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# Radiative and Multiphonon Relaxation of Rare-Earth Ions in $Y_2O_3^{\dagger}$

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Spontaneous-emission probabilities for electric- and magnetic-dipole transitions from excited electronic states of Pr3+, Nd3+, Eu3+, Er3+, and Tm3+ impurities in Y2O3 are calculated using eigenstates in intermediate coupling and experimental intensity parameters. The predicted radiative lifetimes are in good agreement with experimental lifetimes measured using pulsed-selective-excitation techniques for those levels where unit quantum efficiency is expected. Discrepancies do exist, however, which indicate the importance of J-state mixing and possible breakdown of the closure approximation used in Judd and Ofelt's treatment. Nonradiative decay rates were determined by subtracting the radiative contribution from the observed lifetime. The rates of multiphonon emission in  $Y_2O_3$  exhibit a systematic variation with proximity of the next-lowest level, and contribute significantly to the decay for levels having energy gaps to the nextlowest level of less than 3000 cm<sup>-1</sup>. Selection-rule restrictions are evident from the reduced relaxation rates for the  ${}^{5}D_{J}$  levels of Eu<sup>3+</sup>. The concentration dependence of the excitation spectra and excited-state lifetimes of Tm<sup>3+</sup> were investigated to establish the importance of ion-pair relaxation; however, these processes were generally avoided.

### INTRODUCTION

T has been shown by Judd<sup>1</sup> and Ofelt<sup>2</sup> that electricdipole transition probabilities between electronic states of rare-earth ions can be expressed and calculated in terms of a small number of phenomenological intensity parameters characteristic of the ion-host system. This theory has received substantial experimental verification from a number of spectral-intensity studies<sup>3-9</sup> of rare-earth ions in both liquids and solids. Although the agreement between theory and experiment has at times been limited by the experimental conditions and approximations used, the approach is of value for inter-

171

preting and predicting intensities<sup>10</sup> of crystal-fieldinduced electric-dipole transitions in absorption and emission spectra of lanthanide ions. In addition, nonradiative decay rates and quantum efficiencies can be readily determined<sup>7-9</sup> by combining calculated radiative decay probabilities with measurements of excited-state lifetimes.

In this paper, the Judd-Ofelt treatment is applied to calculate the spontaneous-emission probabilities for electric- and magnetic-dipole transitions from a large number of excited states of several different lanthanideseries rare-earth ions in Y<sub>2</sub>O<sub>3</sub>. The interest is twofold: first, to provide a further test of the treatment and its limitations by comparing predicted radiative lifetimes with observed lifetimes for a number of different states where radiative quantum efficiencies of unity are expected, particularly for higher excited states where breakdown of the closure approximation used to sum over states of the opposite-parity configuration may occur; and, second, to combine calculated radiative lifetimes and experimental lifetimes to determine rates of nonradiative decay by multiphonon emission and their dependence on eigenstates, proximity of lower levels, and temperature. Recent investigations of multi-

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phonon relaxation in LaCl<sub>3</sub>, LaBr<sub>3</sub>, and LaF<sub>3</sub> have shown very clearly the sensitivity of the rate of multiphonon emission to the number of phonons required to conserve energy, the phonon-frequency spectrum, and the strength of the ion-lattice coupling.<sup>7,11-13</sup> The present results for rare-earth ions in yttria corroborate these findings and provide an example where strong crystalfield interactions and higher-energy phonons are more active than in the other crystals studied thus far.

The spectroscopic properties of most rare earths in Y<sub>2</sub>O<sub>3</sub> are well known. The Racah and spin-orbit parameters which yield the best fit between energy levels calculated in intermediate coupling and experimental centers of gravity of J levels have also been determined for several ions.

Trivalent rare-earth impurities enter the Y<sub>2</sub>O<sub>3</sub> lattice as an isomorphic substitution for yttrium without charge compensation. There are two different types of substitutional sites in the unit cell, three of point-group symmetry  $C_2$  and one of point-group symmetry  $C_{3i}$ . Because the  $C_{3i}$  sites have inversion symmetry, electricdipole transitions are forbidden. The observed spectra have, in general, been attributed to ions in sites of  $C_2$ symmetry, and this is implicitly assumed throughout.

#### PROBABILITIES FOR RADIATIVE DECAY

Radiative decay of excited rare-earth ions in crystals occurs predominantly by magnetic- and electric-dipole transitions. Whereas magnetic-dipole transitions are allowed between states of the ground  $4f^N$  configuration, electric-dipole transitions are parity-forbidden. If the ion resides in a lattice site lacking inversion symmetry, odd harmonics in the expansion of the crystalfield potential can admix states of opposite parity from higher configurations, such as  $4f^{N-1}5d$ , into  $4f^N$ , and thereby electric-dipole transitions become possible. Judd<sup>1</sup> and Ofelt<sup>2</sup> have shown that by ascribing an average energy to all states of a higher, opposite-parity configuration, closure can be invoked in the summation over the states of the excited configuration. The line strength for electric-dipole transitions between SLJ states can then be expressed simply as a sum of products of matrix elements of unit tensor operators  $\mathbf{U}^{(\lambda)}$ and intensity parameters  $\Omega_{\lambda}$  of the form

$$S = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} (f^N \alpha SLJ \mid |U^{(\lambda)}| \mid f^N \alpha' S' L'J')^2.$$
(1)

The strength of the crystal field, energy of the higher configuration, and integrals involving radial wave functions of the 4f and opposite-parity configurations are all included in the phenomenological parameters  $\Omega_{\lambda}$ . These parameters are usually determined experimentally from measured absorption intensities and

have been evaluated by Krupke<sup>6</sup> for Pr<sup>3+</sup>, Nd<sup>3+</sup>, Eu<sup>3+</sup>,  $Er^{3+}$ , and  $Tm^{3+}$  in  $Y_2O_3$ .

Calculations of the total transition probabilities between different J levels were made using eigenstates in intermediate coupling obtained from diagonalization of the combined spin-orbit and electrostatic energy matrices. These states are composed of a linear combination of Russell-Saunders states of the form

$$|f^{N}[\alpha SL]J\rangle = \sum_{\alpha SL} C(\alpha SL) |f^{N}\alpha SLJ\rangle, \qquad (2)$$

where the bracket denotes that in the labeling of states, S and L are no longer good quantum numbers. J-state mixing caused by even-order terms in the crystalline potential is neglected in this approximation. Using Eq. (1), the probability for spontaneous emission of electric-dipole radiation is given by

$$A_{\rm ed} = 64\pi^4 e^2 \bar{\sigma}^3 \chi/3h(2J+1) \\ \times \sum_{\lambda=2,4,6} \Omega_{\lambda} (f^N [\alpha SL] J || \mathbf{U}^{(\lambda)} || f^N [\alpha' S'L'] J')^2, \quad (3)$$

where  $\bar{\sigma}$  is an average transition frequency (cm<sup>-1</sup>), and  $\chi$  is a correction factor for the refractive index of the medium and is approximated by  $\frac{1}{9}n(n^2+2)^2$ . Since the variation of the index of refraction n for Y<sub>2</sub>O<sub>3</sub> over the spectral region of interest is large ( $\sim 50\%$ ), this correction is significant. For consistency, n for Y<sub>2</sub>O<sub>3</sub> was derived from the same Cauchy formula used by Krupke,  $n(\lambda) = 1.780 + 0.0598\lambda^{-2}(\mu)$ . The probability for magnetic-dipole transitions can be calculated from

$$4_{\rm md} = 4\pi^2 e^2 \bar{\sigma}^3 n^3 h / 3m^2 c^2 (2J+1) \\ \times (f^N [\alpha SL]J || L+2S || f^N [\alpha' S'L']J')^2.$$
(4)

Expressions for evaluating the reduced matrix elements of  $\hat{\mathbf{U}}^{(\lambda)}$  and  $(\mathbf{L}+2\mathbf{S})$  are given elsewhere.<sup>5,7</sup> In Eqs. (3) and (4), all Stark components of the initial J level are assumed to be equally populated.

The probability for vibronic transitions involving a single phonon has the same form as Eq. (3).<sup>1</sup> The experimental parameters  $\Omega_{\lambda}$  used in subsequent calculations include contributions from both static and vibrational crystal-field-induced electric-dipole transitions.

#### Praseodymium, Neodymium, Erbium, and Thulium

A complete set of intermediate coupled states was computed for each of these ions using reported Racah  $E^1$ ,  $E^2$ ,  $E^3$ , and spin-orbit  $\zeta$  parameters. These parameters, together with Krupke's intensity parameters  $\Omega_{\lambda}$ and pertinent references,<sup>6,14-17</sup> are given in Table I. Spontaneous-emission probabilities were calculated from Eqs. (3) and (4) for levels having large energy

<sup>&</sup>lt;sup>11</sup> W. D. Partlow and H. W. Moos, Phys. Rev. 157, 252 (1967). <sup>12</sup> L. A. Riseberg, W. B. Gandrud, and H. W. Moos, Phys. Rev.

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 &</sup>lt;sup>17</sup> J. B. Gruber, W. F. Krupke, and J. M. Poindexter, J. Chem. Phys. 41, 3363 (1964).

| Parameter  | r Pr <sup>3+</sup>   | Nd³+  | Eu <sup>3+</sup>   | Er <sup>3+</sup>  | Tm <sup>3+</sup>  |  |
|--|--|---|--|---|---|--|
| $E^1 \ ({ m cm}^{-1}) \ E^2 \ ({ m cm}^{-1}) \ E^3 \ ({ m cm}^{-1}) \ \zeta \ ({ m cm}^{-1}) \ \zeta \ ({ m cm}^{-1}) \ \Omega_2 \ (10^{-20} \ { m cm}^2) \ \Omega_4 \ (10^{-20} \ { m cm}^2) \ \Omega_6 \ (10^{-20} \ { m cm}^2) \ { m References}$ | $\begin{array}{r} 4670.3\\21.26\\457.13\\733.11\\17.21\pm0.16\\1.98\pm0.14\\4.88\pm0.09\\6\end{array}$ | $\begin{array}{r} 4853.9\\ 24.20\\ 471.87\\ 877.59\\ 8.55\pm0.43\\ 5.25\pm0.80\\ 2.89\pm0.61\\ 6,14\end{array}$ | $5886.0 \\ 30.82 \\ 595.3 \\ 1320.0 \\ 9.86 \\ 2.23 \\ \approx 0.32 \\ 15$ | $\begin{array}{c} 6597.16\\ 31.611\\ 629.54\\ 2383.17\\ 4.59{\pm}0.25\\ 1.21{\pm}0.21\\ 0.48{\pm}0.33\\ 6,16\\ \end{array}$ | $\begin{array}{c} 6959.47\\ 31.995\\ 656.94\\ 2617.0\\ 4.07{\pm}0.27\\ 1.46{\pm}0.16\\ 0.61{\pm}0.13\\ 6,17\end{array}$ |  |

TABLE I. Racah, spin-orbit, and intensity parameters used in calculations for rare-earth ions in Y2O3.

gaps to the next-lowest level, from which some observable emission might be anticipated, and other nearby J levels which either become thermally populated at elevated temperatures or may be strongly admixed. Transitions to all lower levels were considered. The total spontaneous-emission probabilities and the predicted radiative lifetimes, given by  $\left[\sum (A_{\rm ed} + A_{\rm md})\right]^{-1}$ , are tabulated in Table II. The probable errors of the latter arise only from the uncertainties in the  $\Omega_{\lambda}$  parameters.

Calculated spontaneous-emission probabilities, TABLE II. predicted radiative lifetimes, and observed lifetimes for excited states of trivalent rare earths in Y<sub>2</sub>O<sub>3</sub>.

| Excited<br>state  | $A_{\rm ed}$ (sec <sup>-1</sup> )  | $A_{\mathrm{md}}$ (sec <sup>-1</sup> )  | Radiative<br>lifetime<br>(µsec)  | Observed<br>lifetime<br>(µsec)   |  |  |  |  |  |
|---|--|---|--|--|--|--|--|--|--|
| Praseodymium  |  |   |  |  |  |  |  |  |  |
| <sup>1</sup> G <sub>4</sub><br><sup>1</sup> D <sub>2</sub><br><sup>1</sup> I <sub>6</sub><br><sup>3</sup> P <sub>0</sub><br><sup>3</sup> P <sub>1</sub><br><sup>3</sup> P <sub>2</sub>                            | $\begin{array}{c}1 & 718 \\ 19 & 700 \\ 368 & 300 \\ 331 & 000 \\ 301 & 500 \\ 283 & 900 \end{array}$                          | $14.4 \\10.2 \\6.4 \\0.0 \\1.1 \\4.2$   | $577 \pm 4$<br>$50.7 \pm 0.3$<br>$2.7 \pm 0.2$<br>$3.0 \pm 0.1$<br>$3.3 \pm 0.1$<br>$3.5 \pm 0.1$  |  |  |  |  |  |  |
| <sup>4</sup> F <sub>3/2</sub>   | 3 700  | Ne<br>0.0   | odymium<br>270±33  | ≈260   |  |  |  |  |  |
| Europium  |  |   |  |  |  |  |  |  |  |
| <sup>5</sup> D <sub>0</sub><br><sup>5</sup> D <sub>1</sub><br><sup>5</sup> D <sub>2</sub>   | 930<br>878<br>777  | 109<br>105<br>95  | 963<br>1020<br>1150  | 860±20<br>160±5 (77°K)<br>≈100   |  |  |  |  |  |
| Erbium  |  |   |  |  |  |  |  |  |  |
| ${}^{4}I_{13/2}$<br>${}^{4}I_{11/2}$<br>${}^{4}I_{9/2}$<br>${}^{4}F_{9/2}$<br>${}^{4}S_{3/2}$<br>${}^{2}H_{11/2}$<br>${}^{2}H_{9/2}$<br>${}^{4}G_{11/2}$<br>${}^{2}P_{3/2}$<br>${}^{4}D_{5/2}$<br>${}^{4}D_{7/2}$ | $\begin{array}{c} 73\\ 135\\ 220\\ 1\ 537\\ 1\ 432\\ 12\ 655\\ 3\ 998\\ 65\ 170\\ 16\ 026\\ 109\ 624\\ 230\ 121\\ \end{array}$ | $59.3 \\11.9 \\1.3 \\14.7 \\0.0 \\129.2 \\132.4 \\116.3 \\95.0 \\60.7 \\21.0 \\$      | $\begin{array}{c} 7750 \pm 2150 \\ 6810 \pm 2470 \\ 4520 \pm 790 \\ 644 \pm 140 \\ 698 \pm 471 \\ 78 \pm 4 \\ 242 \pm 77 \\ 15 \pm 1 \\ 62 \pm 32 \\ 9.1 \pm 0.7 \\ 4.3 \pm 0.6 \end{array}$ | $\begin{array}{c} 8000 \pm 500 \\ 3900 \pm 400 \\ \gtrless 200 \\ \approx 30 \\ \left\{ 155 \pm 10 \ (77^{\circ} \mathrm{K}) \\ 88 \pm 7 \ (296^{\circ} \mathrm{K}) \\ \approx 5 \\ \gtrless 2 \\ 3700 \pm 5 \ (296^{\circ} \mathrm{K}) \\ \gtrless 1 \end{array} \right.$ |  |  |  |  |  |
| Thulium   |  |   |  |  |  |  |  |  |  |
| ${}^{3}H_{4}$<br>${}^{3}H_{5}$<br>${}^{3}F_{4}$<br>${}^{3}F_{3}$<br>${}^{1}G_{4}$<br>${}^{1}D_{2}$<br>${}^{1}I_{6}$   | 277<br>237<br>1 534<br>2 467<br>2 682<br>58 280<br>29 170  | $\begin{array}{c} 0.0 \\ 84.1 \\ 31.2 \\ 67.8 \\ 212.7 \\ 166.8 \\ 201.4 \end{array}$ | $3610\pm200$<br>$3310\pm190$<br>$639\pm43$<br>$394\pm40$<br>$286\pm7$<br>$17\pm1$<br>$34\pm3$  | $3700\pm 200$<br>$\approx 300$<br>$410\pm 30$<br>$\approx 2$<br>$240\pm 20$<br>$9\pm 1$<br>$32\pm 3$   |  |  |  |  |  |

#### Europium

In contrast to the relatively simple  $4f^2$  and  $4f^3$  configurations of (Pr<sup>3+</sup>, Tm<sup>3+</sup>) and (Nd<sup>3+</sup>, Er<sup>3+</sup>), detailed calculations of transition probabilities between states of Eu<sup>3+</sup> are very extensive because of the large number of component states involved. There are 199 basis states of the  $4f^6$  configuration giving rise to 295 J-levels. Ofelt<sup>15</sup> has diagonalized the combined spin-orbit and electrostatic energy matrices, using hydrogenic ratios of the Slater integrals and neglecting singlet states. A more complete calculation including all states and Racah and spin-orbit parameters obtained from fitting experimental energy levels of Y<sub>2</sub>O<sub>3</sub>: Eu<sup>3+</sup> was performed by Chang and Gruber.<sup>18</sup> Their results for the higher excited states, where contributions from triplet and singlet states are important, differ from Ofelt's values by several hundred cm<sup>-1</sup> or more.

Matrix elements of  $\mathbf{U}^{(\lambda)}$  between  ${}^{5}D_{J}$  and  ${}^{7}F_{J}$  states were calculated<sup>8</sup> previously using Ofelt's eigenstates, which contained only the quintet- and septet-state components. Although the coefficients of the triplet and singlet components of the  $| [ {}^{5}D_{J} ] \rangle$  and  $| [ {}^{7}F_{J} ] \rangle$  states are generally small, sample calculations were made using the more complete and appropriate eigenstates of Chang and Gruber<sup>19</sup> to examine the effect of this truncation. The new  $([{}^{7}F_{4}] \parallel \mathbf{U}^{(4)} \parallel [{}^{5}D_{0}])^{2}$  value, for example, was  $\approx 10\%$  smaller than that calculated using Ofelt's eigenstates. Magnetic-dipole matrix elements calculated using the two different sets of eigenstates revealed similar small differences. Since these differences were not greater than other uncertainties which were present, the calculations were completed using the simpler Ofelt eigenstates. The effect of further truncation of the eigenstates can be more significant, however. The value of the above  $[\mathbf{U}^{(4)}]^2$  matrix element calculated by Axe,<sup>3</sup> using states composed only of  ${}^{5}D$ and <sup>7</sup>F components, is smaller by a factor of  $\approx 4$ .

The eigenstates and resulting  $\mathbf{U}^{(\lambda)}$  matrix elements used by Krupke to determine the intensity parameters for  $Y_2O_3$ : Eu<sup>3+</sup> were not given explicitly; however, it was stated that they agreed with Axe's values. The

<sup>&</sup>lt;sup>18</sup> N. C. Chang and J. B. Gruber, J. Chem. Phys. 41, 3227

<sup>(1964).</sup> <sup>19</sup> I am grateful to Dr. N. C. Chang for kindly providing a set of these eigenstates.



FIG. 1. Observed energy levels of Eu<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup> in Y<sub>2</sub>O<sub>3</sub>.

 $\Omega_{\lambda}$ 's were therefore reevaluated using the above matrix elements. The relative fluorescence intensities from  ${}^{5}D_{0}$  to levels of the  ${}^{7}F$  ground term were measured and were in essential agreement with Krupke's values, although weak transitions to  ${}^{7}F_{5}$  were detected and a lower limit was set on the intensity to  ${}^7F_6$ . The  $\Omega_{\lambda}$  values in Table I were determined, as described previously,<sup>6,8</sup> from these relative intensities and the calculated magnetic-dipole intensity for  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ . The present results differ from Krupke's values because  $A_{\rm md}({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ was approximately 10% larger and different  $\mathbf{U}^{(\lambda)}$ matrix elements were used. Since the observed intensity from  ${}^{5}D_{0}$  to  ${}^{7}F_{2}$  is almost an order of magnitude larger than that to  ${}^{7}F_{1}$ , mixing of these two terminal states by second-order harmonics in the crystal-field potential may have an important effect on the accuracy of the final parameter values. The calculated spontaneousemission probabilities for transitions from  ${}^{5}D_{0}$ ,  ${}^{5}D_{1}$ , and  ${}^{5}D_{2}$  are included in Table II. No calculations were made for  ${}^{5}D_{3}$  because of the proximity of other levels and probable strong *J*-mixing. The final radiative lifetime for  $\lceil {}^{5}D_{0} \rceil$  is slightly smaller than Krupke's predicted value<sup>6</sup> of 1.08 msec.

#### EXPERIMENTAL

The fluorescence excitation and decay properties of  $Tm^{3+}$ ,  $Er^{3+}$ , and  $Eu^{3+}$  in  $Y_2O_3$  were investigated, since these ions have several fluorescing levels. The lowerenergy-level schemes and labeling of states for these ions are shown in Fig. 1. The thickness of the levels indicates the extent of the crystal-field splitting; an arrow denotes levels from which fluorescence was observed at low temperatures.

Excited-state lifetimes were measured using selective excitation techniques and an experimental arrangement

described previously.<sup>20</sup> A narrow band of radiation from a xenon flashtube was isolated with a monochromator and applied to pump ions into selected excited states; the resulting transient fluorescence was observed with a second monochromator and appropriate photomultiplier or PbS detector. The fluorescence lifetimes were determined from semilog plots of the exponential decay following selective excitation into the level of interest. The lifetimes of nonfluorescent levels were determined by exciting ions into these levels and analyzing<sup>20</sup> the growth of fluorescence from the nextlowest fluorescent level. In cases where the decay was fast compared with the excitation pulse width or PbSdetector response time, only an upper lifetime limit is given. When necessary, the signal-to-noise ratio was improved by (a) digital signal averaging using a CAT-1024 computer, or (b) using a PAR CW-1 boxcar integrator. Excitation and fluorescence spectra were recorded using the above optical arrangement, a xenon arc lamp, and phase-sensitive detection.

The samples were float-zone-melted, isopressed rods of rare-earth-doped  $Y_2O_3$  prepared by the Materials Research Corporation, using a hollow-cathode-electronbeam technique. The quoted concentrations are the mole percent of rare-earth oxide added to the initial melt.

The observed lifetimes are given in Table II and are the values measured at or extrapolated to low concentrations, where decay by ion-pair relaxation is believed to be negligible, and low temperatures, where decay by multiphonon emission is reduced to its spontaneousemission rate. For isolated levels where these competing processes are absent, the lifetimes were measured at higher temperatures, thereby populating all Stark levels of the multiplet more equally, as assumed in the calculations. The lifetime for Nd ( ${}^{4}F_{3/2}$ ) is that reported by Hoskins and Soffer<sup>21</sup> at 77 and 300°K. Additional comments pertaining to the excitation and decay properties, concentration and/or temperature dependences, and comparison with previous results are given below.

#### Thulium

Fluorescence was observed from five different J levels:  ${}^{3}H_{4}$ ,  ${}^{3}F_{4}$ ,  ${}^{1}G_{4}$ ,  ${}^{1}D_{2}$ , and  ${}^{1}I_{6}$ . The lifetimes of these levels were measured directly from their decay; the upper limits for the  ${}^{3}H_{5}$  and  ${}^{3}F_{3}$  lifetimes were determined from the risetime of the fluorescence from  ${}^{3}H_{4}$  and  ${}^{3}F_{4}$ , respectively.

To investigate the presence and importance of ionpair relaxation,<sup>22</sup> the fluorescence lifetimes were measured as a function of concentration. The results are shown in Fig. 2. The lifetimes of  ${}^{3}F_{4}$ ,  ${}^{1}G_{4}$ ,  ${}^{1}D_{2}$ , and  ${}^{1}I_{6}$ all exhibit a decrease with increasing concentration.

<sup>&</sup>lt;sup>20</sup> M. J. Weber, Phys. Rev. 156, 231 (1967).

<sup>&</sup>lt;sup>21</sup> R. H. Hoskins and B. H. Soffer, Appl. Phys. Letters 4, 22 (1964).

<sup>&</sup>lt;sup>22</sup> For a discussion of energy transfer between rare-earth ions, see, for example, L. G. Van Uitert and L. F. Johnson, J. Chem. Phys. **44**, 3514 (1966), and references therein.

In addition, the decays observed for the 1.0% sample were not simple exponential functions. This behavior is characteristic of a distribution of relaxation times arising from a range of ion-ion interactions. One or more pairs of transitions involving the above states exist which conserve energy to within a single phonon frequency ( $\gtrsim 500 \text{ cm}^{-1}$ ) and may lead to ion-pair relaxation. Possible pairs of transitions include

$${}^{3}F_{4} \longrightarrow {}^{3}H_{4}: {}^{3}H_{6} \longrightarrow {}^{3}H_{4},$$
 (5a)

$${}^{1}G_{4} \rightarrow ({}^{3}F_{4}, {}^{3}H_{5}) : {}^{3}H_{6} \rightarrow ({}^{3}H_{5}, {}^{3}F_{4}),$$

$${}^{1}G_{4} \rightarrow ({}^{3}F_{2}, {}^{3}H_{4}) : {}^{3}H_{6} \rightarrow ({}^{3}H_{4}, {}^{3}F_{2}),$$
(5b)  
$${}^{1}D_{4} \rightarrow ({}^{3}F_{4}, {}^{3}F_{4}) : {}^{3}H_{6} \rightarrow ({}^{3}H_{4}, {}^{3}F_{2}),$$

$${}^{1}I_{6} \rightarrow ({}^{1}G_{4}, {}^{3}F_{4}): {}^{3}H_{6} \rightarrow ({}^{3}F_{4}, {}^{1}G_{4}),$$

$${}^{1}I_{6} \rightarrow ({}^{1}D_{2}, {}^{3}H_{4}) : {}^{3}H_{6} \rightarrow ({}^{3}H_{4}, {}^{1}D_{2}).$$
 (5d)

Self-resonant transfer such as  ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ :  ${}^{3}H_{6} \rightarrow {}^{3}H_{4}$ does not lead to relaxation but can give rise to energy migration. Since the  ${}^{3}H_{4}$  lifetime shows no variation over the concentration range studied, energy migration and transfer to other quenching centers is not important. Radiation trapping may account for the slight increase in  ${}^{3}H_{4}$  lifetime for the 1.0% sample.

Ion-pair relaxation at higher concentrations was also evident from excitation spectra, an example of which is shown in Fig. 3. About 10% of the ions excited into the  ${}^{1}G_{4}$  and  ${}^{1}D_{2}$  levels are predicted to decay radiatively to levels of the  ${}^{3}F$  term, and thus they excite only a weak  ${}^{8}F_{4}$  fluorescence at low Tm concentrations. These excitation peaks are larger for the 1.0% Tm sample because new decay modes to  ${}^{3}F_{J}$  involving ion-pair tran-



FIG. 2. Fluorescence lifetimes of Y<sub>2</sub>O<sub>3</sub>: Tm<sup>3+</sup> at 296°K as a function of Tm content.



FIG. 3. Excitation spectra of the  ${}^{8}F_{4}$  fluorescence from Y<sub>2</sub>O<sub>8</sub>: Tm<sup>3+</sup> at 296°K for two different Tm concentrations. The dashed curve indicates the spectral variation of the exciting radiation.

sitions, such as Eqs. (5b) and (5c), become important. Although the interest here is only to establish the presence of the processes so that their contribution to the total decay can be estimated, further measurements of the relative fluorescence intensities and quantum efficiencies can provide quantitative information about the rates of ion-pair relaxation.

The Tm<sup>3+</sup> lifetimes in Table II are room-temperature values extrapolated to a concentration-independent limit. The upper lifetime limit for the  ${}^{3}F_{3}$  level was determined at 77°K.

#### Erbium

Transient fluorescence from  ${}^{4}I_{13/2}$ ,  ${}^{4}F_{9/2}$ ,  ${}^{4}S_{3/2}$ , and  ${}^{2}P_{3/2}$  was used to measure the lifetimes of these states and the upper limits thereof for  ${}^{2}H_{9/2}$ ,  ${}^{4}G_{11/2}$ , and  ${}^{4}D_{5/2}$ . The lifetimes given in Table II are for a 0.2% Er sample and were measured at 77°K unless noted otherwise. Based upon steady-state intensity measurements of the  ${}^{4}S_{3/2}$  fluorescence as a function of concentration<sup>23</sup> and the preceding findings for Tm<sup>3+</sup>, any contribution to the above decay rates from ion-pair relaxation should be small.

The  ${}^{4}S_{3/2}$  lifetime is temperature-dependent. Although the calculated radiative lifetime of  ${}^{2}H_{11/2}$  is much shorter than that for  ${}^{4}S_{3/2}$ , thermal population of this level at higher temperatures is insufficient to account for the observed decrease in total lifetime. The observation<sup>24</sup> that the integrated fluorescence intensity for  ${}^{4}S_{3/2}$  at

<sup>&</sup>lt;sup>23</sup> V. L. Levshin and R. K. Pirinchieva, Opt. i Spektroskopiya **21**, 319 (1966) [English transl.: Opt. Spectry. (USSR) **21**, 184 (1966)].

<sup>(1966)].</sup> <sup>24</sup> V. L. Levshin and R. K. Pirinchieva, Opt. i Spektroskopiya 22, 69 (1967) [English transl.: Opt. Spectry. (USSR) 22, 135 (1967)].

TABLE III. Excited-state lifetimes (in  $\mu$ sec) of Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> measured at room temperature.

| Excited<br>state                                | 10% Eu<br>(Ref. 29) | 1.0% Eu<br>(Ref. 28) | (Ref. 27)   | 0.1% Eu<br>(Present<br>work) |
|---|---------------------|----------------------|-------------|------------------------------|
| ${}^{5}D_{0}$<br>${}^{5}D_{1}$<br>${}^{5}D_{2}$ | 820<br>50<br>4      | 960<br>≈70<br>       | 870<br>≈100 | 860<br>120<br>≈95            |

77°K is greater than that from  ${}^{4}S_{3/2} + {}^{2}H_{11/2}$  at 295°K confirms that an additional temperature-dependent quenching mechanism is active at higher temperatures. The  ${}^{4}I_{11/2}$  lifetime is also temperature-dependent and exhibits a monotonic decrease from 3.9 msec at 77°K to 0.9 msec at 600°K. This may arise from a combination of a changing population distribution within the  ${}^{4}I_{11/2}$  multiplet and/or weak temperature-dependent multiphonon emission to  ${}^{4}I_{13/2}$ .

Several excited-state lifetimes for Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup> have been reported which differ from our results. Barasch and Dieke<sup>25</sup> list a  ${}^{4}S_{3/2}$  lifetime for a 1% Er sample of  $300 \ \mu sec$  at  $4^{\circ}K$ ; however, at this temperature only the lower Kramers doublet of  ${}^{4}S_{3/2}$  would be populated and radiation trapping may occur. The concentration dependence of the  ${}^{4}S_{3/2}$  lifetime is evident from the shorter lifetimes observed by others<sup>16,26</sup> using more heavily doped samples. Richman and Chang<sup>26</sup> report a  ${}^{4}F_{9/2}$ lifetime of 60  $\mu$ sec at 77°K and a  ${}^{4}I_{11/2}$  lifetime of 1 msec. No details of the excitation conditions and transitions observed were given. In our experiments, the  ${}^{4}F_{9/2}$  lifetime was determined by observing the  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ emission following pulsed excitation into the  ${}^{4}S_{3/2}{}^{-2}H_{11/2}$ group of levels. The transient response therefore consisted of a buildup and decay characteristic of the difference of two exponential terms, one corresponding to the relaxation of  ${}^{4}S_{3/2}$  and the other the relaxation of  ${}^{4}F_{9/2}$ . The  ${}^{4}F_{9/2}$  lifetime was extracted from an analysis of the time dependence, using the  ${}^{4}S_{3/2}$  lifetime measured independently from the  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  emission.

#### Europium

Fluorescence was observed from  ${}^{5}D_{0}$ ,  ${}^{5}D_{1}$ ,  ${}^{5}D_{2}$ , and  ${}^{5}D_{3}$  following excitation into  ${}^{5}D_{3}$  and higher levels. The transient fluorescences exhibited time dependences composed of a linear combination of exponential terms indicative of level-by-level cascade. The effects were similar to but not as striking as those observed<sup>8</sup> for LaF<sub>3</sub>:Eu<sup>3+</sup>.

Excited-state lifetimes reported by several investigators<sup>27-29</sup> are summarized in Table III, together with the present results. Whereas the  ${}^{5}D_{0}$  lifetime shows no

<sup>25</sup> G. E. Barasch and G. H. Dieke, J. Chem. Phys. 43, 988 (1965) <sup>26</sup> I. Richman and N. C. Chang, Appl. Phys. Letters 10, 218 (1967).

 <sup>20</sup> N. C. Chang, J. Appl. Phys. **34**, 3500 (1963).
 <sup>28</sup> J. D. Axe and P. F. Weller, J. Chem. Phys. **40**, 3066 (1964).
 <sup>29</sup> Y. Kobayashi and T. Takamura, Japan J. Appl. Phys. **6**, 114 (1967).

variation with Eu concentration, the  ${}^{5}D_{1}$  and  ${}^{5}D_{2}$  lifetimes are shorter in more heavily doped samples. This is consistent with the observation that pairs of transitions suitable for ion-pair relaxation exist for the higher <sup>5</sup> $D_I$  levels (J > 0) but not for the <sup>5</sup> $D_0$  level.

The lifetimes of  ${}^{5}D_{0}$  and  ${}^{5}D_{1}$  measured as a function of temperature are shown in Fig. 4. Temperaturedependent decay from  ${}^{5}D_{0}$  by multiphonon emission is very improbable because of the large energy gap  $(\sim 12\ 000\ \mathrm{cm}^{-1})$  to  ${}^7F_6$ . The constancy of the  ${}^5D_0$  lifetime with temperature therefore indicates, in addition, that decay by phonon-assisted transitions is not significant. The temperature dependence of the  ${}^{5}D_{1}$  lifetime arises from multiphonon emission to  ${}^{5}D_{0}$ , as discussed later.

# DISCUSSION

For low impurity concentrations, where ion-pair relaxation or energy migration and transfer to other quenching centers are improbable, excited electronic states relax radiatively by purely electronic and phononassisted transitions and nonradiatively by the emission of one or more phonons. The rate of the latter is very dependent upon the number of phonons needed to conserve energy, and hence upon the size of the energy gap to the next-lowest level. Studies of nonradiative decay of rare-earth ions in LaCl<sub>3</sub>,<sup>10-12</sup> LaBr<sub>3</sub>,<sup>12</sup> LaF<sub>3</sub>,<sup>7,12</sup> and Y<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub><sup>30</sup> have demonstrated that multiphonon re-



FIG. 4. Temperature dependences of the  ${}^5D_0$  and  ${}^5D_1$  fluorescence lifetimes of Y<sub>2</sub>O<sub>3</sub>: Eu<sup>3+</sup>. The dashed curve is the temperature dependence predicted for emission of four 430-cm<sup>-1</sup> phonons.

<sup>&</sup>lt;sup>30</sup> J. R. Chamberlain, D. H. Paxman, and J. L. Page, Proc. Phys. Soc. (London) 89, 143 (1966).

laxation involving the emission of as many as five phonons can effectively compete with radiative transitions for decay. Although the phonon spectrum for  $Y_2O_3$  is not known in detail, a band at 561 cm<sup>-1</sup> is observed<sup>31</sup> in the infrared lattice absorption spectrum and probably corresponds to phonons of the highestenergy optical branch at  $\mathbf{k}=0$ . Therefore nonradiative decay from levels having energy gaps greater than 3000 cm<sup>-1</sup> would require the simultaneous emission of more than five phonons.

#### **Radiative Probabilities**

In Fig. 5, the calculated radiative decay probability and the total decay probability, the latter given by the reciprocal of the measured lifetime, are plotted as a function of energy gap to the next-lowest level for several excited states of Er<sup>3+</sup>, Tm<sup>3+</sup>, and Nd<sup>3+</sup>. For levels having energy gaps greater than 3000 cm<sup>-1</sup>, the agreement between the radiative and observed lifetimes is generally within experimental error. Of course, one does not know a priori whether decay from these levels should be solely radiative with a quantum efficiency of unity. For example, nonradiative decay by ion-pair relaxation or other energy-transfer mechanisms may not be entirely negligible, and vibronic transitions involving more than one phonon, which can become important for strong ion-lattice coupling, have not been treated explicitly. There are also experimental uncertainties arising from the intensity measurements, determination of rare-earth concentrations, assumption that all Stark levels of the initial J multiplet were equally populated, and the statistical significance of the  $\Omega_{\lambda}$  parameters.<sup>6</sup> The good agreement found for isolated low-lying levels such as  $Er^{3+}({}^{4}I_{13/2})$  and  $Tm({}^{3}H_{4})$ , however, strongly suggests that these factors have received proper consideration.

J-state mixing arising from even-order terms in the crystal-field potential, which has been neglected thus far, can affect the calculated probabilities for transitions involving closely spaced levels and, in cases such as the  ${}^{4}S_{3/2} - {}^{2}H_{11/2}$  levels of Er<sup>3+</sup>, must be treated before meaningful comparisons between calculated and observed lifetimes can be made. The over-all Stark splittings of the J levels and the crystal-field parameters for rare earths in  $Y_2O_3$  are large, and hence J mixing can be significant.<sup>32</sup> Gruber, Krupke, and Poindexter<sup>16</sup> obtained an improvement in fitting the crystal-field spectra when J mixing was considered, one example being the  ${}^{3}F_{J}$  group of Tm<sup>3+</sup>. From Table II, the spontaneous-emission probability from  ${}^{3}F_{3}$  is greater than that from  ${}^{3}F_{4}$ ; therefore admixing may reduce the effective radiative lifetime of  ${}^{3}F_{4}$  and bring it into closer agreement with the observed lifetime. While the ex-



FIG. 5. Comparison of calculated radiative probabilities (solid points) and measured decay probabilities (open points) versus energy gap to the next-lowest level for excited states of  $Er^{3+}$  ( $\blacktriangle$ ,  $\bigtriangleup$ ),  $Tm^{3+}$  ( $\blacklozenge$ ,  $\bigcirc$ ), and  $Nd^{3+}$  ( $\blacksquare$ ,  $\square$ ) in  $Y_2O_3$ .

tension of the present calculations using crystal-field eigenstates and the determination of the additional intensity parameters thereby required is straightforward, the labor involved is greatly increased when treating crystals having sites of low point-group symmetry.

Although high quantum efficiencies are expected for the Nd( ${}^{4}F_{3/2}$ ), Er( ${}^{2}P_{3/2}$ ), and Tm( ${}^{1}I_{6}$ ) levels, the good agreement between calculated and observed lifetimes in Table II may be somewhat fortuitous in view of the neglect of J mixing. The radiative lifetimes of high-lying excited states, however, are usually determined by transitions to many terminal states of different basis character; therefore the effects of admixing are, to some degree, averaged out.

The large difference between the radiative and observed lifetimes for the  ${}^{1}D_{2}$  level of Tm<sup>3+</sup> is puzzling (1) because this level is separated by approximately 6000  $cm^{-1}$  from both upper and lower levels, and hence J mixing and multiphonon emission should be negligible, and (2) the results obtained for other Tm<sup>3+</sup> levels are generally satisfactory.<sup>33</sup> The  ${}^{1}D_{2}$  level at  $\approx 27500$  cm<sup>-1</sup> is one of the highest energy levels studied, and since it is closer to the excited, opposite-parity configuration, the degree of admixing of these states into  ${}^{1}D_{2}$  may be greater than for lower levels. In the Judd-Ofelt theory all states of the opposite-parity configuration were assumed to be degenerate. This is admittedly a weak point in the theory (the range of energies for the  $4f^{N-1}5d$ configuration, for example, is very large)<sup>34</sup> but was introduced to invoke closure in the summation over the states of the excited configuration. Since the intensity

<sup>&</sup>lt;sup>31</sup> N. T. McDevitt and A. D. Davidson, J. Opt. Soc. Am. 56, 636 (1966).

<sup>&</sup>lt;sup>32</sup> J mixing is also evident from the appearance of electric- and magnetic-dipole forbidden transitions such as  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ ,  ${}^{7}F_{5}$  in Eu<sup>3+</sup>.

<sup>&</sup>lt;sup>33</sup> A similar discrepancy has been obtained for the  ${}^{1}D_{2}$  level of LaF<sub>3</sub>: Tm<sup>3+</sup> (unpublished) and the  ${}^{1}D_{2}$ ,  ${}^{3}P$  levels of LaF<sub>3</sub>: Pr<sup>3+</sup> (Ref. 9).

<sup>&</sup>lt;sup>34</sup> G. H. Dieke and H. M. Crosswhite, Appl. Opt. 2, 675 (1963).

parameters are usually determined from a best over-all fit of spectral intensities for transitions from the ground state to low-lying excited states of the  $4f^N$  configuration, the resulting values may be expected to underestimate the degree of admixing for excited states near or overlapping states of the higher configuration.

There is a paucity of levels at high energies for which J mixing and multiphonon emission are negligible or known with sufficient accuracy to test the above hypothesis. The lifetime of the  ${}^{1}G_{4}$  level of Tm<sup>3+</sup>, which is well isolated at  $\approx 21400$  cm<sup>-1</sup>, is again smaller than the calculated lifetime, but the difference is only slightly beyond the probable experimental error. The  ${}^{5}D_{4}$  level of Tb<sup>3+</sup> at  $\approx 20\ 300\ \mathrm{cm}^{-1}$  is also well isolated; there are no pairs of transitions suitable for resonant energy transfer, and therefore the decay should be radiative. Hoshina<sup>35</sup> has calculated the electric- and magneticdipole transition probabilities from  ${}^{5}D_{4}$  to levels of the  $^{7}F$  ground term. The predicted radiative lifetime is 2.28 msec compared with an observed lifetime of 1.2 msec. Since the  $4f^{7}5d$  bands of Tb<sup>3+</sup> are among the lowest of the lanthanide series (the lowest  $4f \rightarrow 5d$  transition for CaF<sub>2</sub>: Tb<sup>3+</sup> is<sup>36</sup>  $\approx$ 46 500 cm<sup>-1</sup>), this discrepancy<sup>37</sup> may again indicate the inadequacy of the Judd-Ofelt theory when applied to higher-lying excited states. While the above results are suggestive, they are not conclusive. A search for other examples and a reexamination of the theory are needed to establish whether a modification of the present approach and parameter determination is in order or whether further development of the treatment of crystal-field-induced electricdipole transitions and consideration of the importance of higher-order configuration interactions are required.

#### **Multiphonon Emission**

The large differences between radiative and total lifetimes for levels having energy gaps less than 3000 cm-1 arise from the increased importance of multiphonon emission. The rates of multiphonon emission were found by subtracting the radiative contribution from the total decay rate and are plotted in Fig. 6 as a function of the energy gap to the next-lowest level. The error bars reflect the estimated errors of the calculated spontaneous-emission probabilities and lifetime measurements. When the differences between radiative and observed lifetimes are comparable with the asso-

ciated errors, as for  ${}^{4}I_{11/2}$ , the fractional errors resulting from this approach become large.

The strong, systematic decrease in the rate of multiphonon emission with increasing energy gap for Y<sub>2</sub>O<sub>3</sub> is similar to that found previously<sup>7,11-13</sup> for rare-earth ions in LaCl<sub>3</sub>, LaBr<sub>3</sub>, and LaF<sub>3</sub>. The dependence on energy gap, and hence the number of phonons required to conserve energy, is in qualitative accord with predictions made by Kiel.<sup>37</sup> Because phonons of higher energy are present in  $Y_2O_3$  than in the other crystals above, transitions requiring the emission of fewer phonons, and hence involving lower-order processes, are possible. This, combined with the strong ionlattice coupling, accounts for the larger rate of multiphonon emission in  $Y_2O_3$  for a given size energy gap.

Transition probabilities for high-order multiphonon emission formally involve contributions from many different terms in the expansion of the dynamic crystalfield interaction and summations over various intermediate states and phonon modes. Although order-ofmagnitude estimates of the rates can be made, detailed calculations entail many difficulties.37 The approximately linear correlation found<sup>13</sup> between the logarithm of the rate of multiphonon emission and the energy gap to the next-lowest level indicates that variations in the magnitudes of individual matrix elements are to some degree averaged out. Thus the line drawn in Fig. 6 can, within experimental limits, be used for order-of-mag-



FIG. 6. Rates of multiphonon emission from several excited states of  $Er^{3+}$  ( $\bigcirc$ ) and  $Eu^{3+}$  ( $\blacktriangle$ ) plotted as a function of energy gap to the next-lowest level.

<sup>&</sup>lt;sup>35</sup> T. Hoshina, Japan J. Appl. Phys. 6, 1203 (1967).
<sup>36</sup> E. Loh, Phys. Rev. 147, 332 (1966).
<sup>37</sup> The significance of the calculated radiative lifetime can be questioned on two counts: (1) The reduced matrix elements were evaluated using eigenstates derived by assuming hydrogenic ratios for the Slater integrals and neglecting singlet states; thus the com-ments made earlier with respect to  $Eu^{3+}$  are again apropos; (2) the intensity parameters for  $Tb^{3+}$  were not measured but ob-tained by interpolation of Krupke's experimental values for other rare earths in  $V_2O_3$ . This estimate should be satisfactory, since the largest contribution to the radiative decay of the  ${}^{5}D_{4}$  level arises from the  $\Omega_2$  term, and this parameter exhibits only a small variation throughout the middle of the  $4f^N$  series.

nitude estimates of the rates of multiphonon emission and, combined with calculated radiative probabilities, for predictions of quantum efficiencies for other excited states of different rare-earth ions in  $Y_2O_3$ .

Such a guideline cannot be applied indiscriminately, however.<sup>7</sup> This is demonstrated by the data for the  ${}^{5}D_{1}$  and  ${}^{5}D_{2}$  levels of Eu<sup>3+</sup> which are also included in Fig. 6 and which differ from the rates of multiphonon emission found for Er<sup>3+</sup> levels having comparable energy gaps. In the limit that J is a good quantum number, terms of order  $\lambda$  in the orbit-lattice interaction couple states satisfying the triangle rule  $|J-J'| \leq \lambda \leq$ |J+J'|, where  $\lambda$  is restricted to even integers. Therefore multiphonon emission between states of J=1 and J=0 is forbidden, and only second-order terms are active in the  ${}^{5}D_{2} \rightarrow {}^{5}D_{1}$  relaxation. Weak  ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$  transitions can arise from admixing of  ${}^{5}D_{2}$  into  ${}^{5}D_{1}$  and  ${}^{5}D_{0}$ , or from processes involving virtual transitions to  ${}^{5}D_{2}$ as an intermediate state. Similar selection rules restrict the number and types of terms which contribute to the relaxation of the  ${}^{4}S_{3/2}$  and  ${}^{2}P_{3/2}$  levels of Er<sup>3+</sup>, and thus must in general be considered when applying the results in Fig. 6 to other rare-earth excited states.

The rates of multiphonon emission in Fig. 6 are those at low temperatures corresponding to spontaneous phonon emission. With increasing temperature, induced phonon emission becomes important. The temperature dependence of the transition probability for processes involving the emission of  $\mathbf{n}$  phonons of a single frequency  $\nu$  is given by

$$W_n = W_0 [1 - \exp(-h\nu/kT)]^{-n}$$
 (6)

and varies from a constant  $W_0$  at low temperatures to a  $T^n$  dependence at high temperatures,  $T \gg h\nu/k$ . Data for the temperature dependence of multiphonon emission rates have been fitted<sup>30,11,12</sup> to expressions of the form in Eq. (6), assuming that the relaxation arises predominantly from a small number of high-energy phonons consistent with energy conservation. This approach was applied to the Eu( ${}^{5}D_{1}$ ) data in Fig. 4.  $W_{0}$ was determined by subtracting the radiative probability from the temperature-independent lifetime measured at low temperatures. As illustrated in Fig. 4, substantial agreement is obtained, assuming that four phonons of 430 cm<sup>-1</sup> (the infrared absorption spectra of all rare-earth oxides exhibit a broad, intense absorption in the region of 400 cm<sup>-1</sup>) conserve the 1715-cm<sup>-1</sup> energy of the  ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$  transition. Although higher-energy phonons exist in  $Y_2O_3$ , the use of three phonons of 570 cm<sup>-1</sup> (which is at the extreme upper limit of the phonon spectrum) yields a reasonable fit only over a small range at low temperatures. The total rate of multiphonon emission arises from contributions from many different combinations of phonon modes and frequencies through Brillouin zone. Therefore, unless a single narrow-frequency band of high-density phonons dominates the relaxation over an extended temperature range, a simple expression such as Eq. (6) is not expected to be totally adequate and some composite temperature-dependence curve should be more appropriate.

#### CONCLUSIONS

Spontaneous-emission probabilities calculated in intermediate coupling using the Judd-Ofelt theory and experimental intensity parameters are in good agreement with observed lifetimes for low-lying excited states of lanthanide ions in Y<sub>2</sub>O<sub>3</sub>, thereby attesting again to the general success and usefulness of this approach. More extensive calculations, including transitions between individual Stark levels and J-state mixing, combined with measurements of more transition intensities and use of a statistically weighted fitting procedure to reduce the uncertainties in the intensity parameters, should contribute to a further improvement in the final results. Discrepancies do exist, however, such as found for the  ${}^{1}D_{2}$  level of Tm<sup>3+</sup>, which suggest the possible breakdown for higher excited states of the closure approximation used and/or the need to extend the theory to include other higher-order configuration interactions. The combination of calculated spontaneous-emission probabilities and measured excited-state lifetimes provides a straightforward method for determining nonradiative decay rates and quantum efficiencies. Although this approach is limited by the uncertainties associated with the calculated radiative lifetimes, the accuracy of the results is certainly adequate when compared with the present ability to calculate nonradiative transition probabilities arising from multiphonon emission or ion-pair relaxation.

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