Spectroscopy and calculations for $4f^N \rightarrow 4f^{N-1}5d$ transitions of lanthanide ions in LiYF₄

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Excitation spectra of transitions between the $4f^N$ and $4f^{N-1}5d$ configurations of Ce^{3+} , Pr^{3+} , and Nd^{3+} in LiYF₄ have been measured using UV and VUV synchrotron radiation. Both zero-phonon lines and vibronic bands are observed. The energy levels and transitions intensities are reproduced by a theoretical model that extends established models for the $4f^N$ configuration by including crystal-field and spin-orbit interactions for the 5*d* electron and the Coulomb interaction between the 4*f* and 5*d* electrons.

I. INTRODUCTION

Over the past several decades energy levels and transition intensities for the $4f^N$ configurations of lanthanide ions in a variety of solids have been characterized and understood in terms of detailed theoretical models.^{1–3} Since the $4f^N$ transitions consist of sharp lines, a large number of energy and intensity measurements may be obtained from each spectrum. The transitions between the $4f^N$ configuration and the $4f^{N-1}5d$ configuration have not received as much attention. This is partly because the transitions generally lie in the UV and VUV regions, making them experimentally less accessible. In addition, since the 5d orbitals are much more extended than the 4f orbitals, most of the intensity is in broad vibronic bands, making the spectra more difficult to analyze.

Recently there has been considerable interest in UV and VUV spectra of lanthanide compounds as part of the effort to design new phosphors for lamps and displays.⁴ $4f^N \leftrightarrow 4f^{N-1}5d$ spectra of lanthanide ions in LiYF₄ and other hosts have been measured at the HIGITI facility at the DESY synchrotron laboratory.⁵ Both absorption and emission spectra for transitions within $4f^N$ and between $4f^N$ and $4f^{N-1}5d$ have been obtained for most lanthanide ions in several host crystals.

Most modeling of $4f^N \leftrightarrow 4f^{N-1}5d$ transitions has either been for simple one-electron cases,^{6–9} or has treated the excited configuration as a 5*d* electron, which couples strongly to the lattice, plus a $4f^{N-1}$ core.¹⁰ However, there is significant Coulomb interaction between the 4*f* and 5*d* electrons, so this is a rather poor approximation,¹⁰ as illustrated by a recent analysis of excited-state absorption spectra of Pr^{3+} in LiYF₄.¹¹

In this paper we demonstrate that the energy levels and transition intensities of the $4f^N \rightarrow 4f^{N-1}5d$ transitions for Ce^{3+} , Pr^{3+} , and Nd^{3+} in LiYF₄ can be consistently modeled by extensions to the standard calculations for $4f^N$ to include the $4f^{N-1}5d$ states. Literature values of atomic and crystal-field parameters for the $4f^N$ configuration are used and other atomic parameters for the $4f^{N-1}5d$ configuration are estimated by standard atomic calculations¹² and crystal-field parameters for the 5d electrons are fitted to the Ce^{3+} spectrum. Calculated energies and intensities of zero-phonon lines and

vibronic bands are compared with the experimental data.

II. EXPERIMENT

Excitation spectra for LiYF₄ crystals doped with Ce³⁺, Pr³⁺, and Nd³⁺ were measured at liquid helium temperature at the HIGITI UV/VUV beamline at the DESY synchrotron laboratory by monitoring $4f^{N-1}5d \rightarrow 4f^N$ emission. The experimental methods have been described previously.⁵ The measurements reported here are from powder samples, so the spectra are unpolarized.

The experimental spectra are the solid lines in Fig. 1. The energy scales for the three ions are displaced so that for each ion the first zero-phonon lines for the $4f^N \rightarrow 4f^{N-1}5d$ transitions are at the same horizontal position. This makes the common structure of the $4f^{N-1}5d$ configurations apparent. In the S_4 site symmetry of the Y^{3+} sites that the Ce^{3+} ions substitute into the $5d^1$ configuration is split into five doubly degenerate crystal-field levels and this is what is observed for Ce^{3+} , as will be discussed in detail below. The excitation monochromator used on the synchrotron beamline is optimized for the VUV region and the relative intensities of the lowest two bands in the Ce³⁺ spectrum are not accurately measured by this equipment. Measurements with more conventional equipment give a much higher intensity for the lowest-energy band (see, for example, Refs. 7 and 13). The band at $46\,000$ cm⁻¹ does not appear in the spectra of Refs. 7 and 13 and is probably a defect or impurity. For Pr^{3+} and Nd³⁺ there is additional structure that, as we discuss below, can be attributed to the presence of 4f electrons in the excited configuration.

III. THEORY

To calculate the $4f^{N-1}5d$ energy levels the established theoretical model for $4f^N$ energy levels must be extended. The energy levels of the $4f^N$ configurations of lanthanide ions in solids may be parametrized by a Hamiltonian that describes the atomic interactions within the ion and the

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FIG. 1. Experimental and simulated spectra for the $4f^{N} \rightarrow 4f^{N-1}5d$ excitation of (a) Ce³⁺, (b) Pr³⁺, and (c) Nd³⁺ in LiYF₄. In each case the solid curve is the experimental spectrum, the vertical lines are predicted positions of zero-phonon lines, with heights proportional to predicted intensities, and the dashed curve is a simulated spectrum, including zero-phonon lines and vibronic bands.

crystal-field interaction with the host lattice.^{1,2} This Hamiltonian may be written as

$$H(ff) = H_{\rm A}(ff) + H_{\rm CF}(ff), \tag{1}$$

where $H_A(ff)$ denotes an "atomic" Hamiltonian defined to include all relevant interactions *except* those associated with nonisotropic components of the crystal-field potential, and $H_{CF}(ff)$ is the crystal-field interaction defined below. The atomic Hamiltonian is expressed explicitly as

$$H_{A}(ff) = \sum_{k} F^{k}(ff)f_{k}(ff) + \zeta(ff)A_{so}(ff) + \alpha(ff)L(L+1)$$
$$+ \beta(ff)G(G_{2}) + \gamma(ff)G(R_{7}) + \sum_{i} T^{i}(ff)t_{i}(ff)$$
$$+ \sum_{k} P^{k}(ff)p_{k}(ff) + \sum_{i} M^{j}(ff)m_{j}(ff), \qquad (2)$$

where k = 2, 4, 6; i = 2, 3, 4, 6, 7, 8; and j = 0, 2, 4. Both the notation and meanings of the various operators and parameters in this expression are defined according to standard practice.^{1,2} The $F^k(ff)$ parametrize the Coulomb interaction between the 4f electrons. The $\alpha(ff)$, $\beta(ff)$, and $\gamma(ff)$ parameters are associated with two-electron correlation corrections to the Coulomb repulsion. The $T^{\prime}(ff)$ parametrize three-electron correlation. The parameter $\zeta(ff)$ parametrizes the spin-orbit interaction, the $P^k(ff)$ electrostatically correlated spin-orbit interaction, and the $M^{j}(ff)$ spin-spin and spin-other orbit interactions. For N < 3 the three-body operators $t_i(ff)$ cannot contribute and for N < 2 there is no contribution from the Coulomb interaction, the spin-spin interaction, or the spin-other orbit interaction, and the only atomic interaction in this Hamiltonian is the spin-orbit interaction.

The $H_{CF}(ff)$ operator is defined to represent the *anisotropic* components of the *one-electron* crystal-field interactions, and may be expressed in the following form:

$$H_{\rm CF}(ff) = \sum_{kq} B_q^k(ff) C_q^{(k)}(ff),$$
(3)

where the $B_q^k(ff)$ parameters contain the radially dependent parts of the one-electron crystal-field interactions, and the $C_q^{(k)}(ff)$ are spherical tensor operators acting within the $4f^N$ electronic configuration. The allowed values of k are limited to 2, 4, and 6. The site symmetry of the Y^{3+} sites in LiYF₄, for which the lanthanide ions substitute, is S_4 . In this symmetry the allowed values of q are limited to 0, and ± 4 . In many treatments the symmetry is approximated by D_{2d} ,² since the deviation from D_{2d} is small. In that case only real parameters with $q \ge 0$ are required. All reported calculations in this paper use this approximation, which will be discussed more fully below.

The values for the atomic and crystal-field parameters have been established in a wide variety of crystals. For the LaF₃ host parameters are available for the entire lanthanide series.¹ Parameters for most lanthanides in LiYF₄ are also available,² though these have not been the subject of such a consistent study as for LaF₃.

For the excited $4f^{N-1}5d$ configuration the H(ff) Hamiltonian discussed above still contributes (except in the case of Ce³⁺, where the excited configuration is $5d^1$). However, since one of the 4f electrons has been excited to a 5d orbital, there are several additional contributions to the Hamiltonian. The atomic Hamiltonian is supplemented by the spin-orbit interaction for the 5d electron and the Coulomb interaction between the 5d electron and the 4f electrons (in the cases where N > 1). We define the additions to the atomic Hamiltonian as

$$H_{A}(fd) = \sum_{k} F^{k}(fd)f_{k}(fd) + \sum_{j} G^{j}(fd)g_{j}(fd) + \zeta(dd)A_{so}(dd), \qquad (4)$$

with k=2, 4, and j=1, 3, 5. The $F^k(fd)$ and $G^j(fd)$ are direct and exchange Slater parameters for the Coulomb interaction between the 4f and 5d electrons.¹² The $\zeta(dd)$ parameter is associated with the spin-orbit interaction of the 5d electron. The 5d electron is also affected by the crystal-field interaction

$$H_{\rm CF}(dd) = \sum_{kq} B_q^k(dd) C_q^{(k)}(dd),$$
 (5)

with k=2 and 4, and the same restrictions on q as for $H_{CF}(ff)$.

The $4f^{N-1}5d$ configuration has a higher average energy than the $4f^N$ configuration. This energy difference contains contributions from several sources,¹² including kinetic energy, Coulomb, and (isotropic) crystal-field effects. These effects cannot be distinguished experimentally and can be considered to contribute to a single term $\Delta_E(fd) \delta_E(fd)$ in the Hamiltonian, where the operator $\delta_E(fd)$ is diagonal, with unit matrix elements for $4f^{N-1}5d$ and zero matrix elements for $4f^N$.

Since the $4f^N$ and $4f^{N-1}5d$ configurations have opposite parity, there is no Coulomb configuration interaction between them. However, the odd-parity crystal-field interaction can couple the $4f^N$ and $4f^{N-1}5d$ configurations. This contribution to the Hamiltonian is

$$H_{\rm CF}(fd) = \sum_{kq} B_q^k(fd) C_q^{(k)}(fd),$$
(6)

with k=1, 3, and 5. For S_4 or D_{2d} symmetry q is restricted to ± 2 . This mixing of configurations is one of the major contributions to electric dipole transition intensities within the $4f^N$ configuration.³ However, as we shall discuss below, it has only a small effect on the spectra considered in this work.

In our calculations we used established $4f^N$ crystal field parameters² and $4f^N$ atomic parameters.¹ For Ce³⁺ the determination of crystal-field parameters is difficult, due to the limited number of energy levels in the $4f^1$ configuration. The analysis of Ref. 13 is based on a limited number of optical and EPR measurements. We found that crystal-field parameters reported for for Pr³⁺ in LiYF₄ gave ground-state eigenfunctions almost identical to the eigenfunctions derived in Ref. 13. Since in this work we only consider spectra that involve transitions from the ground state, we used those parameters in our final calculations.

For $4f^{N-1}5d$, we used literature values for the parameters in $H_A(ff)$ for the same ion. These parameters are not required to be identical for the $4f^N$ and $4f^{N-1}5d$ configurations but there is not enough information in the spectra to definitively test the effect of varying these parameters from the $4f^N$ values. For $H_A(fd)$ we used atomic (Coulomb and spin-orbit) parameters calculated from standard atomic computer programs.¹² The only fitted parameters in our calculations are the $B_a^k(dd)$ crystal-field parameters, which we fitted

TABLE I. Observed and calculated energies for the 5*d* states of Ce^{3+} in LiYF₄, in cm⁻¹. The energies given here are for the zero-phonon lines. Apart from the first state, these have been deduced by assuming a 400 cm⁻¹ displacement between the zero-phonon lines and the peak of the vibronic band. Octahedral and D_{2d} irreducible representations for the states are given.

| Experimental | Calculated | Octahedral | D_{2d} |
|--------------|------------|------------|------------|
| 33433 | 33433 | E | Γ_7 |
| 41101 | 41090 | E | Γ_6 |
| 48564 | 48590 | T_2 | Γ_7 |
| 50499 | 51093 | T_2 | Γ_6 |
| 52790 | 52178 | T_2 | Γ_7 |

to the Ce^{3+} spectrum. These crystal-field parameters were then used for the Pr^{3+} and Nd^{3+} calculations.

The transitions from $4f^N$ to $4f^{N-1}5d$ 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.³ However, because the 5*d* orbitals are more extended than the 4*f* orbitals, there is a displacement of the equilibrium positions of the ligands in the excited states and most of the intensity is in the vibronic bands.^{10,14} In our modeling we made the standard approximation that the intensities of the vibronic bands are proportional to the squares of the electric dipole moment operator evaluated between the initial and final electronic states.

IV. RESULTS

Experimental spectra and the results of our simulations are presented in Fig. 1. The solid curves are experimental spectra. Calculated positions and intensities of zero-phonon lines are indicated by vertical lines. The dotted curves are simulated spectra that approximate the vibronic bands by Gaussian curves, displaced from the zero-phonon lines by 400 cm^{-1} , with width 1200 cm^{-1} with intensity proportional to the zero-phonon lines. There are many vibrational modes for LiYF₄ crystals¹⁵ and the spectra contain superpositions of several vibronic progressions,¹⁴ giving rather featureless vibronic bands.

A. Ce³⁺

The excitation spectrum of the Ce³⁺ emission in LiYF₄:Ce³⁺ is shown in Fig. 1(a). The five strongest bands are assigned to $4f \rightarrow 5d$ vibronic progressions. Only the zero-phonon line for the first band is seen. The other zero-phonon lines lie in the conduction band, so photo-ionization gives lifetime broadening and no sharp zero-phonon line can be observed. The width [full width at half maximum (FWHM)] of all the bands is approximately 1200 cm⁻¹ and the peak of the first band is offset from the zero-phonon line by 400 cm⁻¹. Since the width of the bands is constant, it is a reasonable assumption that the peaks of the four higher-energy bands are offset by this same energy from the (unobserved) zero-phonon lines. With this assumption we obtain the energies given in Table I for the zero-phonon

TABLE II. Energy parameters for $4f^N$ and $4f^{N-1}5d$ configurations of Ce³⁺, Pr³⁺, and Nd³⁺ in LiYF₄. Units are cm⁻¹. See text for details.

| | Ce ³⁺ | Pr ³⁺ | Nd ³⁺ |
|------------------------|------------------|------------------|------------------|
| $F^2(ff)$ | | 68878 | 73018 |
| $F^4(ff)$ | | 50347 | 52789 |
| $F^6(ff)$ | | 32901 | 35757 |
| $\alpha(ff)$ | | 16.23 | 21.34 |
| $\beta(ff)$ | | -566.6 | - 593 |
| $\gamma(ff)$ | | 1371 | 1445 |
| $T_2(ff)$ | | | 298 |
| $T_3(ff)$ | | | 35 |
| $T_4(ff)$ | | | 59 |
| $T_6(ff)$ | | | -285 |
| $T_7(ff)$ | | | 332 |
| $T_8(ff)$ | | | 305 |
| $\zeta(ff)$ | 614.9 | 751.7 | 885.3 |
| $M_0(ff)^a$ | | 2.08 | 2.11 |
| $P_2(ff)^{\mathrm{b}}$ | | -88.6 | 192 |
| $B_0^2(ff)$ | 481 | 481 | 409 |
| $B_{0}^{4}(ff)$ | -1150 | -1150 | -1135 |
| $B_4^4(ff)$ | -1228 | -1228 | -1216 |
| $B_0^6(ff)$ | - 89 | - 89 | 27 |
| $B_4^6(ff)$ | -1213 | -1213 | -1083 |
| $\Delta_E(fd)$ | 43754 | 51815 | 57749 |
| $F^2(fd)$ | | 30271 | 30300 |
| $F^4(fd)$ | | 15094 | 15038 |
| $G^1(fd)$ | | 12903 | 12914 |
| $G^3(fd)$ | | 11160 | 11135 |
| $G^5(fd)$ | | 8691 | 8659 |
| $\zeta(dd)$ | 1082 | 1148 | 1216 |
| $B_0^2(dd)$ | 10519 | 10519 | 10519 |
| $B_0^4(dd)$ | -24549 | -24549 | -24549 |
| $B_4^4(dd)$ | - 18966 | -18966 | - 18966 |

^a M^2 and M^4 parameters were included with the ratios $M^2/M^0 = 0.56$ and $M^4/M^0 = 0.31$.

 ${}^{b}P^{4}$ and P^{6} parameters were included with the ratios $P^{4}/P^{2}=0.5$ and $P^{6}/P^{2}=0.1$.

lines. We estimate the uncertainties for these energies to be 200 cm^{-1} .

The only terms in Hamiltonian that split the $5d^1$ configuration are the spin-orbit and crystal-field interactions. The 5dcrystal-field parameters were fitted to the observed splitting, using standard nonlinear least-squares methods,¹ giving the calculated energies of Table I and the parameters of Table II. The crystal-field splitting may be interpreted as a distortion of a cubic field with the two *E* components lowest and the three T_2 components highest. The standard deviation for the fit is 850 cm⁻¹ and the uncertainties of the 5*d* crystal-field parameters $B_0^2(dd)$, $B_0^4(dd)$, and $B_4^4(dd)$ are 1600, 2200, and 1600 cm⁻¹, respectively, i.e., about 10%. The spin-orbit parameter $\zeta(dd)$ was not varied, but fixed at the value calculated by standard atomic-physics computer programs.¹²

The splitting of the two highest-energy states is not well reproduced by our calculation. This discrepancy has been extensively discussed previously^{7,9} and is thought to be a result of distortions in the excited state. Detailed *ab initio*

calculations of excited-state distortions of Ce^{3+} systems have been recently published.⁸ The splitting could be better reproduced by doubling the spin-orbit parameter $\zeta(dd)$. However, experimental spin-orbit parameters for the 5*d* configuration¹⁶ are similar to those quoted in Table II, so such a large spin-orbit parameter seems unlikely.

Our calculations make two approximations that might be expected to have an influence on the quality of the fit. The first approximation is that the site symmetry is D_{2d} , whereas the actual site symmetry is S_4 . In S_4 symmetry there is an additional parameter since the $B_4^4(dd)$ parameter is not restricted to be real. The additional contributions to the Hamiltonian from lowering the symmetry to S_4 are imaginary offdiagonal matrix elements whose influence on the energies is only subtly different from the influence of the D_{2d} Hamiltonian and, in fact, a suitable rotation about the Z axis will eliminate the imaginary part of one of the parameters $B_4^4(ff)$, $B_4^6(ff)$, or $B_4^4(dd)$, so if we consider the $5d^1$ configuration in isolation, the reduction to S_4 symmetry has no effect on the energy-level calculation. For further discussion the reader is referred to the literature.^{17,3} The second approximation is that the odd-parity crystal-field that couples the 4f and 5d states was set to zero. The major effect of the interconfigurational $B_2^3(fd)$ and $B_2^5(fd)$ crystal-field parameters is a second-order perturbation correction to the $B_a^k(dd)$ and $B_q^k(ff)$ parameters. Extensive calculations were carried out using S_4 symmetry and with nonzero values for the interconfigurational crystal-field parameters $B_2^3(fd)$ and $B_2^{5}(fd)$. It was clear from these calculations that the discrepancies between calculated and experimental energies cannot be resolved by lowering the symmetry to S_4 or by including the odd-parity crystal field.

The fitted 5*d* crystal-field parameters have the same signs as the 4*f* parameters, but are about 20 times larger, which is expected because the 5*d* orbitals are much more extended than the 4*f* orbitals.^{7,9} Note that the ratios between the fourth-rank parameters for 4*f* and 5*d* are different. A simple point-charge model of the crystal field would predict these ratios to be the same, but in realistic *ab initio* calculations⁹ the 4*f* and 5*d* orbitals have very different interactions and admixtures with the ligand orbitals.

We show only unpolarized results in Fig. 1. However, our calculated polarization dependence is consistent with the polarized measurements of Ref. 13 and our calculated ground-state (4*f*) eigenfunctions are the same as those calculated in that paper. These eigenfunctions give a good reproduction of the ground-state electron paramagnetic resonance (EPR) measurements reported in that work. As explained above, the experimental intensity of the lowest two transitions in our spectrum is not accurate, probably because the intensity of the excitation beam is very low in this region. Other measurements^{7,13} give a much larger intensity for the lowest energy transition.

B. Pr³⁺

Experimental and calculated $4f^2 \rightarrow 4f5d$ spectra for Pr^{3+} are presented in Fig. 1(b). Only for the lowest $4f^2 \rightarrow 4f5d$ transition is the zero-phonon line observed, but the calculated shapes of the vibronic bands match the observed spectrum quite well. The spectrum consists of the 5*d* crystal-field



FIG. 2. Splitting of the lowest 5*d* crystal field component of the 4f5d configuration of Pr^{3+} in LiYF₄. The parameter *A* represents the the 4f5d Coulomb and 5*d* spin-orbit interactions, as explained in the text. On the left (*A*=0) the parameters for these interactions are set to zero and on the right (*A*=1) they take on their full calculated values, as used in the simulation of Fig. 1(b).

levels plus fine structure arising from the presence of the 4felectron. It is tempting to try to analyze this fine structure in terms of the splitting of the 4f states by the spin-orbit and crystal-field interactions.¹⁰ However, this is not a very good approximation. The Coulomb interaction between the 4f and 5*d* electrons has a significant effect. To visualize this effect, in Fig. 2 we show the splitting of 4f5d states corresponding to the lowest 5d crystal-field level as the 4f5d atomic Hamiltonian parameters $[F^k(fd), G^j(fd), \zeta(dd)]$ are increased from zero to the values used in our simulations [Fig. 1(b)]. The parameter A used as the horizontal axis of the graph multiplies the operator $H_{A}(fd)$ defined in Eq. (4). When A = 0, which corresponds to setting all the parameters in $H_A(fd)$ equal to zero, the multiplet structure of $4f^1$ is clearly discernible. As A is increased from 0 to 1 the energy levels take on the structure used in the simulation [Fig. 1(b)]. The Coulomb interaction between the 4f and 5d electrons is responsible for most of the additional splitting. The atomic parameters that we have used are similar to those obtained from free-ion spectra¹⁶ and those used to fit 4f5d states determined from excited-state absorption measurements,¹¹ the main difference being that our $F^2(fd)$ parameter is larger. The alternative parameter values^{11,16} gave very similar results. We would expect these parameters to be somewhat reduced in the crystal from their free-ion values, as is the case for the $4f^N$ configuration.¹ However, we found that if the parameters were reduced by more than about 30%, the calculated splittings become too small to reproduce the experimental spectrum.

C. Nd³⁺

Experimental and calculated spectra for Nd³⁺ are shown in Fig. 1(c). As in the case of Pr³⁺ there is fine structure built on top of the 5*d* crystal-field splitting. Again, this fine structure cannot be explained in terms of the multiplet structure of the $4f^{N-1}$ configuration with the Coulomb interaction between the 4*f* and 5*d* electrons having a significant effect on the calculated energy levels of the $4f^25d$ configuration.

We can identify several sharp zero-phonon lines in the spectrum. In the $56\,000-58\,000$ cm⁻¹ region our calculations reproduce the positions and intensities of these features

quite well. The higher-energy zero-phonon lines and vibronic bands are not reproduced so well. The calculated energies are affected by a large number of parameters (see Table II). In addition, the spectra are unpolarized, since they are obtained from powders, so conclusive identification of the symmetry properties of the states for which zero-phonon lines are observed is not possible. It would therefore be premature to try to fit the parameters to the data. However, we note that better agreement between calculation and experiment can be achieved by small reductions of the 4f5d atomic parameters and the 5d crystal-field parameters.

V. CONCLUSIONS

We have demonstrated that it is possible to give a consistent account of the the energy levels and transition intensities for the entire $4f^N \rightarrow 4f^{N-1}5d$ excitation spectra for Ce³⁺, Pr^{3+} , and Nd^{3+} in $LiYF_4$ by extending the standard calculations for $4f^N$ to include the $4f^{N-1}5d$ states. Both the zerophonon lines and the vibronic bands have been considered. In our calculations we have used $4f^N$ parameters from the literature and calculated the atomic 4f5d parameters. We have only adjusted the 5d crystal-field parameters and the same 5d crystal-field parameters have been used for all three ions. In contrast with the case for the $4f^N$ configuration, where the atomic interactions are responsible for the gross features of the spectra, with the crystal-field interactions being a small perturbation, the gross features of the $4f^{N-1}5d$ spectra arise from the 5d crystal-field interactions, with the other terms in the Hamiltonian being responsible for the fine structure.

The success of the calculations presented here gives us confidence that the $4f^N \rightarrow 4f^{N-1}5d$ spectra for all ions in the lanthanide series will be amenable to similar treatment. Detailed comparisons between theory and experiment for the entire lanthanide series in a variety of host crystals should allow the fitting of some of the atomic parameters for the $4f^{N-1}5d$ configuration, the determination of trends for atomic and crystal-field parameters, and more detailed comparisons of the calculations for energy levels and transition intensities with experiment.

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- ¹W.T. Carnall, G.L. Goodman, K. Rajnak, and R.S. Rana, J. Chem. Phys. **90**, 3443 (1989).
- ²C. Görller-Walrand and K. Binnemans, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by J. K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1996), Vol. 23, pp. 121–283.
- ³C. Görller-Walrand and K. Binnemans, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1998), Vol. 25, p. 101.
- ⁴R.T. Wegh, H. Donker, K.D. Oskam, and A. Meijerink, Science 283, 664 (1999).
- ⁵R.T. Wegh and A. Meijerink, Phys. Rev. B **60**, 10 820 (1999).
- ⁶J. Sytsma *et al.*, Phys. Rev. B **47**, 14 786 (1993).
- ⁷C.M. Combes *et al.*, J. Lumin. **71**, 65 (1997).
- ⁸M. Marsman, J. Andriessen, and C.W.E. van Eijk, Phys. Rev. B

61, 16 477 (2000).

- ⁹J. Andriessen et al., in Proceedings of the International Conference on Inorganic Scintillators and their Applications, SCINT95 (Delft University Press, Amsterdam, 1996), pp. 142–143.
- ¹⁰A. Meijerink, R. T. Wegh, and L. van Pieterson, Proc. Electrochem. Soc. **99-40**, 23 (2000).
- ¹¹M. Laroche et al., J. Opt. Soc. Am. B 17, 1291 (2000).
- ¹²R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
- ¹³T. Yoshida et al., J. Phys.: Condens. Matter 9, 3733 (1997).
- ¹⁴B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inor*ganic Solids (Clarendon Press, Oxford, 1989).
- ¹⁵S.A. Miller, H.E. Rast, and H.H. Caspers, J. Chem. Phys. 52, 4172 (1970).
- ¹⁶J. Sugar, J. Opt. Soc. Am. 55, 1058 (1965).
- ¹⁷C. Rudowicz, Chem. Phys. **97**, 43 (1985).