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THEORETICAL FREE-ION ENERGIES, DERIVATIVES AND REDUCED MATRIX E--ETC(U)  
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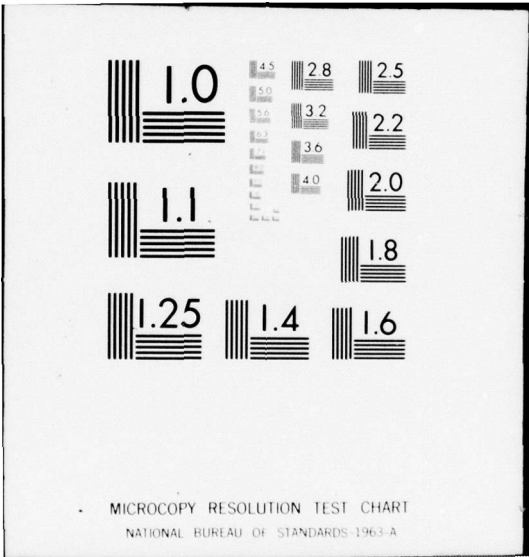
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Theoretical Free-Ion Energies, Derivatives,  
and Reduced Matrix Elements  
I.  $Pr^{2+}$ ,  $Tm^{2+}$ ,  $Nd^{2+}$  and  $Er^{2+}$

July 1977

TR-1814—Theoretical Free-Ion Energies, Derivatives, and Reduced Matrix Elements I.  $Pr^{2+}$ ,  $Tm^{2+}$ ,  $Nd^{2+}$ , and  $Er^{2+}$   
by Clyde A. Morrison, Nicol Kuznetsov, and Donald E. Werthan

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$E_k$ , zeta, alpha, beta, and gamma

cont

calculate the free-ion centroid energies and derivatives with respect to the  $E_k$ ,  $\zeta$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  of Rajnak and Wybourne's seven-parameter Hamiltonian. Reduced matrix elements for the spherical harmonics in low-lying multiplets of these ions are given.



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## 1. INTRODUCTION

Much effort in recent years has been devoted to formulating an accurate, yet tractable, theoretical procedure for analyzing the optical spectra of triply ionized lanthanides in crystals. Owing to the many levels in the  $f^N$  ground configurations of these ions and to the relatively few low-lying levels whose Stark splittings are observed, it is undesirable and often infeasible to require simultaneous diagonalization of the free-ion Hamiltonian,  $H$ , and the crystal field Hamiltonian,  $H_X$ . It is preferable first to diagonalize  $H$ , the larger interaction, and then to calculate the crystal field splittings by diagonalizing  $H_X$  in the low-lying levels. This report examines this procedure, specifically for calculating  $\text{Pr}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$ .

Theory cannot yet determine the free-ion Hamiltonian *ab initio*, but its form,  $H(P_i)$ , is adequately defined by a set of  $P_i$  that determine the strengths of the Coulomb, the spin-orbit, and other interactions. Values for these parameters are defined as minimizing the difference between theoretical free-ion centroids evaluated in a basis of intermediate coupled eigenfunctions and experimental free-ion centroids. Since few experimental data are available for the  $f^N$  configurations of free, triply ionized lanthanides,<sup>1-3</sup> the  $P_i$ , in practice, are determined to give a best fit to Stark-level centroids in aqueous solution or in crystals.<sup>4</sup> Unfortunately, the crystal field affects centroid energies so that, even if all Stark components of a given J-multiplet are determined experimentally, the weighted centroid is not the free-ion energy resulting if the crystal field were "turned off." As a second problem, even the most elaborate free-ion Hamiltonian often cannot give an adequate fit to the J-multiplet centroids once they are determined. The seven-parameter Hamiltonian defined by Rajnak and Wybourne<sup>5,6</sup> and used extensively by Carnall, Fields, and Rajnak (CFR),<sup>4</sup> for example, often gives centroid discrepancies of  $100 \text{ cm}^{-1}$ .

This report describes a method that circumvents the first of these difficulties. The method is based on the fact that, in perturbation theory, changes in wave functions give second-order changes in energy. Conversely, known small changes in energy determine the perturbing Hamiltonian to first order. Thus, any reasonable set of  $P_i$  presumably

<sup>1</sup>J. Sugar, *Phys. Rev. Lett.*, 14 (1965), 731.

<sup>2</sup>N. Spector and J. Sugar, *J. Opt. Soc. Am.*, 66 (1976), 436.

<sup>3</sup>V. Kaufman and J. Sugar, *J. Opt. Soc. Am.*, 66 (1976) 439.

<sup>4</sup>W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, 49 (1968), 4412-55.

<sup>5</sup>K. Rajnak and B. G. Wybourne, *Phys. Rev.*, 132 (1963), 280.

<sup>6</sup>B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience Publishers, New York (1965).

determines an adequate set of J-multiplet wave functions and reduced matrix elements, even though the energies they determine,  $E_j$ , may be incorrect. An appropriate subset of these "free-ion" J-multiplet wave functions (usually 10 to 15 of the lowest lying) may then be chosen as a basis to calculate Stark splittings, and the energies,  $E_j^i$ , of these multiplets may be treated as parameters (along with the crystal field parameters,  $B_{km}$ , in  $H_X$ ) to be varied, as suggested by Margolis,<sup>7</sup> for obtaining a fit between theoretical and experimental Stark levels.<sup>8,9</sup> The resultant  $E_j^i$ , which, in general, differ (by  $\Delta E_j$ ) from the initial centroids, may finally be used to determine new  $P_i' = P_i + \Delta P_i$ , as suggested by Wong,<sup>10</sup> by minimizing the function

$$Q = \sum_j \left[ \sum_i (\partial E_j / \partial P_i) \Delta P_i - \Delta E_j \right]^2 \quad (1)$$

with respect to  $\Delta P_i$ . If the  $\Delta P_i$  determined in this way are not large, then the linearity assumption in Wong's expression is valid, and also it is unnecessary to rediagonalize the free-ion Hamiltonian to determine new reduced matrix elements. These results suggest that it is desirable to perform the initial diagonalization of  $H(P_i)$  with  $P_i$  that pertain to some convenient host and not to the true free ion since variations in the  $P_i$  from host to host are expected to be less than the change in the  $P_i$  from the free state to some host.<sup>11</sup>

Accordingly, we have calculated theoretical energies, derivatives, and reduced matrix elements for the  $f^2$ ,  $f^{12}$ ,  $f^3$ , and  $f^{11}$  configurations, respectively, of  $\text{Pr}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$  using the aqueous solution free-ion parameters of CFR.<sup>4</sup> Wong<sup>10</sup> determined the  $\partial E_j / \partial P_i$  for  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  for  $P_i = \{E^1, E^2, E^3, \zeta\}$  by a finite differencing method involving five separate diagonalizations for each ion. We have extended and improved on his work by obtaining derivatives also with respect to

<sup>4</sup>W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

<sup>7</sup>J. S. Margolis, *J. Chem. Phys.*, **35** (1961) 1370.

<sup>8</sup>N. Karayianis, D. E. Wortman, and H. P. Jenssen, *J. Phys. Chem. Solids*, **37** (1976), 676.

<sup>9</sup>P. Grunberg, S. Hufner, E. Orlich, and J. Schmidt, *Phys. Rev.*, **184** (1969), 290.

<sup>10</sup>E. Y. Wong, *J. Chem. Phys.*, **35** (1961), 544.

<sup>11</sup>N. Karayianis and C. A. Morrison, *Rare Earth Ion-Host Crystal Interactions. 2. Local Distortion and Other Effects in Reconciling Lattice Sums and Phenomenological  $B_{km}$* , Harry Diamond Laboratories TR-1682 (January 1975), table II.

Rajnak and Wybourne's<sup>5</sup> higher-order interactions of strengths  $\alpha$ ,  $\beta$ , and  $\gamma$  and by using Feynman's theorem<sup>12</sup> to obtain derivatives. Feynman's theorem, expressed by

$$\partial E_j / \partial P_i = \langle \psi_j | \partial H / \partial P_i | \psi_j \rangle, \quad (2)$$

where  $|\psi_j\rangle$  represents the  $j$ th eigenfunction of  $H$ , has the advantages of having  $|\psi_j\rangle$  greater inherent accuracy and of requiring only one diagonalization per ion. To perform the calculations, electrostatic matrices corresponding to the Russell-Saunders basis states given by Nielson and Koster were hand keypunched from their book of tables.<sup>13</sup> The  $V^{(11)}$  and  $U^{(k)}$  reduced matrix elements that relate, respectively, to spin-orbit and spherical harmonic reduced matrix elements were calculated from a computer tape containing coefficients of fractional parentage kindly provided by H. M. Crosswhite (Argonne National Laboratory). By choosing to diagonalize  $H$  with the aqueous solution parameters of CFR,<sup>4</sup> we were able to check our computer software procedures by comparing our centroid energies with those of CFR.

A summary of the computational procedures and formulas is given in section 2. Section 3 gives tables of the centroid energies and derivatives and notes some discrepancies between our  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  energies and those reported by CFR.<sup>4</sup> Section 4 gives tables of reduced matrix elements of the spherical harmonics and discusses their use in crystal field calculations. Also in section 4, some measure is given of the sensitivity of theoretical Stark levels to the free-ion parameters and wave functions for  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in  $\text{CaWO}_4$ .

## 2. CALCULATIONS

To obtain free-ion wave functions, matrix elements of the Hamiltonian

$$H = H_E + H_{SO} + \alpha L^2 + \beta G_2 + \gamma R_7 \quad (3)$$

<sup>4</sup>W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

<sup>5</sup>K. Rajnak and B. G. Wybourne, *Phys. Rev.*, **132** (1963), 280.

<sup>12</sup>E. Merzbacher, *Quantum Mechanics*, John Wiley and Sons, Inc., New York (1961), 396.

<sup>13</sup>C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the  $p^N$ ,  $d^N$ , and  $f^N$  Configurations*, The MIT Press, Cambridge, MA (1963).

were taken in a given J subspace spanned by the basis functions\*

$$|JMLS\omega\rangle = \sum_m \langle L(m)S(M-m) | J(M) \rangle |Lm S M-m \omega\rangle, \quad (4)$$

where  $\langle j_1(m_1)j_2(m_2) | j(m) \rangle$  is a Clebsch-Gordon coefficient,<sup>14</sup> and the  $|LS\omega\rangle$  are the Russell-Saunders states defined in Nielson and Koster.<sup>13</sup> The additional quantum number  $\omega$  represents the pairs and triplets of quantum numbers  $u_1u_2$  and  $w_1w_2w_3$  given for each state in Nielson and Koster and corresponding, respectively, to the  $G_2$  and  $R_7$  operators.<sup>6</sup>

Since H is a spherical tensor of rank zero in J space, matrix elements of H in a given J subspace are independent of M. If the quantum number M is suppressed, the electrostatic matrix elements are

$$\langle JL'S'\omega' | H_E | JLS\omega \rangle = \delta_{LL'} \delta_{SS'} \langle LS\omega' | H_E | LS\omega \rangle; \quad (5)$$

the spin-orbit matrix elements for N equivalent electrons of orbital angular momentum  $\ell$  are

$$\begin{aligned} \langle JL'S'\omega' | H_{SO} | JLS\omega \rangle &= -\zeta \{ \ell(\ell+1) [\ell] \}^{\frac{1}{2}} \\ &\times W(1S'LJ; SL') (L'S'\omega' || V^{(11)} || LS\omega); \end{aligned} \quad (6)$$

and the matrix elements of the last three operators in equation (3) are

$$\langle JL'S'\omega' | h_i | JLS\omega \rangle = \delta_{LL'} \delta_{SS'} \delta_{\omega\omega'} \langle h_i \rangle, \quad (7)$$

where

$$\langle h_{1;2;3} \rangle = \alpha L(L+1); \beta G_2(u_1u_2); \gamma R_7(w_1w_2w_3). \quad (8)$$

\*Note the order of L and S in this definition since it does make a difference in the matrix elements.

<sup>6</sup>B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience Publishers, New York (1965).

<sup>13</sup>C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the  $p^N$ ,  $d^N$ , and  $f^N$  Configurations*, The MIT Press, Cambridge, MA (1963).

<sup>14</sup>M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols*, Technology Press, Cambridge, MA (1959).

M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols*, Technology Press, Cambridge, MA (1959). In terms of their tabulated 3-j symbols,  $\langle j_1(m_1)j_2(m_2) | j(m) \rangle [j]^{-\frac{1}{2}} = (-)^{-j_1+j_2-m} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}$ .

The symbol  $W(abcd;ef)$  in equation (6) is a Racah coefficient<sup>14</sup> and  $[x] \equiv 2x + 1$ . Values for the electrostatic matrix elements and the  $V^{(11)}$  reduced matrix elements are given in Nielson and Koster;<sup>13</sup> however, we keypunched only the former. A generalized  $v^{(\kappa k)}$  defined by

$$\begin{aligned} \langle L'S'\omega' || v^{(\kappa k)} || LS\omega \rangle &= N\{s(s+1)[s][L][L'][S][S']\}^{\frac{1}{2}} \\ &\times \sum_{\bar{L}\bar{S}} W(L'\bar{L}k\ell; \ell L) W(S'\bar{S}\kappa s; sS) \\ &\times \sum_{\bar{\omega}} F(L'S'\omega'N; \bar{L}\bar{S}\bar{\omega} N-1) F(LS\omega N; \bar{L}\bar{S}\bar{\omega} N-1), \end{aligned} \quad (9)$$

where  $s = 1/2$ , allows one to calculate a variety of reduced matrix elements once the coefficients of fractional parentage,<sup>15</sup>  $F$ , are available. From H. M. Crosswhite's (Argonne National Laboratory) computer tape containing the  $F$  for the  $f^N$  configurations, we calculated the  $V^{(11)}$ , as well as the reduced matrix elements of the spherical harmonics,  $C_k$ , according to

$$\begin{aligned} \langle J'L'S'\omega' || \sum_i C_k(i) || JLS\omega \rangle &= \delta_{SS'} \left\{ \frac{[L][J][J']}{s(s+1)[S]} \right\}^{\frac{1}{2}} \\ &\times \langle \ell(0)k(0) | \ell(0) \rangle W(JkSL'; J'L) \langle L'S'\omega' || v^{(0k)} || LS\omega \rangle, \quad * \end{aligned} \quad (10)$$

where  $\ell = 3$ .

These reduced matrix elements are necessary for the crystal field calculations discussed in section 4. The reduced matrix elements, in general, are defined by

$$\langle j'm' | T_{kq} | jm \rangle = \langle j(m)k(q) | j'(m') \rangle [j']^{-\frac{1}{2}} \langle j' || T_k || j \rangle. \quad (11)$$

\*This  $v^{(0k)}$  is related to the  $U^{(k)}$  in Nielson and Koster by  $\langle || v^{(0k)} || \rangle = \{s(s+1)[S]\}^{\frac{1}{2}} \langle || U^{(k)} || \rangle$ .

<sup>13</sup>C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the  $p^N$ ,  $d^N$ , and  $f^N$  Configurations*, The MIT Press, Cambridge, MA (1963).

<sup>14</sup>M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols*, Technology Press, Cambridge, MA (1959). In terms of their tabulated 6-j symbols,  $W(abcd;ef) = (-)^{a+b+c+d} \begin{pmatrix} a & b & e \\ d & c & f \end{pmatrix}$ .

<sup>15</sup>B. R. Judd, *Operator Techniques in Atomic Spectroscopy*, McGraw-Hill Book Co., Inc., New York (1963), 166-192.

Values for the eigenvalues of the  $G_2$  and  $R_7$  operators,  $G_2(u_1u_2)$  and  $R_7(w_1w_2w_3)$ , are given in table I, which is a copy of Wybourne's<sup>6</sup> tables 2-6 and 2-7.

Taking matrix elements according to equations (5), (6), and (8) between all  $|LS\omega\rangle$  states that satisfy  $|L-S| \leq J \leq |L+S|$ , one may then choose values for  $E^1, E^2, E^3$  (in  $H_E$ ),  $\zeta$  (in  $H_{SO}$ ),  $\alpha, \beta$ , and  $\gamma$  and diagonalize the subspace to obtain free-ion wave functions,

$$|J(LS\omega)\rangle = \sum_{\overline{LS\omega}} A_{\overline{LS\omega}} |J\overline{LS\omega}\rangle \quad (12)$$

The orbital and spin angular momenta,  $L$  and  $S$ , in  $|J(LS\omega)\rangle$  are not good quantum numbers because of mixing by the spin-orbit interaction, and  $\omega$  is not a good quantum number because of mixing by both the electrostatic and spin-orbit interactions. Thus, the "almost good quantum numbers"  $(LS\omega)$  in parentheses represent values in the limit of the off-diagonal parts of  $H_E$  and  $H_{SO}$  approaching zero. There is such large mixing in many cases, however, that the assignment of  $LS\omega$  values to a given free-ion wave function is arbitrary. The method that we have chosen to make assignments is described in section 3.

TABLE I. VALUES OF  $G_2(u_1u_2)$  AND  $R_7(w_1w_2w_3)$

| $u_1u_2$ | $12G_2$ | $w_1w_2w_3$ | $5R_7$ |
|----------|---------|-------------|--------|
| 00       | 0       | 000         | 0      |
| 10       | 6       | 100         | 3      |
| 11       | 12      | 110         | 5      |
| 20       | 14      | 111         | 6      |
| 21       | 21      | 200         | 7      |
| 22       | 30      | 210         | 9      |
| 30       | 24      | 211         | 10     |
| 31       | 32      | 220         | 12     |
| 40       | 36      | 221         | 13     |
|          |         | 222         | 15     |

<sup>6</sup>B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience Publishers, New York (1965).

### 3. FREE-ION ENERGIES AND DERIVATIVES

Tables II to V give the assignments, energies, and derivatives for each of the free-ion multiplets of  $\text{Pr}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$ , respectively. The arbitrariness in assigning a particular term to some highly mixed multiplet was resolved by scanning the matrix of eigenvectors for the largest magnitude coefficient, assigning the row designation of that coefficient to the column eigenvector, eliminating that row and column from further consideration, and repeating the procedure until the final eigenvector was assigned by default. The square of the designating coefficient is printed under the "PCT. PURE" column of these tables and indicates the percentage of the Russell-Saunders designation present in the free-ion eigenfunction. This procedure is not entirely satisfactory (although it results in a unique one-to-one assignment for a given set of free-ion parameters) because a situation may arise where the Russell-Saunders designation is not the largest component present in an eigenvector. The possible occurrence of this situation is for eigenvectors with a PCT. PURE assignment of less than 50 percent. The  ${}^2\text{G}_{9/2}(1)$  level of  $\text{Er}^{3+}$  (table V) is an example of this occurrence. It contains 24.23 percent of  ${}^4\text{F}_{9/2}$ , but, since that designation had already been assigned to the level at  $15,136 \text{ cm}^{-1}$  which contains 57.64 percent of  ${}^4\text{F}_{9/2}$ , the next largest percentage, 19.06 percent of  ${}^2\text{G}_{9/2}(1)$ , was assigned.

The derivatives with respect to  $\alpha$  yield an added dividend since  $\partial E/\partial \alpha = \langle L^2 \rangle$  according to equations (2) and (3). Thus, the effective orbital angular momentum of an eigenvector given by

$$L_{\text{eff}} = -1/2 + (1/4 + \partial E/\partial \alpha)^{1/2} \quad (13)$$

gives an indication of the L-mixing induced by the spin-orbit interaction. For the  ${}^2\text{G}_{9/2}(1)$  level of  $\text{Er}^{3+}$ ,  $L_{\text{eff}} = 4.32$ , indicating that good percentages of  $\text{H}_{9/2}$  and  $\text{I}_{9/2}$  components also are present.

Table VI gives the free-ion parameters for these ions in aqueous solution determined by CFR.<sup>4</sup> Our calculated energy levels agree with theirs for  $\text{Pr}^{3+}$  and  $\text{Tm}^{3+}$ . For the  ${}^2\text{H}_{11/2}(2)$  level of  $\text{Nd}^{3+}$ , we get  $16,043$  (adding  $130 \text{ cm}^{-1}$  to our value in table IV to adjust for their ground state) compared with their<sup>4</sup> listed  $16,026 \text{ cm}^{-1}$ . In  $\text{Er}^{3+}$ , we get  $47,811$  and  $36,572 \text{ cm}^{-1}$  for the  ${}^2\text{H}_{9/2}(1)$  and  ${}^2\text{H}_{9/2}(2)$  levels, respectively (adding  $109 \text{ cm}^{-1}$  to our values in table V), while they<sup>4</sup> list  $47,822$  and  $36,566 \text{ cm}^{-1}$ --differences of  $11$  and  $6 \text{ cm}^{-1}$ , respectively.

<sup>4</sup>W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

TABLE II. PRASEODYMIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

PR(AQ) C,F,R J. CHEM. PHYS. 49,4412(1968).  
 TOTAL NO. OF STATES = 13  
 EO = 0.  
 ALPHA = 21.255 BETA = -799.940 E2 = 21.937 E3 = 466.73 Z = 740.8  
 GAMMA = 1342.900

| STATE | ENERGY  | PCT. PURE | DE/DE1   | DE/DE2     | DE/DE3   | DE/DZ    | DE/DALPHA | DE/DBETA | DE/DGAMMA |
|-------|---------|-----------|----------|------------|----------|----------|-----------|----------|-----------|
| 3H 4  | 0.0     | 97.21     | 0.05410  | -7.03361   | -8.85668 | -3.52583 | 29.71342  | 1.00406  | 1.01063   |
| 3H 5  | 2077.5  | 100.00    | -0.00000 | -0.00000   | -9.00000 | -0.50000 | 30.00000  | 1.00000  | 1.00000   |
| 3H 6  | 4251.2  | 99.71     | 0.00571  | 0.19984    | -8.95432 | 2.36217  | 30.03426  | 1.00048  | 1.00114   |
| 3F 2  | 4903.6  | 97.64     | 0.04674  | 6.68317    | -0.25040 | -2.70197 | 11.85778  | 0.51568  | 1.00935   |
| 3F 3  | 6295.4  | 100.00    | -0.00000 | -0.00000   | -0.00000 | -0.50000 | 12.00000  | 0.50000  | 1.00000   |
| 3F 4  | 6728.3  | 63.69     | 0.69619  | -90.50445  | -1.52789 | -0.62869 | 15.05583  | 0.73959  | 1.13924   |
| 1G 4  | 9639.9  | 62.49     | 1.24971  | -162.46244 | -2.61548 | 2.65451  | 17.23096  | 0.92302  | 1.24994   |
| 1G 2  | 16595.0 | 89.64     | 1.79287  | 256.38028  | -7.19113 | -0.44908 | 5.81241   | 1.13807  | 1.35857   |
| 3P 0  | 20460.8 | 99.03     | -0.08721 | -0.00000   | 32.68023 | -1.66900 | 1.98062   | 0.99031  | 0.99031   |
| 3P 1  | 21085.0 | 100.00    | -0.00000 | -0.00000   | 33.00000 | -0.50000 | 2.00000   | 1.00000  | 1.00000   |
| 1I 6  | 21255.0 | 99.71     | 1.99429  | 69.80016   | 6.95432  | 0.13783  | 41.96574  | 1.16619  | 1.39886   |
| 3P 2  | 22290.0 | 91.89     | 0.16040  | 22.93656   | 29.44452 | 1.65105  | 2.32981   | 1.01292  | 1.03208   |
| 1S 0  | 46655.5 | 99.03     | 8.91279  | 0.00000    | 0.31977  | 0.66900  | 0.01938   | 0.00969  | 0.00969   |

TABLE III. THULIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

TM(AQ) C,F,R J. CHEM. PHYS. 49,4412(1968).  
 TOTAL NO. OF STATES = 13  
 EO = 0.  
 ALPHA = 14.677 BETA = -631.790 E2 = 33.795 E3 = 674.27 Z = 2628.7  
 GAMMA = 0.000

| STATE | ENERGY  | PCT. PURE | DE/DE1   | DE/DE2     | DE/DE3   | DE/DZ    | DE/DALPHA | DE/DBETA | DE/DGAMMA |
|-------|---------|-----------|----------|------------|----------|----------|-----------|----------|-----------|
| 3H 6  | 0.0     | 99.13     | 0.01738  | 0.60841    | -8.86093 | -2.70564 | 30.10430  | 1.00145  | 1.00348   |
| 3F 4  | 5609.5  | 62.66     | 0.58561  | -76.12922  | -1.89625 | -2.89354 | 15.79252  | 0.73548  | 1.11712   |
| 3H 5  | 8187.6  | 100.00    | -0.00000 | -0.00000   | -9.00000 | 0.50000  | 30.00000  | 1.00000  | 1.00000   |
| 3H 4  | 12518.3 | 59.62     | 0.25997  | -33.79663  | -5.88552 | 1.08381  | 23.77103  | 0.88475  | 1.05199   |
| 3F 3  | 14307.7 | 100.00    | -0.00000 | -0.00000   | -0.00000 | 0.50000  | 12.00000  | 0.50000  | 1.00000   |
| 3F 2  | 14914.4 | 77.36     | 0.41537  | 59.39758   | -1.66538 | -0.69071 | 10.56628  | 0.64784  | 1.08307   |
| 1G 4  | 21172.4 | 57.72     | 1.15442  | -150.07444 | -5.21824 | 3.31573  | 22.43650  | 1.04644  | 1.23089   |
| 1D 2  | 27829.8 | 41.15     | 0.82300  | 117.68943  | 8.75990  | -0.20123 | 5.50551   | 0.97567  | 1.16466   |
| 1I 6  | 34684.3 | 99.13     | 1.98262  | 69.39159   | 6.86093  | 0.20564  | 41.89570  | 1.16522  | 1.39652   |
| 3P 0  | 35435.0 | 95.51     | 0.40444  | 0.00000    | 31.51704 | -0.48024 | 1.91012   | 0.95506  | 0.95506   |
| 3P 1  | 36095.9 | 100.00    | -0.00000 | -0.00000   | 33.00000 | 0.50000  | 2.00000   | 1.00000  | 1.00000   |
| 3P 2  | 37991.1 | 57.87     | 0.76172  | 108.92606  | 14.90686 | 2.32920  | 3.92878   | 1.04327  | 1.15240   |
| 1S 0  | 79390.0 | 95.51     | 8.59556  | 0.00000    | 1.48296  | 1.48024  | 0.08988   | 0.04494  | 0.04494   |

TABLE IV. NEODYMIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

NO(AQ) C.F.R. J. CHEM. PHYS. 49,4412(1968).  
 TOTAL NO. OF STATES = 41    E1 = 4739.30    E2 = 23.999    E3 = 485.96    Z = 884.6  
 ALPHA = 0.561    BETA = -117.150    GAMMA = 1321.300

| STATE  | ENERGY  | PCT. PURE | DE/DE1  | DE/DE2     | DE/DE3    | DE/DZ     | DE/DALPHA | DE/DBETA | DE/DGAMMA |
|--------|---------|-----------|---------|------------|-----------|-----------|-----------|----------|-----------|
| 41 9/2 | 0.0     | 96.97     | 0.09114 | -4.29103   | -20.99855 | -4.236279 | 41.63605  | 1.18203  | 1.21843   |
| 4111/2 | 1876.2  | 98.96     | 0.03125 | -1.55396   | -20.99044 | -1.96187  | 41.88032  | 1.17175  | 1.20636   |
| 4113/2 | 3874.1  | 99.53     | 0.01405 | -0.57561   | -20.94561 | 0.32365   | 42.05801  | 1.16908  | 1.20281   |
| 4115/2 | 5950.0  | 98.62     | 0.04149 | -1.84741   | -20.86103 | 2.50386   | 42.19496  | 1.17473  | 1.20830   |
| 4F 3/2 | 11396.2 | 94.15     | 0.16694 | 4.21498    | -0.75547  | -3.32381  | 11.61840  | 0.53713  | 1.23339   |
| 4F 5/2 | 12443.2 | 97.60     | 0.07616 | -0.61529   | -0.20526  | -1.79769  | 11.87429  | 0.51625  | 1.21319   |
| 2H 9/2 | 12607.8 | 54.97     | 2.46688 | -14.56631  | -14.78460 | 3.08354   | 25.75217  | 1.43045  | 1.69347   |
| 4S 3/2 | 13329.4 | 94.35     | 0.15193 | -0.12750   | -0.54319  | -1.10892  | 0.17725   | 0.05401  | 1.23039   |
| 4F 7/2 | 13434.4 | 93.20     | 0.20708 | -15.45790  | -0.57949  | -0.80360  | 12.52653  | 0.56039  | 1.23923   |
| 4F 9/2 | 14724.1 | 75.55     | 0.71200 | -35.00387  | -4.84186  | 0.69275   | 16.22010  | 0.77437  | 1.34242   |
| 2H11/2 | 15912.9 | 79.80     | 2.79546 | -148.78510 | -18.23532 | 0.80881   | 29.56770  | 1.61035  | 1.75909   |
| 4G 5/2 | 17036.6 | 98.51     | 0.08486 | 1.32322    | 11.65913  | -3.12142  | 19.87890  | 1.16554  | 1.19994   |
| 2G 7/2 | 17203.5 | 30.82     | 1.62063 | -140.84831 | 0.62506   | -1.71073  | 19.63062  | 1.27085  | 1.52344   |
| 2K13/2 | 18886.7 | 98.55     | 2.98680 | -133.34713 | -10.90300 | -1.36786  | 55.79751  | 1.74156  | 1.79737   |
| 4G 7/2 | 18972.6 | 57.87     | 1.21778 | -96.11825  | 3.37477   | -0.15198  | 19.79250  | 1.24289  | 1.43746   |
| 4G 9/2 | 19414.0 | 76.12     | 0.62397 | -51.71769  | 6.82151   | 0.59431   | 20.54267  | 1.21599  | 1.32482   |
| 2K15/2 | 20885.6 | 93.90     | 2.95943 | -121.77497 | -10.75584 | 0.65169   | 56.57185  | 1.74215  | 1.79192   |
| 2G 9/2 | 21041.5 | 39.32     | 2.12189 | -160.43677 | -4.53805  | 3.16336   | 19.93647  | 1.29618  | 1.62453   |
| 2D 3/2 | 21137.0 | 45.82     | 2.72418 | -8.52227   | -9.57206  | -1.97978  | 4.25055   | 1.03321  | 1.74484   |
| 4G11/2 | 21433.2 | 92.43     | 0.22634 | -18.22842  | 10.51101  | 2.18952   | 20.76216  | 1.17635  | 1.24528   |
| 2P 1/2 | 23009.6 | 93.69     | 2.81076 | 0.00000    | -8.22450  | -0.86339  | 2.25232   | 1.01051  | 1.76215   |
| 2P 3/2 | 23735.2 | 97.29     | 2.93988 | -171.59575 | -11.86278 | 0.40755   | 6.13558   | 1.15516  | 1.78659   |
| 2P 5/2 | 26129.6 | 48.44     | 2.87497 | 26.78931   | -11.06838 | 3.14310   | 4.06653   | 1.07143  | 1.77500   |
| 4D 3/2 | 28181.8 | 81.60     | 0.55074 | -6.17097   | 28.45245  | -2.18455  | 5.91728   | 1.25248  | 1.31016   |
| 4D 5/2 | 28346.2 | 79.97     | 0.66633 | 40.41976   | 25.92228  | -2.48234  | 6.15196   | 1.26818  | 1.30601   |
| 2111/2 | 28493.6 | 86.18     | 2.98553 | -6.74711   | 2.73349   | -1.49442  | 40.30040  | 1.15279  | 1.79712   |
| 4D 1/2 | 28762.8 | 93.69     | 0.18924 | 0.00000    | 30.22450  | -0.63661  | 5.74768   | 1.15615  | 1.23785   |
| 2115/2 | 29129.8 | 95.24     | 2.99924 | 93.62158   | -3.38354  | -0.15553  | 71.23685  | 1.74989  | 1.79988   |
| 2113/2 | 29836.0 | 98.94     | 2.99919 | -31.07836  | 2.84855   | 0.54420   | 42.14514  | 1.17271  | 1.79985   |
| 4D 7/2 | 30423.5 | 98.47     | 0.10761 | 0.91471    | 32.26028  | 0.59926   | 6.09647   | 1.16254  | 1.19477   |
| 2L17/2 | 30610.1 | 100.00    | 3.00000 | 105.00000  | -3.00000  | 1.00000   | 72.00000  | 1.75000  | 1.80000   |
| 2H 9/2 | 32437.3 | 86.90     | 2.98685 | 162.83301  | 0.21077   | -0.25940  | 29.84859  | 1.09559  | 1.79738   |
| 2D 3/2 | 33351.0 | 80.56     | 2.53129 | 5.77012    | 12.48684  | 0.95398   | 5.97009   | 1.63510  | 1.70626   |
| 2H11/2 | 33783.0 | 69.99     | 2.96173 | 166.32450  | -1.00209  | 1.98218   | 31.49684  | 1.13899  | 1.79246   |
| 2D 5/2 | 34343.6 | 59.25     | 2.88385 | 160.07582  | 3.88121   | 0.89793   | 7.28120   | 1.53206  | 1.58550   |
| 2F 5/2 | 38374.0 | 43.10     | 4.90492 | 121.46020  | -6.23233  | 1.47740   | 10.68417  | 1.33173  | 1.39905   |
| 2F 7/2 | 39796.4 | 63.10     | 4.99722 | 124.33435  | 4.77751   | 1.74065   | 12.00387  | 1.30336  | 1.37654   |
| 2G 9/2 | 47566.2 | 58.27     | 3.00837 | 126.14798  | 33.13291  | -0.24518  | 20.08042  | 1.50621  | 1.79990   |
| 2G 7/2 | 48455.7 | 58.44     | 3.00595 | 124.36318  | 33.66917  | 0.47261   | 19.89861  | 1.51346  | 1.79828   |
| 2F 7/2 | 66128.5 | 64.17     | 6.84479 | 68.82845   | 38.43763  | -0.14678  | 12.05993  | 0.94517  | 1.02911   |
| 2F 5/2 | 67449.0 | 57.44     | 6.44559 | 82.96251   | 41.84739  | 1.11873   | 11.99918  | 1.03186  | 1.11065   |

TABLE V. ERBIUM AQUEOUS SOLUTION FREE-ION ENERGIES AND DERIVATIVES

ER(AQ) C.F.R. J. CHEM. PHYS. 49,4412(1968).  
 TOTAL NO. OF STATES = 41  
 EO = 0.  
 ALPHA = 0.18,347 BETA = -509,280 E2 = 32,388 GAMMA = 646,62 Z = 2380,7  
 DE/DALPHA = 649,710 DE/DBETA = 2380,7 DE/DGAMMA = 1.21757

| STATE    | ENERGY  | PCT. PURE | DE/DEL  | DE/DE2     | DE/DE3    | DE/DZ    | DE/DALPHA | DE/DBETA | DE/DGAMMA |
|----------|---------|-----------|---------|------------|-----------|----------|-----------|----------|-----------|
| 4I15/2   | 0-0     | 97-07     | 0-08785 | -3-88113   | -20-70475 | -3-62714 | 42-61479  | 1-18375  | 1-21757   |
| 4I13/2   | 6500.7  | 90-10     | 0-02697 | -1-10775   | -20-89597 | -0-70623 | 42-11174  | 1-17132  | 1-20539   |
| 4I11/2   | 10110.7 | 82-22     | 0-49381 | -18-67994  | -20-62226 | -0-34327 | 39-78232  | 1-25134  | 1-29881   |
| 4F 9/2   | 12271.7 | 50-53     | 1-04906 | -72-12450  | -15-87085 | -1-56092 | 32-08203  | 1-19633  | 1-40995   |
| 4F 9/2   | 15136.2 | 57-64     | 0-40105 | -28-90585  | -7-22022  | -1-51839 | 21-68765  | 0-81434  | 1-28023   |
| 4S 3/2   | 18352.7 | 68-41     | 0-78207 | -14-24900  | -2-06483  | -2-72513 | 1-488610  | 0-30289  | 1-35660   |
| 2H11/2 2 | 19149.1 | 68-81     | 1-47848 | -41-84595  | -10-05236 | -1-62794 | 28-28258  | 1-43615  | 1-49571   |
| 4F 7/2   | 20312.9 | 92-33     | 0-23943 | -15-62487  | -0-69610  | -0-70969 | 12-57284  | 0-56629  | 1-24303   |
| 4F 5/2   | 21765.4 | 86-62     | 0-46095 | 24-77997   | -2-13164  | -0-73912 | 11-13845  | 0-61452  | 1-28814   |
| 4F 3/2   | 22312.7 | 62-57     | 0-62567 | -24-47200  | -1-03900  | -0-74972 | 8-74190   | 0-55543  | 1-32515   |
| 2G 9/2 1 | 24400.0 | 19-06     | 1-71019 | -143-01340 | -7-95987  | 0-49886  | 23-02365  | 1-17476  | 1-54216   |
| 4S 9/2   | 26391.1 | 60-29     | 1-11390 | -80-34100  | 0-66591   | -0-11431 | 24-28932  | 1-30324  | 1-42286   |
| 2K15/2   | 27369.4 | 79-02     | 0-47786 | -17-48787  | 4-99170   | 0-11151  | 22-67431  | 1-25178  | 1-29566   |
| 2K15/2   | 27691.4 | 91-39     | 2-91417 | -117-33655 | -10-82793 | -1-31691 | 56-52323  | 1-73341  | 1-78294   |
| 2S 7/2 1 | 27872.0 | 26-18     | 1-74479 | -135-94285 | 1-20751   | -0-66486 | 19-30577  | 1-27834  | 1-50880   |
| 2D 3/2 1 | 31542.5 | 21-61     | 1-82695 | -88-14168  | -0-35396  | 0-41133  | 5-31445   | 0-83036  | 1-56549   |
| 2K13/2   | 32376.2 | 89-66     | 2-98312 | -88-14168  | -9-88801  | 3-48942  | 54-55301  | 1-68971  | 1-79662   |
| 4G 5/2   | 32779.3 | 92-02     | 0-37923 | -123-97877 | 10-91779  | -1-07898 | 19-23514  | 1-17448  | 1-21862   |
| 2P 1/2   | 33343.4 | 91-62     | 2-74871 | -1-34856   | -7-31440  | -0-75041 | 2-33505   | 1-01396  | 1-74974   |
| 4G 7/2   | 33916.1 | 54-44     | 1-29728 | 177-27944  | 2-49634   | -2-27004 | 19-74714  | 1-23726  | 1-45452   |
| 2D 5/2 1 | 34693.4 | 57-46     | 2-17374 | -177-4144  | -9-29904  | -0-39853 | 6-84208   | 1-16230  | 1-63389   |
| 2H 9/2 2 | 36463.0 | 32-00     | 2-39863 | -176-51601 | -10-10773 | 4-64662  | 24-63837  | 1-40382  | 1-67973   |
| 4D 5/2   | 38464.5 | 44-83     | 1-57733 | -191-29273 | 24-32960  | -1-16418 | 6-37021   | 1-30345  | 1-51305   |
| 4D 7/2   | 39048.3 | 95-42     | 0-25154 | 1-63166    | 31-06315  | -1-54718 | 6-36446   | 1-15441  | 1-19105   |
| 2L11/2   | 40898.2 | 66-21     | 2-95808 | 18-66149   | 2-60092   | -1-37998 | 37-83027  | 1-12636  | 1-79167   |
| 2L17/2   | 41576.9 | 100-00    | 3-00000 | 105-00000  | -3-00000  | -1-00000 | 72-00000  | 1-75000  | 1-80000   |
| 4D 3/2   | 42148.9 | 58-06     | 1-07853 | 45-92002   | 13-56552  | 1-49007  | 6-03074   | 1-13291  | 1-41572   |
| 2P 3/2   | 42854.6 | 36-60     | 2-36065 | -143-43999 | 9-51311   | 1-77545  | 4-44192   | 1-20675  | 1-67215   |
| 2I13/2   | 43607.9 | 90-13     | 2-98990 | -39-91349  | 1-58338   | 0-71681  | 4-3-33526 | 1-22230  | 1-79798   |
| 4D 1/2   | 46931.0 | 91-62     | 0-25129 | 0-00000    | 29-31440  | 2-25041  | 5-66495   | 1-15271  | 1-25026   |
| 2H 9/2 1 | 47702.4 | 76-92     | 2-97435 | 199-68165  | -0-94173  | 0-00194  | 29-50156  | 1-16390  | 1-79491   |
| 2D 5/2 2 | 47806.9 | 94-23     | 2-99850 | 91-21539   | -3-46858  | 1-94410  | 71-07326  | 1-74981  | 1-79981   |
| 2D 5/2 3 | 48923.3 | 46-56     | 1-98825 | 53-25441   | 15-25086  | 1-22846  | 7-04350   | 1-45834  | 1-50898   |
| 2H11/2 1 | 50891.3 | 55-41     | 2-95604 | 113-19905  | 0-40630   | 2-16558  | 33-82158  | 1-13314  | 1-79123   |
| 2F 7/2 2 | 52053.0 | 56-22     | 4-85388 | 113-13661  | -4-60826  | 0-19722  | 12-15308  | 1-25821  | 1-34152   |
| 2F 5/2 2 | 55097.5 | 68-98     | 2-32658 | 263-40402  | -0-62083  | 4-29722  | 5-98663   | 1-55528  | 1-66543   |
| 2F 3/2 2 | 53127.6 | 64-43     | 3-82913 | 127-60442  | 4-97369   | 3-70205  | 11-37402  | 1-49909  | 1-56102   |
| 2S 7/2 2 | 65329.0 | 57-33     | 3-00102 | 125-29858  | 33-75629  | -0-93045 | 19-74601  | 1-49850  | 1-79801   |
| 2S 9/2 2 | 63492.4 | 56-19     | 2-98956 | 130-34027  | 32-11037  | 1-22013  | 20-30216  | 1-49359  | 1-79801   |
| 2F 5/2 1 | 93445.5 | 76-73     | 7-59200 | 44-04087   | 31-14574  | -0-20731 | 12-00050  | 0-78812  | 0-87686   |
| 2F 7/2 1 | 97217.3 | 60-45     | 6-61331 | 74-76657   | 39-78626  | 1-38488  | 12-11965  | 0-98764  | 1-07187   |

TABLE VI. FREE-ION PARAMETERS FOR TRIPLY IONIZED Pr, Nd, Er, AND Tm

| Ion             | E <sup>1</sup> | E <sup>2</sup> | E <sup>3</sup> | ζ      | α      | B       | γ      |
|-----------------|----------------|----------------|----------------|--------|--------|---------|--------|
| Pr <sup>a</sup> | 4548.2         | 21.937         | 466.73         | 740.75 | 21.255 | -799.94 | 1342.9 |
| Nd <sup>a</sup> | 4739.3         | 23.999         | 485.96         | 884.58 | 0.5611 | -117.15 | 1321.3 |
| Nd <sup>b</sup> | 4676.4         | 23.764         | 480.25         | 877.25 | 0.336  | -112.52 | 1241.3 |
| Nd <sup>c</sup> | 4988.0         | 24.510         | 493.90         | 906.00 | 0.0    | 0.0     | 0.0    |
| Er <sup>a</sup> | 6769.9         | 32.388         | 646.62         | 2380.7 | 18.347 | -509.28 | 649.71 |
| Er <sup>b</sup> | 6632.0         | 31.128         | 652.18         | 2399.7 | 23.137 | -626.04 | 883.04 |
| Tm <sup>a</sup> | 7142.4         | 33.795         | 674.27         | 2628.7 | 14.677 | -631.79 | 0.0    |

<sup>a</sup>For aqueous solution. See T. Carnall et al, *J. Chem. Phys.*, 49 (1968), 4412-55.

<sup>b</sup>For CaWO<sub>4</sub>.

<sup>c</sup>For LaCl<sub>3</sub>. See E. Y. Wong, *J. Chem. Phys.*, 35 (1961), 544.

Eight other levels differ in energy from 2 to 4 cm<sup>-1</sup> in Er<sup>3+</sup>. We do not know the source of these discrepancies, and we solicit results from an independent calculation. One further contact was made with Wong's Nd<sup>3+</sup> calculations<sup>10</sup> where we found agreement to 0.6 cm<sup>-1</sup> except for his <sup>4</sup>G<sub>7/2</sub> level at 19,288.93 cm<sup>-1</sup>. We calculate this energy as 19,228.9 cm<sup>-1</sup>, strongly indicating a misprint in Wong's table that would be easy to miss in proofreading. We also agree with his ∂E/∂ζ calculations for all his levels with spot checks with his ∂E/∂F<sub>k</sub> values, converting them to our ∂E/∂E<sup>k</sup>.

#### 4. Nd AND Er IN CaWO<sub>4</sub>

Using the procedure described in section 1, we determined<sup>16</sup> free-ion centroids for Nd<sup>3+</sup> and Er<sup>3+</sup> and crystal field parameters in CaWO<sub>4</sub> by fitting, respectively, to 51 (of 64) and 38 (of 48) identified experimental Stark levels. The Nd<sup>3+</sup> centroids for the lowest 14 multiplets\* were fit by using the derivatives of table IV to determine

\*Actually, the <sup>2</sup>K<sub>13/2</sub> multiplet is lower than the <sup>4</sup>G<sub>7/2</sub> multiplet that was the highest multiplet diagonalized (see table IV). However, the number of Stark levels in <sup>2</sup>K<sub>13/2</sub> exceeded the available core capacity in the IBM 7094 computer used to perform these calculations, so the <sup>4</sup>G<sub>7/2</sub> multiplet was used instead.

<sup>10</sup>E. Y. Wong, *J. Chem. Phys.*, 35 (1961), 544.

<sup>16</sup>Donald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Rare Earth Ion-Host Lattice Interactions. 5. Lanthanides in CaWO<sub>4</sub>, Harry Diamond Laboratories TR-1794 (June 1977).

the free-ion parameters for  $\text{CaWO}_4$  given in table VI, line 3. Table VII gives theoretical centroids by using aqueous parameters, theoretical centroids by using  $\text{CaWO}_4$  parameters, and experimental centroids for comparison. The listed centroids corresponding to  $\text{CaWO}_4$  parameters were obtained by Wong's procedure by using our derivatives, yet they differ only by  $0.27 \text{ cm}^{-1}$  rms from the exact values obtained by rediagonalizing the free-ion matrices. The new eigenfunctions and reduced matrix elements obtained by rediagonalizing were then used to recalculate the

TABLE VII.  $\text{Nd}^{3+}$  MULTIPLY CENTROIDS ( $\text{cm}^{-1}$ )

| Multiplet                          | Carnall parameters <sup>a</sup> | Best fit parameters <sup>b</sup> | Experimental <sup>c</sup><br>( $\text{CaWO}_4$ centroids) |
|------------------------------------|---------------------------------|----------------------------------|---|
| $^4I_{9/2}$                        | 84                              | 219                              | 222   |
| $^4I_{11/2}$                       | 1961                            | 2081                             | 2089  |
| $^4I_{13/2}$                       | 3958                            | 4063                             | 4066  |
| $^4I_{15/2}$                       | 6034                            | 6120                             | 6117  |
| $^4F_{3/2}$                        | 11481                           | 11488                            | 11453   |
| $^4F_{5/2}$                        | 12528                           | 12528                            | 12503   |
| $^2H_{9/2}$ (2)                    | 12692                           | 12632                            | 12597   |
| $^4S_{3/2}$                        | 13414                           | 13406                            | 13447   |
| $^4F_{7/2}$                        | 13519                           | 13507                            | 13539   |
| $^4F_{9/2}$                        | 14808                           | 14775                            | 14721   |
| $^2H_{11/2}$ (2)                   | 15997                           | 15903                            | 15947   |
| $^4G_{5/2}$                        | 17121                           | 17065                            | 17102   |
| $^2G_{7/2}$                        | 17288                           | 17196                            | 17228   |
| $^4G_{7/2}$                        | 19057                           | 18959                            | 18910   |
| rms deviation ( $\text{cm}^{-1}$ ) | 85.14                           | 33.34                            |   |

<sup>a</sup>Calculated by using parameters of W. T. Carnall, P. R. Fields, and K. Rajnak (CFR) [*J. Chem. Phys.*, **49** (1968), 4412-55], table VI, line 2, and centered to experimental centroids.

<sup>b</sup>Calculated by using derivatives of centroids with respect to CFR parameters to fit  $\text{CaWO}_4$  centroids. Exact centroids by using parameters table VI, line 3, differ from these by an rms of  $0.27 \text{ cm}^{-1}$ .

<sup>c</sup>Donald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Harry Diamond Laboratories TR-1794 (June 1977).

Stark splittings for  $\text{Nd}^{3+}:\text{CaWO}_4$  by using the crystal field parameters determined by the original fitting procedure. Deviations between the theoretical energy levels of the two calculations were  $1.8 \text{ cm}^{-1}$  or less for the lowest 53 Stark levels and 1.94 rms for the highest 11 levels shown in table VIII. This exercise indicates, fortunately, that the aqueous eigenvectors and reduced matrix elements are adequate for  $\text{Nd}^{3+}$  crystal field calculations at least to the degree of accuracy obtainable by the seven-parameter free-ion Hamiltonian considered here. Because of the inability of this theory, however, to obtain a better fit to free-ion centroids, one cannot at this stage predict the effects on crystal field calculations of a more profound free-ion theory.

TABLE VIII. EFFECT OF  $\text{Nd}^{3+}$  FREE-ION WAVE FUNCTIONS ON THEORETICAL STARK LEVELS FOR THREE EXCITED MULTIPLETS

| Multiplet                            | Stark energies for $\text{CaWO}_4$ ( $\text{cm}^{-1}$ ) |                          |                          |            |
|--------------------------------------|---|--------------------------|--------------------------|------------|
|                                      | $2\mu$  | Theoretical <sup>a</sup> | Theoretical <sup>b</sup> | $ \Delta $ |
| ${}^4\text{G}_{5/2}$<br>(17101.8)    | 3   | 16979.7                  | 16980.9                  | 1.2        |
|                                      | 1   | 17041.3                  | 17041.9                  | 0.6        |
|                                      | 3   | 17098.0                  | 17100.6                  | 2.6        |
| ${}^2\text{G}_{7/2}(1)$<br>(17227.9) | 1   | 17223.1                  | 17225.5                  | 2.4        |
|                                      | 3   | 17251.5                  | 17249.7                  | 1.8        |
|                                      | 1   | 17303.2                  | 17300.2                  | 3.0        |
|                                      | 3   | 17426.6                  | 17423.1                  | 3.5        |
| ${}^4\text{G}_{7/2}$<br>(18911.1)    | 1   | 18809.0                  | 18808.2                  | 0.8        |
|                                      | 3   | 18903.3                  | 18904.5                  | 1.2        |
|                                      | 3   | 18993.7                  | 18993.9                  | 0.2        |
|                                      | 1   | 19013.3                  | 19014.1                  | <u>0.8</u> |
|                                      |   |                          |                          | rms 1.94   |

<sup>a</sup>Free-ion wave functions by using aqueous parameters of W. T. Carnall, P. R. Fields, and K. Rajnak (CFR) [J. Chem. Phys., 49 (1968), 4412-55], table VI, line 2, and  $\text{CaWO}_4$  crystal field parameters  $B_{20} = 496.662$ ;  $B_{40} = -867.308$ ;  $B_{44} = 1032.75$ ;  $B_{60} = -8.09$ ; and  $B_{64} = 900.433 + i255.00 \text{ cm}^{-1}$ .

<sup>b</sup>Free-ion wave functions by using  $\text{CaWO}_4$  parameters (table VI, line 3) and crystal field parameters given above.

In connection with the best-fit free-ion parameters for  $\text{Nd}^{3+}:\text{CaWO}_4$  (table VI, line 3), they are the best-fit parameters only to within certain limitations imposed on their deviation from the aqueous parameters. The rigorous, best-fit parameters gave a fit to  $28.23 \text{ cm}^{-1}$  (instead of the  $33.34 \text{ cm}^{-1}$  fit obtained with the above parameters), but deviated wildly from the aqueous values, for example,  $\alpha$ ,  $\beta$ , and  $\gamma = -40.47$ ,  $727.92$ , and  $-13,284.7$ , respectively. These deviations were pared to deviations compatible with the parameter fluctuations that CFR<sup>4</sup> found over the lanthanide series and then were held constant while best fits with the  $E^k$  and  $\zeta$  were obtained. The result of this exercise, though somewhat arbitrary, was nevertheless physically palatable and was sufficient for performing the tests on the theory described above.

Table IX shows the improved free-ion centroid fit obtained for the lowest 10 multiplets of  $\text{Er}^{3+}:\text{CaWO}_4$  by varying the free-ion parameters. Similar restrictions on  $\alpha$ ,  $\beta$ , and  $\gamma$  to those described above were imposed and resulted in the  $\text{CaWO}_4$  parameters given in table VI, line 6. Perhaps a more liberal leeway on the  $\alpha$ ,  $\beta$ , and  $\gamma$  deviations should have been allowed in this fit because, whereas the rigorous, best fit parameters gave a fit to  $3.32 \text{ cm}^{-1}$ , the constrained parameters gave a fit only to  $47.73 \text{ cm}^{-1}$ . Nevertheless, the  $\text{CaWO}_4$  free-ion parameters obtained with the constraint differ sufficiently from the aqueous parameters of CFR<sup>4</sup> to perform a test of the theory similar to that for Nd described above.

In the 48 Stark-split levels in the 10 lowest multiplets of  $\text{Er}^{3+}$  in  $\text{CaWO}_4$  calculated by the two sets of free-ion wave functions, theoretical differences were only  $1.13 \text{ cm}^{-1}$  rms, even less than differences found in  $\text{Nd}^{3+}$ . This calculation gives further strong evidence of the insensitivity of crystal field calculations to free-ion parameter changes between host materials.

As a result of these exercises, we conclude that, within the limitations of the seven-parameter free-ion Hamiltonian, the reduced matrix elements for the  $C_{km}$  in the crystal field Hamiltonian

$$H_x = \sum_{km} B_{km} \sum_i C_{km}(i) \quad (14)$$

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<sup>4</sup>W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49** (1968), 4412-55.

TABLE IX.  $\text{Er}^{3+}$  MULTIPLET CENTROIDS ( $\text{cm}^{-1}$ )

| Multiplet                          | Carnall parameters <sup>a</sup> | Best fit parameters <sup>b</sup> | Experimental <sup>c</sup><br>( $\text{CaWO}_4$ centroids) |
|------------------------------------|---------------------------------|----------------------------------|---|
| $^4I_{15/2}$                       | 144                             | 124                              | 155   |
| $^4I_{13/2}$                       | 6645                            | 6681                             | 6632  |
| $^4I_{11/2}$                       | 10255                           | 10258                            | 10241   |
| $^4I_{9/2}$                        | 12416                           | 12409                            | 12489   |
| $^4F_{9/2}$                        | 15280                           | 15324                            | 15297   |
| $^4S_{3/2}$                        | 18497                           | 18454                            | 18403   |
| $^2H_{11/2}(2)$                    | 19293                           | 19190                            | 19146   |
| $^4F_{7/2}$                        | 20457                           | 20532                            | 20519   |
| $^4F_{5/2}$                        | 22109                           | 22092                            | 22178   |
| $^4F_{3/2}$                        | 22457                           | 22489                            | 22492   |
| rms deviation ( $\text{cm}^{-1}$ ) | 68.10                           | 47.73                            |   |

<sup>a</sup>Calculated by using parameters of W. T. Carnall, P. R. Fields, and K. Rajnak (CFR) [J. Chem. Phys., 49 (1968), 4412-55], table VI, line 5, and centered to experimental centroids.

<sup>b</sup>Calculated by using derivatives of centroids with respect to CFR parameters to fit  $\text{CaWO}_4$  centroids. Exact centroids by using parameters of table VI, line 6, differ from these by an rms of  $3.42 \text{ cm}^{-1}$ .

<sup>c</sup>Donald E. Wortman, Clyde A. Morrison, and Nick Karayianis, Harry Diamond Laboratories TR-1794 (June 1977).

evaluated in the aqueous free-ion basis wave functions may be used independently of host. These reduced matrix elements are given for  $\text{Pr}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Er}^{3+}$  for  $k = 2, 4, 6$  in tables X to XXI. These tables give  $(J'(L'S'\omega') || \sum_i C_k(i) || J(LS\omega))$ ,\* where a general crystal field matrix element is evaluated according to

$$\begin{aligned} \langle J'M'(L'S'\omega') | \sum_i C_{km}(i) | JM(LS\omega) \rangle &= \langle J(M)k(m) | J'(M') \rangle \\ &\times [J']^{-1/2} (J'(L'S'\omega') | \sum_i C_k(i) | J(LS\omega)) . \end{aligned} \quad (15)$$

\*Multiply these reduced matrix elements, respectively, by  $-\sqrt{15/28}$ ,  $\sqrt{22/28}$ , and  $-\sqrt{429/700}$ --values of  $(\langle 3(0)k(0) | 3(0) \rangle \sqrt{7})^{-1}$ --for  $k = 2, 4,$  and  $6$  to obtain the reduced matrix elements  $(|U^{(k)}|)$ .

TABLE X. Pr<sup>3+</sup> REDUCED MATRIX ELEMENTS (J'(L'S')||ΣC<sub>2</sub>||J(LS))

| n' | ψ <sub>n'</sub> | n <sub>0</sub> | n =            |                   |                   |                   |                   |                   |                   |  |
|----|-----------------|----------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|--|
|    |                 |                | n <sub>0</sub> | n <sub>0</sub> +1 | n <sub>0</sub> +2 | n <sub>0</sub> +3 | n <sub>0</sub> +4 | n <sub>0</sub> +5 | n <sub>0</sub> +6 |  |
| 1  | 3P 0            | 4              | 0.596362       | -0.742609         | -0.165856         |                   |                   |                   |                   |  |
| 2  | 1S 0            | 4              | -0.352898      | -0.085191         | -0.966218         |                   |                   |                   |                   |  |
| 3  | 3P 1            | 3              | -0.547722      | -0.887462         | -0.708172         | 0.379780          | -1.032794         |                   |                   |  |
| 4  | 3P 2            | 4              | 0.855283       | -0.244479         | 0.045818          | -0.693723         | -0.878429         | 0.009562          | -1.121449         |  |
| 5  | 3F 2            | 5              | 0.339609       | 0.159808          | -0.197953         | 0.052284          | -0.974662         | -0.008547         |                   |  |
| 6  | 1D 2            | 6              | 0.836994       | 0.239456          | 1.061070          | -0.070405         | -0.744106         |                   |                   |  |
| 7  | 3F 3            | 7              | 0.341565       | -0.216014         | -0.349532         | -0.088500         | -1.083203         |                   |                   |  |
| 8  | 3F 4            | 8              | 0.158500       | -0.186944         | 0.385431          | -0.233227         | -1.021430         | 0.414422          |                   |  |
| 9  | 3H 4            | 9              | -1.205814      | 0.047739          | 0.452078          | -0.014099         | -0.131521         |                   |                   |  |
| 10 | 1G 4            | 10             | -0.028045      | -0.268138         | -0.705772         | -0.666234         |                   |                   |                   |  |
| 11 | 3H 5            | 11             | -1.309959      | 0.449048          | 0.024027          |                   |                   |                   |                   |  |
| 12 | 3H 6            | 12             | -1.520235      | 0.080881          |                   |                   |                   |                   |                   |  |
| 13 | 1I 6            | 13             | -3.027486      |                   |                   |                   |                   |                   |                   |  |

The (LSω) are the assigned Russell-Saunders designations for the free-ion wave functions according to the discussion in section 3. To save space and avoid printing reduced matrix elements that are identically zero because the triangle condition among J, k, and J' is not met, column 3 in each of these tables gives the number of the first multiplet (n) to which the multiplet in column 2 connects. Across a row, the reduced matrix elements correspond to  $(\psi_{n'} || \Sigma C_k || \psi_n)$  as n increases in steps of unity from the value n listed in column 3. The lower half of the matrix of reduced matrix elements is given by

$$(J || \Sigma C_k || J') = (-)^{J'-J} (J' || \Sigma C_k || J) . \quad (16)$$

With these tables, one does not need to know the specific structure of an individual free-ion wave function. One may (1) take all or any particular subspace of the multiplets; (2) set up crystal subspaces of states with given M that are connected by H<sub>x</sub>; (3) evaluate the interaction matrix according to equation (15) and the centroid energy parameters E(J(LSω)), where

TABLE XI.  $P_{r3^+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S') || \Sigma C_4 || J(LS))$

| $n'$ | $J'_{n'}$ | $n =$     |           |           |           |           |           |           |          |          |         |  |  |          |  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|---------|--|--|----------|--|
|      |           | $n_0$     | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   | $n_0+7$  | $n_0+8$  | $n_0+9$ |  |  |          |  |
| 1    | 3P 0      | -0.369012 | 0.468868  | -0.266779 |           |           |           |           |          |          |         |  |  |          |  |
| 2    | 1S 0      | -0.469102 | 0.094570  | 0.703800  |           |           |           |           |          |          |         |  |  |          |  |
| 3    | 3P 1      | 0.499999  | 0.575542  | 0.466072  | 0.332594  | 0.603022  |           |           |          |          |         |  |  |          |  |
| 4    | 3P 2      | 0.103524  | -0.615506 | 0.306743  | -0.626231 | -0.361316 | 0.214782  | -0.246944 | 0.490479 | 0.797834 |         |  |  | 0.181261 |  |
| 5    | 3F 2      | -0.091695 | 0.327554  | 0.254669  | -0.039648 | 0.716362  | -0.142251 | -0.615599 | 0.144726 | 0.082544 |         |  |  |          |  |
| 6    | 1D 2      | 0.652185  | 0.146191  | -0.002803 | -0.147208 | 0.253955  | -0.047313 | -0.289576 | 0.447794 |          |         |  |  |          |  |
| 7    | 3F 3      | -0.062675 | 0.303376  | 0.664463  | 0.088177  | 0.664346  | -0.636433 | -0.034054 |          |          |         |  |  |          |  |
| 8    | 3F 4      | -0.564849 | 0.252328  | 0.432757  | 0.625681  | 0.874445  | -0.912684 |           |          |          |         |  |  |          |  |
| 9    | 3H 4      | -0.768412 | 0.095408  | 0.506674  | -0.204849 | 0.256516  |           |           |          |          |         |  |  |          |  |
| 10   | 1G 4      | -0.911851 | 0.361568  | 0.585520  | 1.316835  |           |           |           |          |          |         |  |  |          |  |
| 11   | 3H 5      | -0.683293 | 0.544301  | 0.029124  |           |           |           |           |          |          |         |  |  |          |  |
| 12   | 3H 6      | -0.951463 | -0.127825 |           |           |           |           |           |          |          |         |  |  |          |  |
| 13   | 1I 6      | 1.430614  |           |           |           |           |           |           |          |          |         |  |  |          |  |

TABLE XII.  $Pr^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S')) || \Sigma C_6 || J(LS)$

| $n'$ | $\psi_{n'}$ | $n_0$ | $(\psi_{n'}    \Sigma C_6    \psi_n)$ |           |           |           |           |           |           |  |
|------|-------------|-------|---------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|--|
|      |             |       | $n_0$                                 | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   |  |
| 1    | 3P 0        | 12    | 0.344329                              | -0.076765 |           |           |           |           |           |  |
| 2    | 1S 0        | 12    | 0.017784                              | -0.961341 |           |           |           |           |           |  |
| 3    | 3P 1        | 11    | -0.381690                             | -0.450976 | -0.024131 |           |           |           |           |  |
| 4    | 3P 2        | 8     | 0.129430                              | 0.470155  | -0.166139 | 0.464251  | 0.296966  | -0.482656 |           |  |
| 5    | 3F 2        | 8     | 0.382606                              | 0.438258  | 0.105357  | -1.037022 | 0.703888  | -0.231448 |           |  |
| 6    | 1D 2        | 8     | 0.186369                              | -0.291352 | -0.351648 | 0.028572  | -0.103263 | -1.672322 |           |  |
| 7    | 3F 3        | 7     | -0.319345                             | -0.092953 | 1.067449  | -0.291482 | 0.000000  | -1.174953 | -0.062869 |  |
| 8    | 3F 4        | 8     | -0.258766                             | 0.889523  | 0.763671  | 0.841322  | 0.862787  | 0.846305  |           |  |
| 9    | 3H 4        | 9     | 0.658622                              | 0.208546  | -0.998429 | 0.477071  | -0.197532 |           |           |  |
| 10   | 1G 4        | 10    | -1.003319                             | 0.835684  | 0.636235  | -1.037987 |           |           |           |  |
| 11   | 3H 5        | 11    | 0.445123                              | -1.023579 | -0.054769 |           |           |           |           |  |
| 12   | 3H 6        | 12    | 1.134016                              | 0.085047  |           |           |           |           |           |  |
| 13   | 1I 6        | 13    | -0.450876                             |           |           |           |           |           |           |  |

TABLE XIII.  $Tm^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S')) || \Sigma C_2 || J(LS)$

| $n'$ | $\psi_{n'}$ | $n_0$ | $(\psi_{n'}    \Sigma C_2    \psi_n)$ |           |           |           |           |          |           |  |
|------|-------------|-------|---------------------------------------|-----------|-----------|-----------|-----------|----------|-----------|--|
|      |             |       | $n_0$                                 | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$  | $n_0+6$   |  |
| 1    | 3P 0        | 4     | -0.478731                             | 0.812148  | -0.224881 |           |           |          |           |  |
| 2    | 1S 0        | 4     | -0.756045                             | -0.305446 | 0.629148  |           |           |          |           |  |
| 3    | 3P 1        | 3     | 0.547722                              | 0.574662  | 0.512364  | 0.916868  | 1.032794  |          |           |  |
| 4    | 3P 2        | 4     | -0.915430                             | 0.089385  | 0.026101  | 0.513104  | 0.493808  | 0.713875 | -1.064602 |  |
| 5    | 3F 2        | 5     | -0.510792                             | 0.345813  | 0.085387  | -0.747708 | 0.744068  | 0.109043 |           |  |
| 6    | 1D 2        | 6     | -0.605753                             | 0.554295  | 1.036016  | 0.487717  | 0.586714  |          |           |  |
| 7    | 3F 3        | 7     | -0.341565                             | 0.067844  | 0.391384  | 0.137411  | 1.083203  |          |           |  |
| 8    | 3F 4        | 8     | -0.135608                             | -0.491240 | 0.081259  | 0.412849  | 1.001638  | 0.337688 |           |  |
| 9    | 3H 4        | 9     | 0.706724                              | 0.540142  | -0.156614 | 0.665526  | -0.349806 |          |           |  |
| 10   | 1G 4        | 10    | 0.504239                              | -0.368366 | -0.300152 | 0.633915  |           |          |           |  |
| 11   | 3H 5        | 11    | 1.309959                              | -0.447732 | 0.041924  |           |           |          |           |  |
| 12   | 3H 6        | 12    | 1.529082                              | 0.140710  |           |           |           |          |           |  |
| 13   | 1I 6        | 13    | 3.018638                              |           |           |           |           |          |           |  |

TABLE XIV.  $T_{m3+}$  REDUCED MATRIX ELEMENTS ( $J'(L'S')$  ||  $\Sigma C_4$  ||  $J(LS)$ )

| $n'$ | $l' n'$ | $n_0$ | $(\begin{smallmatrix} n' & l' \\ n & l \end{smallmatrix}    \Sigma C_4    \begin{smallmatrix} n & l \\ n_0 & l_0 \end{smallmatrix})$ |           |           |           |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
|------|---------|-------|--|-----------|-----------|-----------|-----------|-----------|-----------|---------|---------|---------|--|--|--|--|--|--|--|--|
|      |         |       | $n_0$  | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   | $n_0+7$ | $n_0+8$ | $n_0+9$ |  |  |  |  |  |  |  |  |
| 1    | 3P 0    | 8     | 0.587180   | -0.163257 | -0.257731 |           |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 2    | 1S 0    | 8     | -0.344826  | 0.279204  | -0.718884 |           |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 3    | 3P 1    | 7     | -0.499999  | -0.371229 | -0.717952 | -0.076303 |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 4    | 3P 2    | 4     | -0.509434  | 0.233106  | 0.442135  | 0.541047  | 0.328013  |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 5    | 3F 2    | 5     | -0.229022  | 0.627656  | -0.306934 | 0.271460  | -0.468068 | -0.603022 |           |         |         |         |  |  |  |  |  |  |  |  |
| 6    | 1D 2    | 6     | 0.074418   | 0.302448  | 0.349665  | -0.122113 | -0.465897 | 0.108779  |           |         |         |         |  |  |  |  |  |  |  |  |
| 7    | 3F 3    | 7     | 0.062675   | -0.024218 | -0.670869 | -0.301113 | -0.664346 | -0.046832 | -0.634568 |         |         |         |  |  |  |  |  |  |  |  |
| 8    | 3F 4    | 8     | 0.721884   | -0.406932 | 0.158103  | -0.403569 | -0.961316 | -0.792554 |           |         |         |         |  |  |  |  |  |  |  |  |
| 9    | 3H 4    | 9     | 0.454544   | -0.071044 | -0.780496 | -0.372530 | 0.622326  |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 10   | 1G 4    | 10    | 1.068679   | -0.082951 | 0.308624  | -1.268054 |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 11   | 3H 5    | 11    | 0.683293   | -0.542705 | 0.050817  |           |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 12   | 3H 6    | 12    | 0.937480   | -0.222381 |           |           |           |           |           |         |         |         |  |  |  |  |  |  |  |  |
| 13   | 1I 6    | 13    | -1.416631  |           |           |           |           |           |           |         |         |         |  |  |  |  |  |  |  |  |

TABLE XV.  $Tm^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S') || \Sigma C_6 || J(LS))$

| $n'$ | $\gamma_{n'}$ | $n_o$ | $(\gamma_{n'}    \Sigma C_6    \gamma_n)$ |           |           |           |           |           |           |  |
|------|---------------|-------|---|-----------|-----------|-----------|-----------|-----------|-----------|--|
|      |               |       | $n_o$                                     | $n_o+1$   | $n_o+2$   | $n_o+3$   | $n_o+4$   | $n_o+5$   | $n_o+6$   |  |
| 1    | 3P 0          | 12    | -0.351265                                 | -0.172700 |           |           |           |           |           |  |
| 2    | 1S 0          | 12    | 0.015921                                  | 0.946299  |           |           |           |           |           |  |
| 3    | 3P 1          | 11    | 0.381690                                  | 0.449655  | -0.042104 |           |           |           |           |  |
| 4    | 3P 2          | 8     | -0.008344                                 | -0.099162 | -0.415045 | -0.553503 | -0.190825 | -1.071767 |           |  |
| 5    | 3F 2          | 8     | -0.264944                                 | -0.359633 | -0.258090 | 0.979178  | -0.648925 | -0.743873 |           |  |
| 6    | 1D 2          | 8     | 0.192071                                  | -0.609645 | -0.037426 | 0.163173  | -0.389119 | 1.169055  |           |  |
| 7    | 3F 3          | 7     | 0.319345                                  | 0.527810  | -0.681971 | -0.699555 | -0.000000 | 1.171510  | -0.109696 |  |
| 8    | 3F 4          | 8     | 0.662111                                  | -0.579100 | 0.343265  | -1.230376 | -0.623448 | 0.794383  |           |  |
| 9    | 3H 4          | 9     | 0.975570                                  | -0.776527 | 0.123402  | -0.985090 | -0.398150 |           |           |  |
| 10   | 1G 4          | 10    | 0.916926                                  | 0.934876  | 0.142744  | 1.020011  |           |           |           |  |
| 11   | 3H 5          | 11    | -0.445123                                 | 1.020578  | -0.095563 |           |           |           |           |  |
| 12   | 3H 6          | 12    | -1.124712                                 | 0.147959  |           |           |           |           |           |  |
| 13   | 1I 6          | 13    | 0.441572                                  |           |           |           |           |           |           |  |

$$\langle J'M'(L'S'\omega') | H | JM(LS\omega) \rangle = \delta_{JJ'} \delta_{MM'} \delta_{(L'S'\omega'), (LS\omega)} E(J(LS\omega)) ; \quad (17)$$

and (4) vary the  $B_{km}$  and centroids,  $E(J(LS\omega))$ , to obtain a least squares fit with experimental levels. Within the approximation of constant basis wave functions, this procedure is tantamount to a simultaneous diagonalization of  $H + H_x$  since, by Wong's method, the "free-ion" Hamiltonian may be inferred from the resultant centroids, and the crystal field Hamiltonian is determined by the resultant  $B_{km}$ .

TABLE XVI.  $Nd^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S')_w') || \Sigma C_2 || J(LS_w))$

| $n'$ | $\psi_{n'}$ | $n_0$ | $n =$     |           |           |           |           |           |           |           |  |  |
|------|-------------|-------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--|--|
|      |             |       | $n_0$     | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   | $n_0+7$   |  |  |
| 1    | 4S 3/2      | 1     | 0.032836  | -0.026214 | 0.005950  | 0.039986  | -0.007244 | -0.063317 | -0.039054 |           |  |  |
| 2    | 4F 3/2      | 2     | 0.339661  | -0.385166 | -0.949571 | 0.110770  | 0.428746  | 0.390132  |           |           |  |  |
| 3    | 4F 5/2      | 3     | 0.287851  | -0.707504 | -0.354338 | -0.664543 | -0.707220 | 0.142775  | 0.042483  | -0.110086 |  |  |
| 4    | 4G 5/2      | 4     | 0.075427  | 0.269469  | 0.004553  | 0.021759  | -0.068006 | 1.294736  | 0.042697  |           |  |  |
| 5    | 4F 7/2      | 5     | 0.524794  | -0.553996 | -0.511694 | -0.421464 | -0.043049 | 0.104467  | -0.033328 | -0.251660 |  |  |
| 6    | 4G 7/2      | 6     | 0.448902  | -0.328195 | 0.032171  | 0.320949  | 0.310972  | 1.083151  | -0.054476 |           |  |  |
| 7    | 2G 7/2 (1)  | 7     | 0.124433  | 0.221964  | 0.375500  | -0.119439 | 0.906681  | 0.111158  |           |           |  |  |
| 8    | 4F 9/2      | 8     | 0.510183  | 0.040488  | 0.299347  | -0.015969 | 0.408135  | 0.081228  |           |           |  |  |
| 9    | 4I 9/2      | 9     | -0.473344 | -0.131237 | 0.190513  | 0.010183  | -0.011184 |           |           |           |  |  |
| 10   | 2H 9/2 (2)  | 10    | 0.459275  | -0.072154 | 0.355319  | -0.268724 |           |           |           |           |  |  |
| 11   | 4I 11/2     | 11    | -0.496846 | -0.089470 | 0.218747  | -0.008758 |           |           |           |           |  |  |
| 12   | 2H 11/2 (2) | 12    | 0.142776  | -0.091398 | -0.494615 |           |           |           |           |           |  |  |
| 13   | 4I 13/2     | 13    | -0.562442 | 0.191108  |           |           |           |           |           |           |  |  |
| 14   | 4I 15/2     | 14    | -0.660762 |           |           |           |           |           |           |           |  |  |

TABLE XVII.  $Nd^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S')\omega') || \sum C_4 || J(LS\omega)$

| $n'$ | $T_{n'}$    | $n_0$ | $(\begin{smallmatrix} n \\ n_0 \end{smallmatrix}    C_4    \begin{smallmatrix} n \\ n_0 \end{smallmatrix})$ |           |           |           |           |           |           |           |           |           |          |
|------|-------------|-------|---|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|
|      |             |       | $n_0$   | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   | $n_0+7$   | $n_0+8$   | $n_0+9$   | $n_0+10$ |
| 1    | 4s 3/2      | 3     | -0.027556   | -0.474735 | 0.024037  | -0.495936 | -0.325212 | -0.058060 | -0.058540 | 0.074617  | 0.006332  | 0.268860  |          |
| 2    | 4f 3/2      | 3     | 0.258154  | -0.237622 | -0.317635 | 0.272881  | 0.238718  | 0.078336  | 0.540335  | 0.135311  | -0.425475 | 0.015378  |          |
| 3    | 4f 5/2      | 3     | 0.163216  | -0.405531 | 0.263965  | -0.043020 | 0.093512  | -0.253355 | 0.549380  | -0.200100 | 0.462519  | 0.061157  |          |
| 4    | 4g 5/2      | 4     | 0.493774  | 0.360100  | -0.535072 | -0.435172 | -0.090004 | 0.721761  | -0.132377 | -0.606808 | 0.019780  | 0.210885  | 0.479148 |
| 5    | 4f 7/2      | 5     | 0.098475  | -0.282687 | -0.287962 | 0.343743  | 0.231893  | 0.208535  | 0.549383  | -0.143407 | 0.646444  | -0.443605 |          |
| 6    | 4g 7/2      | 6     | 0.244690  | -0.076020 | 0.106536  | 0.447771  | 0.253172  | 0.350097  | -0.162776 | -0.540947 | 0.185414  |           |          |
| 7    | 2g 7/2 (1)  | 7     | -0.012113   | 0.257213  | 0.484703  | 0.195826  | 0.484313  | -0.006925 | -0.360749 | 0.046662  |           |           |          |
| 8    | 4f 9/2      | 8     | -0.357564   | 0.108470  | -0.057823 | 0.209565  | 0.177674  | 0.527782  | 0.798536  |           |           |           |          |
| 9    | 4i 9/2      | 5     | -0.469816   | -0.100919 | 0.369643  | 0.058298  | -0.131416 | 0.009105  |           |           |           |           |          |
| 10   | 2h 9/2 (2)  | 10    | 0.045811  | 0.022195  | 0.070246  | 0.088044  | 0.519339  |           |           |           |           |           |          |
| 11   | 4i 11/2     | 11    | -0.384327   | -0.108727 | 0.414927  | -0.118018 |           |           |           |           |           |           |          |
| 12   | 2h 11/2 (2) | 12    | -0.041504   | -0.147838 | -0.297266 |           |           |           |           |           |           |           |          |
| 13   | 4i 13/2     | 13    | -0.463221   | 0.388905  |           |           |           |           |           |           |           |           |          |
| 14   | 4i 15/2     | 14    | -0.487946   |           |           |           |           |           |           |           |           |           |          |

TABLE XVIII.  $Nd^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S'\omega') || \Sigma C_6 || J(LS\omega))$

| $n'$ | $\gamma_{n'}$ | $n =$ |           | $(\gamma_n    \Sigma C_6    \gamma_n)$ |           |           |           |           |           |           |          |           |         |  |
|------|---------------|-------|-----------|--|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|---------|--|
|      |               | $n_0$ | $n_0$     | $n_0$                                  | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   | $n_0+7$  | $n_0+8$   | $n_0+9$ |  |
| 1    | 4s 3/2        | 8     | 0.046623  | 0.619603                               | -0.019383 | 0.582979  | -0.052899 | 0.734585  | 0.733994  |           |          |           |         |  |
| 2    | 4f 3/2        | 8     | -0.430755 | -0.299254                              | -0.188123 | 0.818233  | -0.115150 | -0.583199 | 0.216631  |           |          |           |         |  |
| 3    | 4f 5/2        | 5     | 0.383562  | 0.428742                               | 0.366592  | 0.420304  | -0.804918 | 0.090337  | 0.243854  |           |          |           |         |  |
| 4    | 4g 5/2        | 5     | 0.516628  | 0.287106                               | 0.377538  | -0.467405 | 0.242037  | -0.053441 | -0.397527 | 0.195979  | 0.810306 | -0.613764 |         |  |
| 5    | 4f 7/2        | 5     | -0.411985 | 0.070962                               | -0.123917 | -0.352169 | -0.832544 | -0.076940 | -0.710437 | -0.154512 | 0.277457 | -0.084173 |         |  |
| 6    | 4g 7/2        | 6     | 0.336965  | 0.247842                               | 0.110768  | 0.300511  | 0.796861  | 0.139438  | -0.435347 | -0.454932 | 0.012953 | 1.005682  |         |  |
| 7    | 2g 7/2 (1)    | 7     | 0.196500  | 0.664218                               | 0.225750  | -0.546193 | -0.281440 | 0.752395  | -0.249594 | -0.307016 | 0.067170 |           |         |  |
| 8    | 4f 9/2        | 8     | -0.029358 | -0.260513                              | 0.060935  | -0.774801 | 0.176235  | -0.917710 | -0.872591 | 0.413896  |          |           |         |  |
| 9    | 4i 9/2        | 9     | -1.062671 | -0.434186                              | 1.378836  | 0.129929  | -0.862461 | 0.271728  |           |           |          |           |         |  |
| 10   | 2h 9/2 (2)    | 10    | 0.667681  | -0.200510                              | 0.667282  | -0.434152 | -0.353281 |           |           |           |          |           |         |  |
| 11   | 4i11/2        | 11    | -0.331779 | -0.101115                              | 1.421068  | -0.826117 |           |           |           |           |          |           |         |  |
| 12   | 2h11/2 (2)    | 12    | -0.217820 | 0.067921                               | -0.005544 |           |           |           |           |           |          |           |         |  |
| 13   | 4i13/2        | 13    | -0.616629 | 1.538633                               |           |           |           |           |           |           |          |           |         |  |
| 14   | 4i15/2        | 14    | -1.775096 |  |           |           |           |           |           |           |          |           |         |  |

TABLE XIX.  $Er^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S'\omega') || \Sigma C_2 || J(LS\omega))$

| $n'$ | $\psi_{n'}$ | $n_0$ | $(\psi_{n'}    \Sigma C_2    \psi_n)$ |           |           |           |           |
|------|-------------|-------|---------------------------------------|-----------|-----------|-----------|-----------|
|      |             |       | $n_0$                                 | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   |
| 1    | 4S 3/2      | 1     | -0.262482                             | 0.220321  | -0.123648 | 0.010977  |           |
| 2    | 4F 3/2      | 2     | -0.358546                             | 0.339569  | -0.072840 |           |           |
| 3    | 4F 5/2      | 3     | -0.166956                             | 0.377745  | -0.027622 | -0.141576 |           |
| 4    | 4F 7/2      | 4     | -0.531058                             | 0.150517  | 0.174346  | -0.081189 | -0.478841 |
| 5    | 4F 9/2      | 5     | -0.478750                             | -0.488599 | 0.362506  | 0.823042  | 0.137362  |
| 6    | 4I 9/2      | 6     | 0.059525                              | 0.074883  | 0.622563  | 0.027990  |           |
| 7    | 4I11/2      | 7     | 0.380479                              | -0.258171 | -0.248614 | -0.229408 |           |
| 8    | 2H11/2 (2)  | 8     | 0.064755                              | -0.207437 | -1.153236 |           |           |
| 9    | 4I13/2      | 9     | 0.567533                              | -0.190782 |           |           |           |
| 10   | 4I15/2      | 10    | 0.679091                              |           |           |           |           |

TABLE XX.  $Er^{3+}$  REDUCED MATRIX ELEMENTS  $(J'(L'S'\omega') || \Sigma C_4 || J(LS\omega))$

| $n'$ | $\psi_{n'}$ | $n_0$ | $(\psi_{n'}    \Sigma C_4    \psi_n)$ |           |           |           |           |           |          |
|------|-------------|-------|---------------------------------------|-----------|-----------|-----------|-----------|-----------|----------|
|      |             |       | $n_0$                                 | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$  |
| 1    | 4S 3/2      | 3     | 0.071178                              | -0.085995 | -0.020083 | 0.316716  | 0.073430  | 0.503102  |          |
| 2    | 4F 3/2      | 3     | -0.211138                             | 0.272688  | 0.071543  | -0.540948 | 0.343382  | 0.024375  |          |
| 3    | 4F 5/2      | 3     | -0.079428                             | -0.252989 | 0.554343  | -0.270880 | -0.352943 | 0.273028  | 0.476466 |
| 4    | 4F 7/2      | 4     | -0.110153                             | -0.208608 | -0.348339 | -0.580590 | -0.139612 | -0.655039 | 0.432382 |
| 5    | 4F 9/2      | 5     | 0.318566                              | -0.086966 | 0.119105  | 0.168638  | -0.441658 | -0.825465 |          |
| 6    | 4I 9/2      | 6     | 0.313221                              | -0.292901 | 0.290134  | -0.116014 | -0.469588 |           |          |
| 7    | 4I11/2      | 7     | 0.213348                              | -0.419460 | -0.466250 | -0.019705 |           |           |          |
| 8    | 2H11/2 (2)  | 8     | -0.296091                             | -0.278804 | -0.724416 |           |           |           |          |
| 9    | 4I13/2      | 9     | 0.469379                              | -0.386437 |           |           |           |           |          |
| 10   | 4I15/2      | 10    | 0.696071                              |           |           |           |           |           |          |

TABLE XXI.  $E_r 3^+$  REDUCED MATRIX ELEMENTS  $(J'(L'S'\omega') || \Sigma C_6 || J(LS\omega))$

| $n'$ | $\psi_{n'}$ | $n_0$ | $(\psi_{n'}    \Sigma C_6    \psi_n)$ |           |           |           |           |           |           |
|------|-------------|-------|---------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
|      |             |       | $n_0$                                 | $n_0+1$   | $n_0+2$   | $n_0+3$   | $n_0+4$   | $n_0+5$   | $n_0+6$   |
| 1    | 4s 3/2      | 5     | 0.207436                              | -0.644214 | -0.347284 | 0.128523  | -0.751733 | -0.600759 |           |
| 2    | 4f 3/2      | 5     | 0.311537                              | 0.301793  | -0.890596 | 0.069566  | 0.237355  | -0.455555 |           |
| 3    | 4f 5/2      | 4     | -0.406985                             | -0.763623 | 0.407966  | -0.066968 | 0.545644  | -0.748047 | 0.603501  |
| 4    | 4f 7/2      | 4     | 0.403600                              | -0.156917 | 0.835497  | 0.497156  | -0.809732 | -0.014258 | -1.011190 |
| 5    | 4f 9/2      | 5     | -0.276963                             | -0.213917 | 1.447424  | -0.059624 | 0.341243  | 0.867992  |           |
| 6    | 4i 9/2      | 6     | 1.129530                              | -0.455469 | 0.682982  | 1.081023  | 0.127155  |           |           |
| 7    | 4i 11/2     | 7     | 0.211155                              | -0.245872 | -1.331432 | 0.803101  |           |           |           |
| 8    | 2H11/2 (2)  | 8     | 0.419948                              | 0.293424  | -0.388420 |           |           |           |           |
| 9    | 4i 13/2     | 9     | 0.611945                              | -1.528391 |           |           |           |           |           |
| 10   | 4i 15/2     | 10    | 1.741019                              |           |           |           |           |           |           |

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