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Optical Intensities of Rare-Earth Ions in Yttrium Orthoaluminate[*]

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Optical absorption and emission intensities are investigated for trivalent rare earths in $YAlO_3$. Ions examined included Pr, Nd, Eu, Tb, Ho, Er, Tm, and Yb. Oscillation strengths of $f \rightarrow f$ transitions between J manifolds were measured at room temperature and compared with calculated electric and magnetic dipole oscillator strengths. The Judd-Ofelt approach and phenomenological parameters for each ion were used to derive the electric dipole intensities. The intensity parameters, which were obtained for a least-square-fitting procedure, exhibited a general decrease with increasing number of $4f$ electrons throughout most of the series. The intensities for Pr and Tb were not satisfactorily accounted for in the present theory; some reasons for this are presented.

I. INTRODUCTION

Optical spectra of rare-earth ions arise predominantly from electric and magnetic dipole transitions between states of the ground $4f^n$ electronic configuration. Whereas the probability for magnetic dipole transitions can be readily calculated, given appropriate wave functions, electric dipole transitions are forbidden between states of the same configuration. They become allowed, however, if odd-order terms in the expansion of the static or dynamic crystalline-field potential admix states of higher, opposite-parity configurations into f^n. The intensities of these spectra have been interpreted and accounted for using the treatment of Judd[1] and Ofelt.[2] In this approach, the probability for electric dipole transitions is expressed in terms of a small number of phenomenological intensity parameters. These parameters for a given ion-host combination are usually derived from a best fit of calculated and observed intensities. The validity of the Judd-Ofelt theory has now been tested for most trivalent rare earths both in crystalline environments[3] and in solutions.[4,5]

In this paper the Judd-Ofelt theory is applied to the optical spectra of rare-earth impurities in crystals of yttrium orthoaluminate. The interest is threefold: (a) to test the success and/or the limitations of the treatment for rare earths in $YAlO_3$, (b) to compare the intensity parameters in $YAlO_3$ with those obtained for other hosts, and (c) to examine the variation of the intensity parameters for ions throughout the lanthanide series. This last point has received limited consideration, the only reported measurements for several ions in the same host being those of Krupke[3] for Y_2O_3 and Carnall *et al.*[5] for solutions. Krupke, in addition, sought to explain the trend in parameter values across the series based upon calculations made using free-ion radial wave functions and relevant crystal-field strengths.

Knowledge of the Judd-Ofelt parameters, obtained either directly from measurements or by extrapolation from results for other ions, is of value since, once determined, the parameters can be used to calculate transition probabilities between any $4f$ levels of interest. These include the probabilities for stimulated and spontaneous emission and for excited-state absorption. By subtracting calculated radiative lifetimes from measured excited-state lifetimes, the probabilities for nonradiative processes can also be found.[6,7] The rate of nonradiative decay by multiphonon emission in $YAlO_3$ has been studied using this approach and the present results. This investigation is discussed in a separate paper[8] hereafter referred to as II.

II. THEORY

Since the theory and treatment of radiative transitions of rare earths has been adequately described,[1-3,9] only a brief summary and essential formulas will be given. The free-ion states of an ion having an f^n electronic configuration are composed of a linear combination of Russell-Saunders states

$$|f^n[\alpha SL]J\rangle = \sum_{\alpha,S,L} C_{\alpha SL}\,|f^n\alpha SLJ\rangle\,, \qquad (1)$$

where the coupling coefficients C are obtained from diagonalizing the combined electrostatic, spin-orbit, and configuration interaction energy matrices. (The bracketed quantities indicate that in the labeling of states, S and L are no longer good quantum numbers.) Magnetic dipole and electric quadrupole transitions involve no change in parity between the initial and final states and thus are allowed between states of a given configuration. The line strength for magnetic dipole (md) transitions between J manifolds is given by

$$S_{\text{md}}(aJ;\,bJ') = \mu_B^2\,\langle f^n[\alpha SL]J\,\|\,\vec{\mathrm{L}}+2\vec{\mathrm{S}}\,\|\,f^n[\alpha' S' L']J'\rangle^2\,, \qquad (2)$$

where $\mu_B = e\hbar/2mc$. The probabilities for electric quadrupole transitions of rare earths have generally been found[6,9,10] to be very much smaller than dipolar processes and therefore are not considered. Because rare-earth ions enter the $YAlO_3$ lattice substitutionally at noncentrosymmetric Y^{3+} sites (C_{1h} symmetry),[11] electric dipole transitions are possible. The electric dipole (ed) line strength in the Judd-Ofelt treatment is expressed as a sum of intensity parameters Ω and reduced matrix elements of tensor operators $\underline{U}^{(t)}$ of rank t of the form

$$S_{ed}(aJ;bJ') = e^2 \sum_{t\ \mathrm{even}} \Omega_t \langle f^n[\alpha SL]J \| \underline{U}^{(t)} \| f^n[\alpha' S' L']J' \rangle^2 . \tag{3}$$

The parameters Ω contain the crystal-field strengths, the energy separation of the two opposite-parity configurations, and the interconfigurational radial integrals and include contributions from both static and vibrationally induced electric-dipole transitions. From the selection rule $|\Delta J| \leq 2l$, t in the summation in Eq. (3) is limited to values of 2, 4, 6 for lanthanide ($l=3$) ions.

The oscillator strength f of a transition of average frequency $\bar{\nu}$, in terms of the above line strengths, is given by

$$f(aJ;bJ') = \frac{8\pi^2 m\bar{\nu}}{3(2J+1)he^2} S(aJ;bJ') . \tag{4}$$

The spontaneous emission probability A is calculated from

$$A(aJ;bJ') = \frac{64\pi^4\bar{\nu}^3\chi}{3(2J+1)hc^3} S(aJ;bJ') . \tag{5}$$

For a well-localized center in a medium of isotropic refractive index n, the χ factors in Eq. (5) which correct for the effective field are $\chi_{ed} = n(n^2+2)^2/9$ for electric dipole emission and $\chi_{md} = n^3$ for magnetic dipole emission. The radiative lifetime τ of an excited state i is simply

$$\frac{1}{\tau_i} = \sum_j A(i,j) , \tag{6}$$

where the summation is over electric and magnetic dipole transitions to all terminal states j. The fluorescence branching ratio is given by

$$\beta_{ij} = \frac{A(i,j)}{\sum_j A(i,j)} = \tau_i A(i,j) . \tag{7}$$

Attempts to calculate the intensity parameters Ω are plagued with many of the same difficulties encountered in *ab initio* calculations of electric dipole transition probabilities; these parameters have therefore usually been derived empirically from measurements of integrated absorption cross sections.[3] These are related to the oscillator strengths by

$$\int \sigma(\nu)d\nu = \frac{\pi e^2 \chi}{mcn^2} f . \tag{8}$$

The cross section $\sigma(\nu)$ is defined by

$$\sigma(\nu) = \frac{\ln[I_0(\nu)/I(\nu)]}{Nt} , \tag{9}$$

where N is the number of ions per cm^3 and t is the absorption path length. The spontaneous emission probability can also be found directly from the integrated absorption cross section via the relationship

$$A(aJ, bJ') = \frac{8\pi n^2\bar{\nu}^2}{c^2} \frac{(2J'+1)}{(2J+1)} \int \sigma(\nu)\, d\nu . \tag{10}$$

The comments made below about the assumption of equally populated Stark levels of the initial J manifold are again apropos.

Matrix elements of $\vec{L}+2\vec{S}$ and $\underline{U}^{(t)}$ required in Eqs. (2) and (3) are calculated using formulas given elsewhere.[9] Since the free-ion eigenstates exhibit only small changes with host, matrix elements for absorption transitions which have been tabulated by Carnall *et al.*[12] were used in most instances. The sources of matrix elements used for emission transitions are cited. By using free-ion eigenstates, equal population in the Stark levels of the initial J manifold is assumed, a condition which is only approximately fulfilled at ambient temperatures. In $YAlO_3$, because of the low crystal-field symmetry, each Stark component is composed of a linear combination of many substates. This plus inclusion of transitions to many different states tends to average out the effects of unequal level populations. Admixing of J states, which can be significant for J manifolds with small energy separations, is also neglected.

III. EXPERIMENTAL PROCEDURES

Crystals of rare-earth-doped yttrium orthoaluminate were grown by the Czochralski method.[11] Samples were cut from boules, heated to ~1000 °C for several hours in a reducing atmosphere to remove color centers, and polished using standard techniques. Dopant concentrations were in the range 0.1–1.0 at.%. In $YAlO_3$ the distribution coefficients for rare-earth impurities in the crystal to that in the initial melt range from 0.8 for neodymium to approximately unity for holmium, erbium, and thulium. The actual sample concentrations and distribution coefficient for Nd^{3+} in $YAlO_3$ were determined by x-ray fluorescence analysis; the concentrations of other dopants were determined by spectrochemical analysis and/or by extrapolation from known distribution coefficients. Rare-earth concentrations in the samples used are believed to be accurate to within ±10%.

Absorption spectra were recorded at ambient temperatures using a Cary model 14 spectrophotometer. Absorption pathlengths were typically in the order of a few mm to 1 cm. For weak absorptions, a 0–0.1 optical-density slidewire was used. The spectral resolution was much less than the observed linewidths throughout the visible and infrared. In the ultraviolet region, some line broadening may have been present for the narrower lines but the total contribution was considered to be small. Integrated intensities were measured from the recorded spectra with a planimeter. The spectral baseline could usually be easily established. At wavelengths below ~300 nm, however, underlying absorption bands arising from residual imperfections were sometimes present, thereby making it difficult to determine the correct baseline. Data for the uv region therefore have a greater uncertainty.

Fluorescence spectra were recorded with a 0.5-m grating monochromator equipped with either a S-1 or a S-20 cathode photomultiplier. A xenon arc lamp was the excitation source. The spectral response of the monochromator-photomultiplier combination was calibrated using a quartz-tungsten-iodine lamp standard. Fluorescence lifetimes, where cited, were measured using techniques described in II.

IV. RESULTS

TABLE I. Experimental intensity parameters for trivalent rare earths in $YAlO_3$.

	Nd$(4f^3)$	Eu$(4f^6)$	Tb$(4f^8)$	Ho$(4f^{10})$	Er$(4f^{11})$	Tm$(4f^{12})$
$\Omega_2(10^{-20}\ \mathrm{cm}^2)$	1.24	2.66	3.25	1.82	1.06	0.67
$\Omega_4(10^{-20}\ \mathrm{cm}^2)$	4.68	6.32	7.13	2.38	2.63	2.30
$\Omega_6(10^{-20}\ \mathrm{cm}^2)$	5.85	0.80	2.00	1.53	0.78	0.74

Absorption intensity measurements were made for eight trivalent rare earths: Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+}. Since the crystalline Stark splitting of J manifolds in $YAlO_3$ is moderately large, lines sometimes overlapped or could not be assigned to specific J states. When this occurred, the combined intensity was treated as one experimental datum and attributed to a sum of transitions using a mean frequency. In cases where few absorption data were available, they were supplemented by measurements of fluorescence spectra and lifetimes. Samples containing low rare-earth concentrations were used for these measurements to reduce radiation trapping and nonradiative decay by self-quenching.

Intensity parameters Ω were derived for six ions and are tabulated in Table I. For four of the ions the parameters were found from a least-squares analysis of the observed and calculated spectral intensities. The root-mean-square deviation of the measured and calculated line strengths, defined by

$$\delta_{\mathrm{rms}} = \left(\frac{\text{sum of squares of deviations}}{\text{number of transitions} - \text{number of parameters}}\right)^{1/2} ,$$

was also computed. While the quality of the fits between measured and calculated oscillator strengths and branching ratios provides relative Ω values, it is independent of the ion concentration N. The absolute values of the oscillator strengths, cross sections, and radiative lifetimes, on the other hand, are critically dependent upon N. Therefore as a further test of the Ω values, radiative lifetimes were also calculated and compared with measured lifetimes. This was done for ions and excited states where, based upon results obtained in II, any nonradiative decay contributions to the lifetime were known to be negligible.

A. Praseodymium

The absorption spectra of nominal 0.1- and 1.0-at.% Pr^{3+} samples were recorded from 2.65 to 0.4 μm. Since the energy levels of Pr^{3+} in $YAlO_3$ have not been determined and J mixing is probable, it was frequently not possible to assign intensities to specific J states. Thus the absorption spectra yielded only five data groups corresponding to transitions from $^3H_4$ to $(^3H_6, {}^3F_4)$, $(^3F_3, {}^3F_2)$, $^1G_4$, $^1D_2$, and $(^3P_{0,1,2}, {}^1I_6)$. In addition to the paucity of data, the transitions to $^1G_4$ was weak. The oscillator strength for magnetic dipole transitions to these states are small, ~10^{-8}. Attempts to fit oscillator strengths to electric dipole transitions were unsuccessful; a negative value of Ω_2 was obtained which is incompatible with the Judd-Ofelt theory. Similar results and poor fits for Pr^{3+} spectra have been reported previously. In solutions, negative values of Ω_2 occurred when attempting to fit observed and calculated Pr^{3+} intensities; a fit was obtained only by deleting data.[5] In one case where the Pr^{3+} intensities were fitted, the statistical error for one parameter was greater than its absolute value.[3] In addition, the calculated radiative lifetimes were not in agreement with experiment.[10]

To supplement the absorption data, measurements were made of the fluorescence from the $^1D_2$ and $^3P_0$ states. The lifetimes measured for a 0.1-at.% Pr sample at 77 °K were $^1D_2$, 125 μsec and $^3P_0$, 12 μsec. Since the energy gap to the next-

TABLE II. Measured and calculated oscillator strengths of transitions from $^4I_{9/2}$ for Nd^{3+} in $YAlO_3$.

Excited state $S'L'J'$	Spectral range (nm)	Oscillator strength ($\times 10^6$) Measured	Calculated
$^4F_{3/2}$	863–910	1.36	1.71
$^4F_{5/2}, {}^2H_{9/2}$	775–822	5.50	5.62
$^4F_{7/2}, {}^4S_{3/2}$	730–770	5.84	5.90
$^4F_{9/2}$	670–695	0.54	0.43
$^2H_{11/2}$	620–645	0.15	0.13
$^4G_{5/2}, {}^2G_{7/2}$	570–611	8.08	8.17
$^4G_{7/2}, {}^4G_{9/2}$ $^2K_{13/2}$	500–547	5.27	3.82
$^2K_{15/2}, {}^2D_{3/2}$ $^4G_{11/2}, {}^2G_{9/2}$	455–487	1.43	0.95
$^2P_{1/2}$	431–443	0.46	0.45
$^4D_{3/2}, {}^4D_{5/2}$ $^2I_{11/2}, {}^4D_{1/2}, {}^2L_{15/2}$	350–368	8.82	9.08

lower levels are ~6000 and ~3500 cm^{-1}, respectively, decay by multiphonon emission is negligible[8] and the above lifetimes can be attributed solely to radiative decay. The magnetic dipole contribution to the radiative probability from $^1D_2$ is only 10.6 sec^{-1} and hence also negligible. Magnetic dipole transitions from $^3P_0$ are forbidden by the selection rule $|\Delta J| \leq 1$. In terms of the electric dipole intensity parameters, the radiative lifetimes are, from Eq. (5),

$$\tau(^1D_2)^{-1} = (6.82\Omega_2 + 4.08\Omega_4 + 3.45\Omega_6)\times 10^{22} , \quad (11)$$

$$\tau(^3P_0)^{-1} = (59.6\Omega_2 + 102\Omega_4 + 17.0\Omega_6)\times 10^{22} . \quad (12)$$

The intensity parameters reported for Pr^{3+} have tended to be the largest for the lanthanide series.[3,5] Values for $YAlO_3$: Pr^{3+} of $\Omega_2 = 2$, $\Omega_4 = 6$, and $\Omega_6 = 7\times 10^{-20}$ cm^2 were estimated by extrapolation from the values for $YAlO_3$: Nd^{3+}. Using these parameters in Eqs. (11) and (12) yields predicted lifetimes of 160 and 11.8 μsec. These results are in general agreement with experiment but may be fortuitously good. Whereas several transitions contribute to determining the $^1D_2$ lifetime, the $^3P_0$ lifetime is dominated by the contribution from $A(^3P_0 \rightarrow {}^3H_4)$ and hence is sensitive to only the Ω_4 parameter. If the above Ω's are used to calculate the absorption oscillator strengths, the five data are not fit simultaneously. A possible reason for this is presented in the concluding remarks.

B. Neodymium

Intensity parameters for Nd^{3+} were obtained earlier based upon measurements of transitions to ten different groups of J states.[13] A detailed comparison of the measured and calculated oscillator strengths is given in Table II. The fit is satisfactory with an rms deviation of 0.60×10^{-6}.

Of the three intensity parameters for Nd^{3+} in Table I, Ω_2 is the least well determined. The matrix elements of $\underline{U}^{(2)}$ from the $^4I_{9/2}$ ground state to all states studied are very small with the exception of the transition to $^4G_{5/2}$. Thus Ω_2 is fitted predominantly by this single datum (the contribution of the second-order term to this transition is also less than that of the fourth-order term).

The intensity parameters were also used to calculate the radiative lifetime and fluorescence branching ratios from $^4F_{3/2}$ to the ^4I ground multiplet.[13] The predicted lifetime was in good agreement with experiment; the predicted branching ratios, however, exhibited less satisfactory agreement.

C. Europium

Determination of the intensity parameters for Eu^{3+} from absorption spectra is difficult because there are a large number of closely spaced excited states which made assignments of J quantum numbers difficult for hosts having medium to large crystalline Stark splittings. In addition, the number of terms in Eq. (3) which contribute to transitions from the $^7F_0$ ground state and the thermally populated $^7F_1$ and $^7F_2$ states is restricted by the triangle rule $|J-J'| \leq t \leq |J+J'|$. Intensity parameters were therefore derived instead from measurements of the fluorescence lifetime and branching ratios.

The radiative lifetime of the $^5D_0$ level is $1/\tau(^5D_0) = \sum A(^5D_0 \rightarrow {}^7F_J)$, where the summation is over the terminal levels of the ^7F multiplet. The spontaneous emission probabilities A are related by the fluorescence branching ratios in Eq. (7). These ratios, determined from measurements of the relative fluorescence intensities from $^5D_0$ at 300 °K were $^7F_1$, 0.165; $^7F_2$, 0.328; $^7F_3$, 0.033; $^7F_4$, 0.428; $^7F_6$, 0.047. The intensity to $^7F_5$ was not measured since it was masked by $^2E \rightarrow {}^4A_2$ vibronic emission from unintentional Cr^{3+} impurities in the crystal used; the intensity, however, is believed to be small—less than a few percent of the total. In the absence of J-state mixing, the only allowed transitions from $^5D_0$ are $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) and $^5D_0 \rightarrow {}^7F_2$, $^7F_4$, $^7F_6$ (electric dipole). The magnitude of the $^5D_0 \rightarrow {}^7F_3$ intensity indicates that J mixing is not negligible, a conclusion reached previously by others.[14] Combining the above branching ratios with the measured radiative lifetime for $^5D_0$ of 1.5 msec yields the measured spontaneous emission probabilities given in Table III.

The probability for $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transitions calculated using eigenstates for Eu^{3+} in an immediate coupling scheme was 107 sec^{-1}, which is in good agreement with the measured val-

TABLE III. Measured and calculated spontaneous emission probabilities from the $^5D_0$ state of Eu^{3+} in $YAlO_3$.

Terminal state $S'L'J'$	Spectral range (nm)	Spontaneous emission probability (sec^{-1}) Measured	Calculated
$^7F_0$	580–585	~1	0
$^7F_1$	590–602	110	107
$^7F_2$	612–635	219	230
$^7F_3$	648–660	22	0
$^7F_4$	680–712	285	297
$^7F_5$	~750	...	0
$^7F_6$	806–842	31	32

ue. Electric dipole transitions from $^5D_0$ to $^7F_2$, $^7F_4$, $^7F_6$ each involve only a single intensity parameter. These parameters were found by neglecting J mixing and setting the total calculated radiative probability equal to the observed decay rate. The resulting Ω's are given in Table I; the A's calculated from this set of parameters are included in Table III.

Because Ω_2, Ω_4, and Ω_6 were each derived from a single datum, no fitting was possible. As a test of the parameter values, the absorption intensities from $^7F_{0,1}$ to $^7F_6$ and to $^5D_2$, which are proportional to Ω_6 and Ω_2, respectively, were measured. A sample containing a nominal 0.25-at.% Eu and a pathlength of 0.31 cm was used. In deriving the separate contributions from $^7F_0$ and $^7F_1$, the appropriate Boltzmann population was used. (At 300 °K there is also a small population in $^7F_2$; however, the matrix elements from $^7F_2$ are also small, which renders any contribution from $^7F_2$ less than the experimental uncertainties). The intensity parameters found were $\Omega_2 = 4.9 \times 10^{-20}$ cm^2 and $\Omega_6 = 0.94 \times 10^{-20}$ cm^2. These values are somewhat larger than those in Table I, particularly Ω_2.

D. Terbium

Attempts to perform a detailed analysis of Tb^{3+} intensities are plagued by some of the same difficulties encountered for Eu^{3+}. Higher excited states are closely spaced and J labeling is uncertain. Matrix elements of $\underline{U}$ are small for many transitions of interest and sensitive to the eigenstates used.[12,15,16] In addition, the lowest 5d bands of Tb^{3+} are low and the potential admixing with 4f states is large (although spin selection rules may reduce the degree of 4f-5d admixing).[12,16]

Because of the above, measurements of the absorption spectra were restricted to transitions to the well-isolated $^5D_4$ level at ≈20 500 cm^{-1} and to the $^7F_{3,2,1,0}$ levels in the region ≈2500–6000 cm^{-1}. A $TbAlO_3$ crystal having a thickness of 0.048 cm was used for these measurements, thus eliminating uncertainties associated with the Tb concentration. The $^7F_6 \rightarrow {}^5D_4$ oscillator strength at 295 °K was 2.9×10^{-8}. This corresponds to a $^5D_4 \rightarrow {}^7F_6$ spontaneous emission probability of 87 sec^{-1}.

Fluorescence was observed from the $^5D_4$ and $^5D_3$ states. The lifetimes for a 0.1-at.% Tb sample were 1.7 and 0.7 msec, respectively. Both lifetimes were temperature independent from 77 to 700 °K and are attributed solely to radiative decay. The fluorescence branching ratios from $^5D_4$ to the ^7F_J manifolds were measured at 300 °K using a powdered 0.1-at.% Tb sample. Combining these results with the $^5D_4$ lifetime and assuming a radiative quantum efficiency of unity yields the measured A's given in Table IV. If the $A(^5D_4 \rightarrow {}^7F_6)$ derived from the $^7F_6 \rightarrow {}^5D_4$ oscillator strength found in absorption is combined with the measured branching ratios, a radiative lifetime of 2.07 msec is predicted. The agreement with experiment is only fair.

A set of Ω parameters for Tb^{3+} was derived from the following experimental results: (a) the $^7F_6 \rightarrow {}^5D_4$ oscillator strength, (b) the $^7F_6 \rightarrow {}^7F_{3,2,1,0}$ oscillator strengths, and (c) the radiative lifetime of $^5D_4$. These three data could all be fitted very well using the matrix elements of Kuboniwa and Hoshina[16] and the Ω parameters given in Table I. However, the calculated spontaneous emission probabilities from $^5D_4$ shown in Table V are not in good agreement with measured values. (Others have cited an inability to obtain a consistent set of Ω's for Tb^{3+} from fluorescence intensities.[16]) Note that the $\underline{U}^{(t)}$ matrix elements from $^5D_4$ to $^7F_6$ are all larger than to $^7F_4$, yet the observed intensity to $^7F_4$ is greater. J mixing is undoubtedly present for several states. Because of the limited number of data used and the sensitivity of the matrix elements of Tb^{3+} to the eigenstates, the Tb^{3+} Ω values must be considered with reservations.

E. Holmium

The measured intensities and analysis of the absorption spectrum of Ho^{3+} in $YAlO_3$ have been reported in a separate paper[17] and will not be repeated here. Transitions to 19 different J states

TABLE IV. Measured and calculated spontaneous emission probabilities from the $^5D_4$ state of Tb^{3+} in $YAlO_3$.

Terminal state $S'L'J'$	Spectral range (nm)	Spontaneous emission probability (sec^{-1}) Measured	Calculated
$^7F_6$	0.48–0.51	106	87
$^7F_5$	0.54–0.56	259	230 ed 102 md
$^7F_4$	0.58–0.60	123	54 ed 1 md
$^7F_3$	0.62–0.63	71	34 ed 12 md
$^7F_{2,1,0}$	0.64–0.69	29	68

TABLE V. Measured and calculated oscillator strengths of transitions from $^4I_{15/2}$ for Er^{3+} in $YAlO_3$.

Excited state $S'L'J'$	Spectral range (nm)	Oscillator strength ($\times 10^6$) Measured	Calculated
$^4I_{13/2}$	1450–1640	1.27	0.63 ed 0.59 md
$^4I_{11/2}$	959–1020	0.31	0.23
$^4I_{9/2}$	782–842	0.25	0.43
$^4F_{9/2}$	644–677	1.15	1.75
$^4S_{3/2}$	540–556	0.41	0.21
$^2H_{11/2}$	510–538	2.43	2.41
$^4F_{7/2}$	482–502	1.12	1.20
$^7F_{5/2}$ $^7F_{3/2}$	441–461	0.60	0.41
$^2H_{9/2}$	403–417	0.42	0.38
$^4G_{11/2}$	376–389	4.31	4.34
$^4G_{9/2}$, $^2K_{15/2}$ $^2G_{7/2}$	355–373	1.67	1.77
$^2P_{3/2}$	316–322	0.043	0.029
$^4G_{7/2}$	293–299	1.46	2.06
$^2D_{5/2}$	287–292	0.058	0.041
$^2G_{9/2}$	272–279	0.30	0.32
$^4D_{5/2}$, $^4D_{7/2}$	253–265	7.33	6.27

or groups of J states were investigated. A very good fit between measured and calculated oscillator strengths (≈± 10%) was obtained. The Ω parameters are included in Table I.

F. Erbium

Integrated absorption cross sections were measured using crystals having an erbium concentration of 1.1-at.% and path length of 0.47 cm. Sixteen J or groups of unresolved J states with energies up to 40 000 cm^{-1} were investigated. The measured oscillator strengths, given in Table V, ranged over two orders of magnitude.

Least-squares-fitted oscillator strengths calculated from the Er^{3+} intensity parameters in Table I are included in Table V. The rms deviation was 0.35×10^{-6}, which, in terms of percentage, was the largest for the ions studied. By examining the relative magnitudes of the matrix elements and contributions from the various terms, it is evident that some intensities are especially sensitive to the values of particular parameters. For example, the intensities to $^2P_{3/2}$, $^4I_{9/2}$, and $^4I_{11/2}$ (none of which were fitted very well) are governed predominantly by a single term in Eq. (3), the second-, fourth-, and sixth-order terms, respectively.

The lifetimes of the $^4I_{13/2}$ and $^2P_{3/2}$ states, measured at low temperatures and low-Er^{3+} concentration, are slightly longer than the predicted radiative lifetimes.[8] This suggests that the Ω parameters for Er^{3+} in Table V may be somewhat large, due either to the quality of the fitting or possibly an inaccurate concentration determination.

G. Thulium

Measurements of absorption cross sections were made using a nominal 1.0-at.% thulium-doped crystal. The agreement between measured and calculated oscillator strengths, shown in Table VI, is very good with an rms derivation of 0.11×10^{-6}. The calculated radiative lifetime of the $^3H_4$ state is 4.7 msec.

H. Ytterbium

Trivalent ytterbium has only two free-ion states, $^2F_{7/2}$ and $^2F_{5/2}$, and a single $f\rightarrow f$ transition. The oscillator strength of the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition, measured in absorption, was 2.53×10^{-6}. This includes both electric and magnetic dipole contributions. The calculated magnetic dipole contribution is $f_{md}=0.34\times10^{-6}$, thereby leaving an oscillator strength of 2.19×10^{-6} attributable to electric dipole transitions.

With only one transition it is not possible to determine the individual intensity parameters for Yb^{3+}. Table I reveals a gradual decrease in the values of the Ω's for progressively heavier ions in the latter half of the $4f$ series. Extrapolating this trend to Yb^{3+}, approximate values of $\Omega_2\approx0.4$, $\Omega_4\approx2.3$, $\Omega_6\approx0.6\times10^{-20}$ cm^2 were obtained. Using these values in Eqs. (3) and (4) gives a calculated oscillator strength of $f_{ed}=2.08\times10^{-6}$. The radiative lifetime of $^2F_{5/2}$ predicted from Eq. (5) is 0.70 msec versus a measured lifetime of 0.74 msec. Thus the extrapolated values of Ω_t provide satisfactory estimates of the optical transition probabilities for $YAlO_3:Yb^{3+}$.

TABLE VI. Measured and calculated oscillator strengths of transitions from $^3H_6$ for Tm^{3+} in $YAlO_3$.

Excited state $S'L'J'$	Spectral range (nm)	Oscillator strength ($\times 10^6$) Measured	Calculated
$^3H_4$	1600–2000	1.07	1.08
$^3H_5$	1140–1270	1.28	0.75 ed 0.53 md
$^3F_4$	760–840	0.96	0.90
$^3F_3$	680–720	1.57	1.62
$^3F_2$	650–680	0.25	0.24
$^1G_4$	458–490	0.38	0.38
$^1D_2$	350–371	2.05	1.84

V. CONCLUDING REMARKS

The phenomenological Judd-Ofelt theory accounts reasonably well for the intensities observed in the optical spectra of most rare-earth ions studied in $YAlO_3$. One notable exception is praseodymium. There is now an increasingly well-documented record of inadequacy when the Judd-Ofelt treatment is applied to Pr^{3+}.[3,5,10] The reason for these discrepancies, as suggested previously,[5,10] may be the proximity of the $5d$ bands which for Pr^{3+} are among the lowest of the $4f^n$ series.[18] If the degree of f-d admixing is significantly different for low- and high-lying levels of the $4f^2$ configuration, then the Judd-Ofelt use of an averaged $4f$-$5d$ energy denominator and a single set of intensity parameters to account for all transitions may be insufficient.

In the Judd-Ofelt approach, measured oscillator strengths are related to products of intensity parameters and reduced matrix elements. Generally the latter are insensitive to the eigenstates used for their computation. However, when the matrix elements are small, as for many transitions of Eu^{3+} and Tb^{3+}, they can become sensitive to the eigenstates used. For an intermediate coupling scheme, the eigenstates are dependent upon the spin-orbit parameter and three Racah parameters. Different matrix elements are obtained if simple hydrogenic ratios of Racah parameters are assumed or if parameters are derived from fitting the centers of gravities of J manifolds.[15,16] Truncation of the eigenstates may also seriously affect the final matrix elements.[7] The results for Eu^{3+} and Tb^{3+} are therefore subject to uncertainties associated with the available matrix elements, since they were not derived explicitly for $YAlO_3$.

The intensity parameters obtained for trivalent rare earths in $YAlO_3$ are large, of similar magnitude to those for Y_2O_3[3] and generally larger than those of LaF_3[3,17] and $Y_3Al_5O_{12}$.[19] This correlates with the greater absorption and shorter radiative lifetimes observed in $YAlO_3$. Of the three parameters, Ω_2 is usually the least well defined. This occurs because the matrix elements of $U^{(2)}$ are zero for transitions involving $|\Delta J| > 2$, which limits the number of intensities contributing to the fit.

The variation of the intensity parameters across the $4f^n$ series is unclear (i) because the only results obtained toward the first-half of the series are those for Nd^{3+} and (ii) because of uncertainties associated with the values for Eu^{3+} and Tb^{3+}. The results for $YAlO_3$ differ from those for Y_2O_3, where Ω_4 and Ω_6 had their smallest values near the center of the series.[3] The over-all behavior is more similar to that reported for rare earths in solutions,[5] although some major differences do occur.

There does appear to be a systematic gradual decrease in the Ω's with increasing atomic number in the latter half of the lanthanide series. This trend is qualitatively consistent with calculations of Krupke made using lattice sums and free-ion radial wave functions.[3] The relative static and vibronic contributions to the parameters can affect the trend. These individual contributions were not established for $YAlO_3$ but are expected to differ for different hosts. The appearance of vibronic transitions is increasing evident in the spectra of heavier ions such as Yb^{3+} and Tm^{3+}. If the intensities were restricted to only the purely electronic transitions, the Ω's would be smaller and would probably exhibit a greater decrease with increasing Z.

Extrapolation of the observed decreasing trend of Ω's to Yb^{3+} yielded satisfactory predictions of the radiative lifetime. Thus the extrapolation of measured Judd-Ofelt parameters to adjacent ions should provide valid estimates of optical intensities.

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[1] B. R. Judd, Phys. Rev. **127**, 750 (1962).

[2] G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

[3] W. F. Krupke, Phys. Rev. **145**, 325 (1966).

[4] W. T. Carnall, P. R. Fields, and B. G. Wybourne, J. Chem. Phys. **42**, 3797 (1965).

[5] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4412 (1968).

[6] M. J. Weber, Phys. Rev. **157**, 262 (1967).

[7] M. J. Weber, Phys. Rev. **171**, 283 (1968).

[8] M. J. Weber, following paper, Phys. Rev. B **8**, 54, (1973).

[9] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965).

[10] M. J. Weber, J. Chem. Phys. **48**, 4771 (1968).

[11] M. J. Weber, M. Bass, K. Andringa, R. R. Monchamp, and E. Comperchio, Appl. Phys. Lett. **15**, 342 (1969).

[12] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4424 (1968); J. Chem. Phys. **49**, 4443 (1968); J. Chem. Phys. **49**, 4447 (1968); J. Chem. Phys. **49**, 4450 (1968).

[13] M. J. Weber and T. E. Varitimos, J. Appl. Phys. **42**, 4996 (1971).

[14] M. Kajiura and K. Shinagawa, J. Phys. Soc. Jap. **28**, 1041 (1970).

[15] T. Hoshina, Jap. J. Appl. Phys. **6**, 1203 (1967).

[16] S. Kuboniwa and T. Hoshina, J. Phys. Soc. Jap. **32**, 1059 (1972).

[17] M. J. Weber, B. H. Matsinger, V. L. Donlan, and G. T. Surratt, J. Chem. Phys. **57**, 562 (1972).

[18] Strong $f \rightarrow d$ absorption is observed beginning below 230 nm for $YAlO_3$:Pr^{3+}.

[19] W. F. Krupke, IEEE J. Quantum Electron. **QE-7**, 153 (1971).