation with a cluster of this size can not properly represent the conduction band, it does confirm that interactions with the conduction band are important for the 4f\(^{N-1}\)5d configuration. This is well-known from the lack of structure observed in the spectra for high-energy states, and from direct measurements of photoconductivity [7].

Mixing with the conduction band may be part of the reason why it is sometimes difficult to reproduce the spectra of the 4f\(^{N-1}\)5d configuration with a simple crystal-field model. Another possible perturbation is electron-phonon coupling, which has been discussed by Malkin and co-workers [47].

4 Probing electronic and geometrical structure with excited-state absorption

The ab-initio calculations by Seijo and co-workers [21, 22, 23] have challenged some common assumptions. It is often assumed that the bond lengths always increase when a lanthanide ion is excited from 4f\(^N\) to 4f\(^{N-1}\)5d. However, the recent first-principles calculations cited above suggest that for the lowest-energy 4f\(^{N-1}\)5d states the bond lengths are shorter than for the 4f\(^N\) configuration. Only the magnitude, not the sign, of this change in bond length may be easily estimated from ground-state absorption (GSA) spectra. Various evidence, such as pressure measurements, may be used to confirm these calculations [48]. Another approach is to test these calculations by performing excited-state absorption (ESA) measurements.

For ions with \(N > 7\) the lowest 4f\(^{N-1}\)5d states have a higher spin than the ground 4f\(^N\) states and the lowest states with the same spin as the ground state lie a few thousand cm\(^{-1}\) higher. Luminescence is observed in many cases from both the “High Spin” (HS) and the higher-energy “Low Spin” (LS) states [18]. Thus, if we populate the HS states we will be able to observe ESA when scanning with a second excitation source by monitoring the emission from the LS states.

Transitions where the 5d electron stays in the same orbital should be sharp, whereas those for which the 5d electron changes to a different orbital will be broad. If the bond lengths when the 5d electron is in the lowest 5d orbitals are more contracted than when it is in a 4f orbital and the bond lengths when the electron is in a higher 5d orbital are more expanded, as indicated by the calculations of Seijo and co-workers [21, 22, 23], then some of the transitions within the 4f\(^{N-1}\)5d configuration will have even broader vibronic bands than the 4f\(^N\) to 4f\(^{N-1}\)5d transitions.

We illustrate the information that might be obtained from ESA measurements by considering the case of Yb\(^{2+}\) in SrCl\(_2\). This system has been analysed in detail by Piper et al. [11], and more recently by Pan et al. [49].
In Figure 2 we show the effect of “switching on” the Hamiltonian, apart from the 5d crystal field. In O\textsubscript{h} symmetry there is only one independent 5d crystal-field parameter, \(B^{4}_{0}(d)\), and the Hamiltonian may be written as:

\[
H_{\text{Yb}} = B^{4}_{0}(d) \left[ C^{(4)}_{0} + \sqrt{\frac{5}{14}} \left( C^{(4)}_{4} + C^{(4)}_{-4} \right) \right] + AH_{\text{atomic}},
\]

where \(H_{\text{atomic}}\) contains all other interactions apart from the 5d crystal field (and thus is not truly “atomic”, since it contains the 4f crystal field). In Figure 2 the parameter \(A\) is varied from 0 to 1. When \(A = 0\) we have only the 5d crystal-field splitting, with the lowest states having the 5d electron in an \(e\) orbital and the higher states having the 5d electron in a \(t_{2}\) orbital. When \(A = 1\) we reproduce the calculation of Ref. [49].

Though the lowest \(4f^{13}5d\) state has the 5d electron in an \(e\) orbital, it is clear that some states for which the d electron is in an \(e\) or a \(t_{2}\) orbital overlap and mix when \(A = 1\). We may calculate this mixing by expressing the eigenvectors for \(A = 1\) as linear combinations of the eigenvectors for \(A = 0\). This allows us to simulate the ESA spectrum by assigning appropriate line-widths for the various transitions.

In Figure 3 we show calculated GSA along with ESA spectra. The GSA transitions are assigned a vibronic linewidth of 650 cm\(^{-1}\). We assume, for simplicity, that the 5d:\(e\) states are contracted and the 5d:\(t_{2}\) states expanded by the same amount relative to the 4f\(^{14}\) ground state. Therefore, we assign a small linewidth (50 cm\(^{-1}\)) to ESA transitions to pure 5d:\(e\) states and a linewidth \(\text{twice}\) the GSA linewidth to ESA transitions to pure 5d:\(t_{2}\) states. Mixed states have intermediate linewidths according to their proportion of 5d:\(t_{2}\). In the O\textsubscript{h} site symmetry of Yb\(^{2+}\) in SrCl\(_{2}\) the ESA transitions within the \(4f^{13}5d\) configuration are only magnetic-dipole allowed, and so their dipole strengths are about 1000 times smaller than the electric-dipole allowed GSA transitions. However, they are still strong compared to typical 4f\(^{N}\) transitions, and we note that ESA experiments similar to those discussed here have been carried out for transitions within the 4f\(^{N}\) configuration of Gd\(^{3+}\) [50].

The transition to the HS state is forbidden, so does not appear in the simulated GSA spectrum at about 25,000 cm\(^{-1}\). It is clear from Figure 3 that an ESA spectrum could give much more information than the GSA spectrum.

Yb\(^{2+}\) in SrCl\(_{2}\) has drawbacks for this sort of experiment. It is difficult to populate the lowest excited state due to the transition from the ground state to the lowest excited state being forbidden and the non-radiative relaxation from higher states being very slow [49]. More promising candidates are Tm\(^{2+}\) systems, for which up-conversion has already been observed [51].
5 Conclusions

It is clear that there are many interesting aspects of excited states of lanthanide ions remaining to be explored. We have demonstrated that it is possible to calculate crystal-field parameters from ab-initio calculations and have suggested excited-state absorption experiments that should allow the exploration of excited states involving 5d electrons in much more detail than in the past.

Acknowledgements

M.F.R. acknowledges travel support from the MacDiarmid Institute and support from the International Conference on f-Elements.
L.H. acknowledges support from a Chinese Government Scholarship for his visit to New Zealand.
C.-K.D acknowledges the National Science Foundation of China for financial support.
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Table 1: Experimental and calculated energy levels for the $4f^1$ and $5d^1$ configurations of Ce$^{3+}$ in LiYF$_4$.

|          | Experiment [52] | Calculation (this work) | Calculation (Ref. [39]) |
|----------|-----------------|-------------------------|-------------------------|
|          | Small cluster   | Large cluster           |                         |
|          | (CeF$_8$)$_{5-}$| (CeLi$_8$Y$_4$F$_{12}$)$_{11+}$ | (CeF$_8$)$_{5-}$        |
| $4f^1$   | 0               | 0                       | 0                       |
|          | 616             | 1025                    | 129                     |
|          | 672             | 1549                    | 492                     |
|          | 2604            | 3350                    | 2807                    |
|          | 2971            | 3947                    | 2896                    |
|          | 3316            | 4656                    | 3041                    |
|          | 3461            | 4783                    | 3646                    |
| $5d^1$   | 41101           | 33764                   | 31745                   |
|          | 48564           | 43078                   | 40757                   |
|          | 50499           | 48145                   | 49089                   |
|          | 52790           | 48739                   | 49745                   |
|          | 53000           | 52662                   | 55051                   |
| $5d$ average | 45277           | 30864                   | 81176                   |
|          |                 |                         | 49490                   |
Table 2: Crystal-field and spin-orbit parameters for the 4f\(^1\) and 5d\(^1\) configurations of Ce\(^{3+}\) in LiYF\(_4\).

| Parameter | Calculation | Experiment |
|-----------|-------------|------------|
|           | Small Cluster | Large Cluster | Ce\(^{3+}\) | Pr\(^{3+}\) | Nd\(^{3+}\) |
| B\(_0^2\)(f) | (Ce\(_8\))\(^{5-}\) | (Ce\(_8\)Li\(_8\)Y\(_4\)F\(_{12}\))\(^{11+}\) | | | |
| B\(_0^4\)(f) | 1228 | 2404 | 481 | 489 | 409 |
| B\(_4^0\)(f) | -538 | 1350 | -1150 | -1043 | -1135 |
| B\(_4^4\)(f) | -1001 | -874 | -1228 | -1242 | -1216 |
| B\(_6^0\)(f) | 12 | -345 | -89 | -42 | 27 |
| B\(_6^4\)(f) | -723 | -1071 | -1213 | -1213 | -1083 |
| ζ(f) | 748 | 910 | 615 | 731 | 871 |

| B\(_0^2\)(d) | | | | | |
| B\(_0^4\)(d) | 5338 | 3339 | 4673 | 7290 |
| B\(_4^0\)(d) | -12155 | -19136 | -18649 | -14900 |
| B\(_4^4\)(d) | -23448 | -29128 | -23871 | 17743 |
| ζ(d) | 894 | 365 | 1082 | 906 |

\(^a\) Extrapolated and fitted parameters from Ref. [52].
\(^b\) Fitted parameters from Ref. [16].
\(^c\) Fitted parameters from Ref. [53].
Figure 1: Calculated percentages of 5d orbitals for excited states of Ce$^{3+}$ in LiYF$_4$. 
Figure 2: Calculated energy levels for Yb\(^{2+}\) in SrCl\(_2\). The parameter \(A\) represents all of the 4f\(^{13}\)5d Hamiltonian apart from the 5d crystal field (see text). When \(A = 1\) the energies reproduce the calculation of Ref. [49].
Figure 3: Simulated ground-state absorption (GSA) and excited-state absorption (ESA) spectra for Yb$^{2+}$ in SrCl$_2$. The horizontal axes have units of cm$^{-1}$. The ESA is shifted so that the final states are at the same position on both graphs. Note that the transitions from the ground state to the lowest 4f$^{13}$5d state at approximately 25000 cm$^{-1}$ is forbidden. Linewidths for the GSA transitions are 650 cm$^{-1}$, linewidths for the ESA transitions range from 50 cm$^{-1}$ to 1300 cm$^{-1}$, depending on the fraction of 5d:$t_2$ in the final state.