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Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. I. Pr³⁺, Nd³⁺, Er³⁺, Tm³⁺, and Yb³⁺ †

W. T. CARNALL, P. R. FIELDS, AND B. G. WYBOURNE

Argonne National Laboratory, Argonne, Illinois

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We have correlated the experimentally measured intensities of the solution absorption spectra of Pr³⁺, Nd³⁺, Er³⁺, Tm³⁺, and Yb³⁺ in three different solvents with a theoretical expression derived by Judd. The expression,

$$P = \sum_{\lambda} T_{\lambda} \sigma (f^N \psi_J || U^{(\lambda)} || f^N \psi'_{J'})^2$$

$$\lambda = 2, 4, 6$$

is derived from a theory in which the ligand-field interactions with the central 3+ ion cause a mixing of higher configurations of opposite parity into the f^N configuration and gives rise to induced electric-dipole transitions. A prerequisite for the intensity calculations is the computation of complete intermediate coupling eigenvectors for the energy levels investigated. Other possible mechanisms such as magnetic-dipole and electric-quadrupole transitions are considered. The oscillator strengths of important magnetic-dipole transitions are tabulated.

The results give the first experimental verification of the ability of the theory to account for large changes in certain bands of the same lanthanide observed in different solvents. Conclusions are drawn respecting the T_{λ} 's obtained in a given medium for all the lanthanides studied, and also for those obtained for a given lanthanide in different media. The J dependence of the T_{λ} 's is removed to facilitate their intercomparison, and the resulting parameters are tabulated. The T_{λ} 's for Yb³⁺ are obtained by an extrapolation of the values computed for Tm³⁺ and Er³⁺. The nature of the model required by the theory is discussed.

1. INTRODUCTION

UNTIL quite recently, the main emphasis in the theoretical interpretation of trivalent lanthanide and actinide absorption spectra has been upon the correlation of the experimentally observed energy levels with those calculated by diagonalization of the complete energy matrices of the appropriate f^N electron configurations.¹⁻⁷ These calculations have been surprisingly successful and have led to the establishment of reasonably reliable intermediate coupling eigenvectors for most of the low-lying energy levels. It is thus an appropriate time to consider the calculation of the intensities of the absorption bands that result from intra- f^N electronic transitions.

Early estimates of the relative importance of the different modes by which electronic transitions can occur within the f^N configuration were made by Van Vleck.⁸ Subsequently, Broer *et al.*⁹ revised and extended these estimates, and presented as well, a considerable amount of experimental data on the intensities of

lanthanide spectra in aqueous solutions. The actual calculation of intensities has been made feasible by the recent work of Judd¹⁰ and Ofelt.¹¹

In the present paper, we have examined the validity of the intensity relationships deduced by Judd and Ofelt. The energies and intensities of the absorption bands have been studied for the Pr³⁺(4f²), Nd³⁺(4f³), Er³⁺(4f¹¹), Tm³⁺(4f¹²), and Yb³⁺(4f¹³) ions in several different solution media. The observed spectral intensities were analyzed using the eigenvectors obtained from the energy-level calculations, in a manner similar to that employed by Judd¹⁰ in his treatment of Nd³⁺ and Er³⁺. Judd was able to obtain good agreement between theory and experiment for these two ions in dilute aqueous solution in terms of three parameters, T_{λ} ($\lambda = 2, 4, 6$). Our particular interest is in the behavior of these parameters under the influence of different ligand fields and in the relationship that they bear to each other for different lanthanides or actinides.

We first consider the various modes by which the optical transitions may occur and the calculation of their contributions to the total oscillator strength. This is followed by a discussion of the experimental methods and a comparison of the measured oscillator strengths with those calculated. Finally, we review the basis of the models used and the interpretation of our results.

2. CALCULATION OF OSCILLATOR STRENGTHS

The intensity of an absorption band is measured by its oscillator strength, which is directly proportional to

† Based on work performed under the auspices of the U.S. Atomic Energy Commission.

¹ B. G. Wybourne, *J. Chem. Phys.* **32**, 639 (1960); **34**, 279 (1961).

² M. H. Crozier and W. A. Runciman, *J. Chem. Phys.* **35**, 1392 (1961).

³ B. G. Wybourne, *J. Chem. Phys.* **36**, 2295, 2301 (1962).

⁴ G. S. Ofelt, *J. Chem. Phys.* **38**, 2171 (1963).

⁵ H. Lämmermann and J. G. Conway, *J. Chem. Phys.* **38**, 259 (1963).

⁶ J. B. Gruber, *J. Inorg. Nucl. Chem.* **25**, 1093 (1963).

⁷ W. T. Carnall and B. G. Wybourne, *J. Chem. Phys.* **40**, 3428 (1964).

⁸ J. H. Van Vleck, *J. Phys. Chem.* **41**, 67 (1937).

⁹ L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, *Physica* **11**, 231 (1945).

¹⁰ B. R. Judd, *Phys. Rev.* **127**, 750 (1962).

¹¹ G. S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).

the area under the absorption curve. The oscillator strength P can be expressed in terms of the molar extinction coefficient ϵ , the energy of the transition in wavenumbers σ , and the refractive index of the medium η , by the relationship¹²

$$P = \frac{2303 mc^2}{N\pi e^2} \frac{9\eta}{(\eta^2+2)^2} \int \epsilon_i(\sigma) d\sigma$$

$$= 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2+2)^2} \right] \int \epsilon_i(\sigma) d\sigma. \quad (1)$$

The molar extinction coefficients of lanthanide absorption bands in dilute aqueous solutions are seldom >10 , and on the average are nearer to unity. A typical oscillator strength is $\sim 10^{-6}$.

The electronic transitions of the trivalent lanthanides and actinides can be of electric-dipole, magnetic-dipole, or electric-quadrupole character; some transitions have appreciable contributions from more than one mode. Electric-dipole transitions within a pure f^N configuration are strictly parity forbidden. However, weak, induced electric-dipole transitions can occur as a result of the interaction of the central ion with the surrounding ligand-field mixing into the f^N configuration states from configurations of opposite parity and thus relaxing the parity restriction. Electric-dipole transitions may also be induced as a result of the asymmetries produced by means of the vibronic coupling of the central ion with its ligands. In contrast to the foregoing, electric-quadrupole and magnetic-dipole transitions within the f^N configuration are parity-allowed.

The oscillator strengths for pure electric-quadrupole transitions are estimated to be several orders of magnitude too low to account for the observed intensities of lanthanide and actinide absorption bands and hence they are not discussed further.^{9,13,14}

In the Russell-Saunders approximation, magnetic dipole transitions are restricted by the selection rules

$$\Delta J \leq 1, \quad \Delta L = 0, \quad \Delta S = 0,$$

and

$$\Delta I = 0. \quad (2)$$

Thus in the extremum of LS coupling, magnetic-dipole transitions by absorption will be limited to transitions from the ground state to the first excited state of the ground multiplet. The selection rules on the L and S quantum numbers will be relaxed, even in the free ion, if there is an appreciable spin-orbit coupling and hence, at least a few additional magnetic-dipole transitions could be anticipated. The details of the intermediate coupling calculations follow shortly.

¹² W. Kauzmann, *Quantum Chemistry* (Academic Press Inc., New York, 1957), p. 581.

¹³ C. K. Jørgensen and B. R. Judd, *Mol. Phys.* **8**, 281 (1964).

¹⁴ M. A. El'yashevich, "Spectra of the Rare Earths," U.S. Atomic Energy Commission, AEC-tr-4403 (1953) has pointed out that the value of P for pure quadrupole radiation, Ref. 9, p. 235, should read 2×10^{-11} instead of 2×10^{-9} .

Judd¹⁰ has shown that the oscillator strength of an induced electric-dipole transition may be related to the energy of the transition σ (expressed in our case in cm^{-1}) and the square of the matrix elements of the unit tensor operators $\mathbf{U}^{(\lambda)}$ connecting the initial and final states (ψ_J and $\psi_{J'}$) via three phenomenological parameters T_λ ($\lambda=2, 4$, and 6). These three parameters are related to the radial wavefunctions of the states, the refractive index of the medium, and the ligand-field parameters that characterize the environmental field. Judd's result may be written as

$$P = \sum_{\lambda \text{ even}} T_\lambda \sigma (f^N \psi_J || \mathbf{U}^{(\lambda)} || f^N \psi_{J'})^2. \quad (3)$$

We note that in developing this expression the relevant matrix elements have been summed over the M projection quantum numbers and it has been assumed that the states of the initial level are equally populated. In Judd's expression the parameters T_λ contain the weighting factor $(2J+1)^{-1}$. To facilitate the comparison of the parameters for different ions it is desirable to extract this factor and rewrite Eq. (3) as

$$P = \sum_{\lambda \text{ even}} \mathfrak{J}_\lambda \sigma (f^N \psi_J || \mathbf{U}^{(\lambda)} || f^N \psi_{J'})^2 / (2J+1), \quad (4)$$

where

$$\mathfrak{J}_\lambda = (2J+1) T_\lambda. \quad (5)$$

Eigenvectors were calculated for all the ions of interest by diagonalizing the complete energy matrices using parameters that were chosen to minimize the deviations between the centers of gravity of the observed absorption bands and the calculated "free-ion" levels. These parameters are given in Table I. The eigenvectors were of the form

$$|f^N \alpha SLJ\rangle = \sum_{\alpha, S, L} C(\alpha, S, L) |f^N \alpha SLJ\rangle, \quad (6)$$

where $C(\alpha, S, L)$ are the intermediate coupling coefficients and $|f^N \alpha SLJ\rangle$ are the basis states in the LS coupling scheme. These eigenvectors were used to transform matrix elements, calculated in the LS basis, into the physical coupling scheme.¹⁵

The matrix elements of Eq. (4) were calculated in the LS basis using the equation¹⁶

$$(f^N \alpha SLJ || \mathbf{U}^{(\lambda)} || f^N \alpha' SL' J') = (-1)^{S+L'+J+\lambda}$$

$$\times [(2J+1)(2J'+1)]^{\frac{1}{2}} \left\{ \begin{matrix} J & J' & \lambda \\ L & L' & S \end{matrix} \right\}$$

$$\times (f^N \alpha SL || \mathbf{U}^{(\lambda)} || f^N \alpha' SL'). \quad (7)$$

The reduced matrix elements on the right-hand side

¹⁵ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1957), p. 277.

¹⁶ B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963).

of Eq. (7) were taken from the tables of Nielson and Koster.¹⁷ The matrix elements of Eq. (7) were then transformed from the LS -basis states to the physical coupling scheme prior to being squared and substituted into Eq. (4).

The oscillator strength for a magnetic-dipole transition is given by⁹

$$P_{\text{mag}} = (8\pi^2 mc / 3\hbar e^2) \sigma [S(\psi_J; \psi'_{J'}) / (2J+1)] \eta, \quad (8)$$

where S is the line strength whose square root is defined as

$$S^{\frac{1}{2}}(\psi_J; \psi'_{J'}) = (-e/2mc) (\psi_J \parallel \mathbf{L} + 2\mathbf{S} \parallel \psi'_{J'}). \quad (9)$$

(a) $J = J'$

$$(\alpha SLJ \parallel \mathbf{L} + 2\mathbf{S} \parallel \alpha SLJ) = g\hbar [J(J+1)(2J+1)]^{\frac{1}{2}}, \quad (10)$$

where

$$g = 1 + \{[J(J+1) + S(S+1) - L(L+1)] / 2J(J+1)\}, \quad (11)$$

(b) $J' = J-1$

$$(\alpha SLJ \parallel \mathbf{L} + 2\mathbf{S} \parallel \alpha SLJ-1) = \hbar \{[(S+L+J+1)(S+L+1-J)(J+S-L)(J+L-S)] / 4J\}^{\frac{1}{2}}, \quad (12)$$

(c) $J' = J+1$

$$(\alpha SLJ \parallel \mathbf{L} + 2\mathbf{S} \parallel \alpha SLJ+1) = \hbar \{[(S+L+J+2)(S+J+1-L)(L+J+1-S)(S+L-J)] / 4(J+1)\}^{\frac{1}{2}}. \quad (13)$$

The matrix elements calculated from Eqs. (10) to (13) were transformed into the physical scheme and the magnetic-dipole oscillator strengths computed using Eq. (8). These quantities, including the refractive indices of the media used, are given in Table II.

The calculated magnetic-dipole oscillator strength is directly proportional to the refractive index η , and hence it was necessary to include this factor so as to ensure that the residual oscillator strength was a true measure of the induced electric-dipole oscillator strength. Strictly, a refractive index factor $9\eta/(\eta^2+2)^2$ should also be used in computing the electric-dipole oscillator strengths as indicated in Eq. (1). Provided the refractive index does not show appreciable variation over the spectral range considered the neglect of this factor will only affect the absolute magnitude of \mathfrak{J}_λ . As we are mainly concerned with the relative values of the \mathfrak{J}_λ 's and since the correction is small and relatively independent of the media we chose to neglect this factor in our calculations.

The experimental data were analyzed by resolving each observed absorption band into one or more Gaussian components to enable evaluation of the total area under the curve. The oscillator strength was then computed using Eq. (1). Each magnetic-dipole oscillator strength was subtracted from the experimental value, in the few instances where this correction was

TABLE I. Slater parameters (F_k) and spin-orbit coupling constants (ζ) in units of cm^{-1} used to generate the electronic energy level schemes of Pr^{3+} , Nd^{3+} , Er^{3+} , and Tm^{3+} .

	F_2	F_4	F_6	ζ
Pr^{3+}	315.0	51.0	5.65	775
Nd^{3+}	327.5	48.7	5.36	884
Er^{3+}	433.2	67.1	7.36	2393
Tm^{3+}	460.0	69.0	8.00	2670

The nonzero matrix elements will be those diagonal in the quantum numbers α , S , and L . Equation (9) was evaluated for all the three cases permitted by the $\Delta J = 0, \pm 1$ selection rule using the relationships⁹

appreciable, and the residual oscillator strength used as a measure of the induced electric-dipole oscillator strength.

A least-squares analysis was used to obtain the optimum set of the three parameters \mathfrak{J}_λ . The statistical significance of the parameters was gauged by computing their standard errors in the usual manner.¹⁸ The root-mean-square (rms) deviation of the observed (P_{obs}) and calculated (P_{calc}) oscillator strengths was defined as

$$\text{rms} = \left(\frac{\text{sum of squares of deviations}}{\text{number of observations} - \text{number of parameters}} \right)^{\frac{1}{2}}. \quad (14)$$

3. EXPERIMENTAL

The absorption spectra reported here were observed using a high-resolution grating-prism recording spectrophotometer with a useful spectral range of 0.2–2.6 μ . The lanthanides used were supplied as oxides of >99.9% purity. The choice of solvents was influenced by a desire to utilize as large a portion of the available spectral range as possible, while at the same time selecting rather different environments in which to observe the absorption bands characteristic of the lanthanides being studied. The three media selected

¹⁷ C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (MIT Press, Cambridge, Massachusetts, 1963).

¹⁸ W. M. Smart, *Combination of Observations* (Cambridge University Press, New York, 1958), Chap. 6.

TABLE II. Calculated magnetic dipole oscillator strengths (P_{MD}) for levels in which $P_{MD} > 10^{-6}$, and which occur in the range 4000–40 000 cm^{-1} .

	Level	$E_{calc}(\text{cm}^{-1})$	$P_{MD} \times 10^6 / \eta^a$
Nd ³⁺	² H _{9/2}	12 527	1.3
Er ³⁺	⁴ I _{13/2}	6 547	31.0
	² K _{15/2}	27 226	3.8
Tm ³⁺	³ H ₅	8 322	27.7
	¹ I ₆	34 551	1.4
Yb ³⁺	² F _{5/2}	10 250	17.8

^a The following values were used for the refractive index (η) of the media: $\eta_{H_2O} = 1.33$, $\eta_{LiNO_3-KNO_3} = 1.43$, $\eta_{EtAc} = 1.37$.

were: (1) Dilute DClO_4 or HClO_4 —the former was useful in extending the region of transmission in the near infrared¹⁹; no difference was observed in measurements in the two solvents in the ultraviolet-visible region. (2) Ethyl acetate-anhydrous lanthanide nitrates were prepared following the method of Addison *et al.*,²⁰ and were dissolved in anhydrous ethyl acetate. Both the dilute perchloric acid and the anhydrous ethyl acetate solutions were studied at 25°C. (3) Molten $\text{LiNO}_3\text{--KNO}_3$ —the efficacy of this solvent in the visible-near infrared regions has already been discussed.²¹ Observations were made at 160°C in a cell system that has been described along with other experimental details, in a previous paper.²¹ At least two or three different concentrations of lanthanide ions were studied in each solvent and the reported oscillator strengths are thus averaged values. The results indicated that for all the bands the oscillator strengths were independent of the concentration in the range investigated.

TABLE III. Matrix elements for Pr^{3+} .

$S'L'J'$	Calculated energy (cm^{-1})	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$
³ H ₆	4 438	0.0001	0.0331	0.1396
³ F ₂	4 829	0.5081	0.4047	0.1189
³ F ₃	6 267	0.0655	0.3474	0.6996
³ F ₄	6 910	0.0174	0.0526	0.4958
¹ G ₄	10 176	0.0019	0.0044	0.0118
¹ D ₂	17 741	0.0029	0.0192	0.0618
³ P ₀	20 683	0	0.1719	0
³ P ₁	21 302	0	0.1708	0
¹ I ₆	21 496	0.0087	0.0482	0.0220
³ P ₂	22 690	~0	0.0333	0.1247
¹ S ₀	52 028	0	0.0072	0

4. RESULTS

 $\text{Pr}^{3+}(4f^2)$

Twelve "free-ion" levels lie above the ³H₄ ground state of $\text{Pr}^{3+}(4f^2)$. We were able to observe, and utilize for purposes of calculation, absorption bands corresponding to eight levels in $\text{HClO}_4\text{--DClO}_4$ and ethyl acetate solutions, and corresponding to 10 levels in $\text{LiNO}_3\text{--KNO}_3$. A band corresponding to the ¹S₀ level was seen in HClO_4 but was not included in the calculations because of a lack of reproducibility of the data. The ³H₆ level lies much beyond the infrared limit of the spectral region studied. Most bands in the melt are weaker, but somewhat broader, than in the aqueous solutions. However, only in the case of the transition to ³P₂ is there a marked difference in intensity—a decrease from $\epsilon = 9.98$ in aqueous solution to $\epsilon = 2.5$ in $\text{LiNO}_3\text{--KNO}_3$. The corresponding difference in oscillator strength amounts to a decrease of ~50%.

TABLE IV. Oscillator strengths for Pr^{3+} .

Spectral region ^a (cm^{-1})	$\text{HClO}_4\text{--DClO}_4$		$P \times 10^6$ $\text{LiNO}_3\text{--KNO}_3$		Ethyl acetate		PrCl_3^b
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.
4 120–5 800			6.84	6.76	4.94	4.55	
5 800–6 620	6.55	6.15	7.34	7.26	10.6	12.0	
6 620–7 690	6.20	7.65	2.12	3.93	3.95	7.42	
9 090–11 100	0.31	–0.11	0.32	0.18	0.36	0.29	0.34
16 050–17 500	3.04	2.47	1.63	1.41	3.14	2.52	3.12
19 800–21 900	14.2	14.4	8.48	8.63	11.1	11.3	9.18
21 900–23 810	11.2	10.2	5.51	3.51	12.9	6.57	14.6
rms deviation] ^c	1.10×10^{-6}		1.36×10^{-6}		3.70×10^{-6}		

^a The range indicated is approximately the same in each solvent.

^b From Ref. 22.

^c Root-mean-square deviation calculated from Eq. (14).

¹⁹ W. T. Carnall, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.* **66**, 2159 (1962).

²⁰ C. C. Addison, J. C. Sheldon, and N. Hodge, *J. Chem. Soc.* **1956**, 3900.

²¹ W. T. Carnall, *Anal. Chem.* **34**, 786 (1962).

The calculated matrix elements consistent with the observed levels of Pr^{3+} are given in Table III, while the calculated and experimental oscillator strengths are compared in Table IV. Uncertainty in determining the zero line for the 3P group (19 800–21 900 cm^{-1}) indicated by Hoogschagen and Gorter as an experimental problem in their work,²² may account for the discrepancies between their results and ours in this range. The \mathfrak{J}_λ values for the different media appear in Table XI. The parameter \mathfrak{J}_2 is seen to be poorly defined in the HClO_4 - DClO_4 and ethyl acetate solutions, since the statistical error was larger than the parameter itself. In LiNO_3 - KNO_3 , \mathfrak{J}_2 is well defined. The cause of this anomaly can be readily seen upon inspection of Table III. The matrix elements in $\mathbf{U}^{(2)}$ are much smaller than those of $\mathbf{U}^{(4)}$ and $\mathbf{U}^{(6)}$ except for the $^3F_2+^3H_6$ group which was observed in LiNO_3 - KNO_3 but not in the other media. The values of \mathfrak{J}_4 and \mathfrak{J}_6 are of the same order of magnitude in all three solvents while \mathfrak{J}_2 appears to be considerably larger in HClO_4 - DClO_4 than in the other two.

As indicated earlier, attempts to measure the oscillator strength of the 1S_0 band were not reproducible. A system of electronic energy levels calculated to be consistent with the absorption bands of Pr^{3+} would place the 1S_0 level near 52 000 cm^{-1} , whereas the center of the observed band is found at 46 700 cm^{-1} . This band is superimposed on the tail of a much larger absorption with its maximum at >53 000 cm^{-1} , which is probably to be identified as an f - d transition. The tail is very broad, extending practically into the visible region. Because of the perturbing effect of this higher configuration it is unlikely that the Judd-Ofelt theory will give a realistic basis for the calculation of the oscillator strength for 1S_0 . From the value of \mathfrak{J}_4 we would predict the 1S_0 level to be characterized by a relatively weak band with $P \simeq 7 \times 10^{-7}$. Measured ϵ values of ~ 40 indicate that experimentally, the transition is much more intense than predicted. The band does appear to be quite sharp, which is consistent with the nature of a 1S_0 state.

$\text{Tm}^{3+}(4f^{12})$

The $4f^{12}$ configuration of Tm^{3+} is the conjugate of the $4f^2$ configuration of Pr^{3+} . Due to the increased spin-orbit interaction in Tm^{3+} , as compared to Pr^{3+} , we were able to observe transitions from the 3H_6 ground state to all of the remaining levels of the 3H and 3F multiplets. The 3P multiplet was also shifted to higher energies as a result of increased electrostatic interaction. It was observed in the ultraviolet region, and was superimposed on the tail of a band whose maximum lies at ~ 50 000 cm^{-1} . As was the case with Pr^{3+} , this superposition of bands introduced a considerable error into the calculation of oscillator strengths in this region.

TABLE V. Matrix elements for Tm^{3+} .

$S' L' J'$	Calculated energy (cm^{-1})	$[\mathbf{U}^{(2)}]^2$	$[\mathbf{U}^{(4)}]^2$	$[\mathbf{U}^{(6)}]^2$
3F_4	5 508	0.5470	0.7355	0.2462
3H_6	8 322	0.1073	0.2313	0.6381
3H_4	12 636	0.2300	0.1032	0.5880
3F_3	14 280	0	0.3162	0.8408
3F_2	14 996	0	~ 0	0.2609
1G_4	21 421	0.0006	0.0355	0.2082
1D_2	28 103	0	0.3352	0.0919

Thus the group of levels including 3P_2 , 1I_6 , 3P_0 , and 3P_1 was not used in the computation of the \mathfrak{J}_λ parameters. An example of the irreproducibility of the results for the foregoing group is indicated by the fact that for 0.35M Tm^{3+} , $P = 4.8 \times 10^{-6}$ while for 0.83M Tm^{3+} , $P = 9.4 \times 10^{-6}$. It should, however, be noted that by combining the matrix elements for $^3P+^1I$ and using the parameters \mathfrak{J}_λ determined from bands observed in the visible-near-infrared regions, a value of $P_{\text{calc}} = 5.4 \times 10^{-6}$ was found, which is certainly of the correct order of magnitude.

The matrix elements consistent with the observed levels of Tm^{3+} are given in Table V while the calculated and experimental oscillator strengths are compared in Table VI. The unreasonably large value of P reported by Hoogschagen and Gorter for the 1D_2 band,²² probably can be attributed both to a lack of resolution and to appreciable background absorption. In addition, their sample of thulium was known to be of low purity.

The \mathfrak{J}_λ values for the different media appear in Table XI. Again, \mathfrak{J}_2 is poorly defined in HClO_4 - DClO_4 in spite of the inclusion of \mathfrak{J}_2 dependent bands that were not observed in Pr^{3+} .

Only the 3H_4 and 3F_4 states have large $\mathbf{U}^{(2)}$ matrix elements. However, these same two states also have large $\mathbf{U}^{(4)}$ and $\mathbf{U}^{(6)}$ matrix elements with the result that the effect of the \mathfrak{J}_4 and \mathfrak{J}_6 parameters is dominant and \mathfrak{J}_2 is of secondary importance in determining the oscillator strength in HClO_4 - DClO_4 . \mathfrak{J}_2 is at least an order of magnitude larger in LiNO_3 - KNO_3 and ethyl acetate with the result that it is well defined in these two media.

$\text{Nd}^{3+}(4f^3)$

Judd¹⁰ used the data of Hoogschagen and Gorter²² for Nd^{3+} in dilute aqueous solutions in testing his interpretation of the intensity of rare earth solution spectra. Although Hoogschagen and Gorter reported oscillator strengths for both NdCl_3 and $\text{Nd}(\text{NO}_3)_3$ solutions, and Stewart²³ has obtained similar information using $\text{Nd}(\text{ClO}_4)_3$ solutions, these results actually

²² J. Hoogschagen and C. J. Gorter, *Physica* **14**, 197 (1948).

²³ D. C. Stewart, Argonne National Laboratory Report ANL-4812, 1952 (unpublished).

TABLE VI. Oscillator strengths for Tm^{3+} .

Spectral region ^a (cm^{-1})	$\text{HClO}_4\text{-DClO}_4$		$P \times 10^6$ $\text{LiNO}_3\text{-KNO}_3$		Ethyl acetate		TmCl_3^b Exptl.
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	
5 560- 6 330	1.06	1.26	4.70	5.00			
7 600- 9 350	1.24	1.41	2.10	2.52	1.82	2.31	
12 000-13 700	2.10	1.83	5.41	4.96	4.36	4.22	1.98
13 890-14 800					3.66	3.69	
	{3.93	3.93	{3.97	4.32			{3.18
14 800-15 670					0.73	0.80	
20 650-22 200	0.74	1.00	2.05	1.04	1.54	1.11	0.45
27 170-29 400	2.31	2.20	3.49	3.24	3.07	3.02	~30.
rms deviation ^c	2.73×10^{-7}		7.45×10^{-7}		3.91×10^{-7}		

^a The range indicated is approximately the same in each solvent.^b From Ref. 22.^c Root-mean-square deviation calculated from Eq. (14).

represent data in only one environment since in all cases the species under study was the hydrated ion $\text{Nd}(\text{H}_2\text{O})_9^{3+}$. Differences in the reported oscillator strengths for the same bands in these different media probably reflect differences in experimental conditions

TABLE VII. Matrix elements for Nd^{3+} .

$S' L' J'$	Calculated energy (cm^{-1})	$[\text{U}^{(2)}]^2$	$[\text{U}^{(4)}]^2$	$[\text{U}^{(6)}]^2$
$^4I_{13/2}$	3 875	0.0001	0.0136	0.4557
$^4I_{15/2}$	5 950	0	0.0001	0.0453
$^4F_{3/2}$	11 232	0	0.2299	0.0547
$^4F_{5/2}$	12 277	0.0009	0.2361	0.3973
$^2H_{9/2}$	12 527	0.0092	0.0076	0.1196
$^4S_{3/2}$	13 113	0	0.0027	0.2354
$^4F_{7/2}$	13 268	0.0010	0.0420	0.4249
$^4F_{9/2}$	14 587	0.0010	0.0096	0.0381
$^2H_{11/2}$	15 864	0.0001	0.0026	0.0104
$^4G_{5/2}$	16 897	0.8968	0.4091	0.0355
$^2G_{7/2}$	17 044	0.0755	0.1848	0.0316
$^2K_{13/2}$	18 803	0.0068	0.0002	0.0313
$^4G_{7/2}$	18 823	0.0551	0.1569	0.0547
$^4G_{9/2}$	19 260	0.0046	0.0611	0.0407
$^2K_{15/2}$	20 806	0	0.0053	0.0144
$^2G_{9/2}$	20 897	0.0010	0.0144	0.0136
$^2D_{3/2}$	21 041	0	0.0181	0.0001
$^4G_{11/2}$	21 272	~0	0.0053	0.0080
$^2P_{1/2}$	22 903	0	0.0381	0
$^2D_{5/2}$	23 549	0	0.0001	0.0024
$^2D_{3/2}$	26 047	0	0.0030	0.0010
$^4D_{3/2}$	27 945	0	0.1954	0.0168
$^4D_{5/2}$	28 164	0.0001	0.0573	0.0280
$^2I_{11/2}$	28 320	0.0049	0.0148	0.0034
$^4D_{1/2}$	28 511	0	0.2570	0
$^2L_{15/2}$	29 074	0	0.0250	0.0096
$^2I_{13/2}$	29 655	0.0001	0.0013	0.0017
$^1D_{7/2}$	30 190	~0	0.0037	0.0080
$^2L_{17/2}$	30 562	0	0.0010	0.0012
$^2H_{9/2}$	32 334	0.0001	0.0086	~0
$^2D_{3/2}$	33 219	0	0.0103	0.0011
$^2H_{11/2}$	33 692	0.0001	0.0001	0.0002
$^2D_{5/2}$	34 488	0.0007	0.0005	0.0028

and in the method of the reduction of the data rather than changes in the environment of the rare-earth ion.

We have re-examined the spectra of Nd^{3+} in dilute aqueous solution and in addition have obtained results in the molten $\text{LiNO}_3\text{-KNO}_3$ eutectic and in ethyl acetate. The experimental results in aqueous solution were taken at higher resolution and over a larger spectral range than has been previously reported, but aside from expected differences in the near-infrared range, they are quite similar to the results given by Hoogschagen and Gorter and by Stewart.

Some background absorption was found in the ultra-violet region of the Nd^{3+} spectrum in $\text{HClO}_4\text{-DClO}_4$ and this precluded an accurate determination of the oscillator strengths of several weak bands occurring there. However, with 10 or more terms from each solvent system, together with the presence of some relatively large matrix elements amongst each of the sets of terms defining \mathfrak{J}_2 , \mathfrak{J}_4 , and \mathfrak{J}_6 , the final values of the \mathfrak{J}_λ were well established.

The matrix elements consistent with the observed levels of Nd^{3+} are given in Table VII while the calculated and experimental oscillator strengths for the three media appear in Table VIII. Again, the \mathfrak{J}_λ values are given in Table XI. The most striking feature of the sets of \mathfrak{J}_λ values for Nd^{3+} is the excellence with which they describe the large variations in the oscillator strengths for the same absorption band in different solvents. The value of \mathfrak{J}_2 in $\text{LiNO}_3\text{-KNO}_3$ is a factor of 10 greater than in aqueous solution while \mathfrak{J}_4 is roughly constant and \mathfrak{J}_6 for $\text{LiNO}_3\text{-KNO}_3$ is half of the value for aqueous solutions. In ethyl acetate \mathfrak{J}_4 and \mathfrak{J}_6 are very nearly the same as in aqueous solution while \mathfrak{J}_2 is larger by about a factor of 10.

$\text{Er}^{3+}(4f^{11})$

The calculated and experimental oscillator strengths for Er^{3+} in the three media are given in Table IX. The matrix elements are contained in Table X while the values of \mathfrak{J}_λ appear in Table XI. The experimental observations for aqueous solutions are in close agreement

TABLE VIII. Oscillator strengths for Nd³⁺.

Spectral region ^a (cm ⁻¹)	HClO ₄ -DClO ₄		$P \times 10^6$ LiNO ₃ -KNO ₃		Ethyl acetate	
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
3 740- 4 760			0.71	1.06		
5 560- 6 890	0.48	0.28	0.34	0.16		
10 810-11 980	2.57	2.08	1.30	1.31	1.95	2.54
11 770-13 100	8.54	8.34	4.56	4.93	8.12	8.97
13 100-14 130	8.78	9.47	5.16	5.24	9.89	9.59
14 180-15 270	0.63	0.66	0.53	0.39	0.70	0.69
15 750-16 260	0.15	0.19	0.12	0.11	0.18	0.20
16 260-18 150	9.34	9.48	30.0	30.1	28.9	29.0
18 150-20 400	6.82	5.02	6.49	4.84	8.29	7.07
20 400-22 470	2.25	1.29	1.19	0.80	1.94	1.48
22 620-24 390	0.53	0.54	0.25	0.35	0.26	0.70
26 110-26 460	0.02	0.07				
27 550-29 700	9.88	10.4	6.50	6.80		
					{13.8	{13.8
29 700-31 350	2.10	0.37				
31 350-32 260	0.12	0.15				
32 570-33 780	0.29	0.23				
33 900-34 840	0.27	0.11				
rms deviation ^b	8.00×10 ⁻⁷		6.08×10 ⁻⁷		6.62×10 ⁻⁷	

^a The range indicated is approximately the same in each solvent.^b Root-mean-square deviation calculated from Eq. (14).

with those already published.²² The parameters \mathfrak{J}_4 and \mathfrak{J}_6 are very nearly the same in all three media, although \mathfrak{J}_4 is not well defined in LiNO₃-KNO₃. As was the case for Nd³⁺, the parameter \mathfrak{J}_2 was found to be approximately 10 times larger in ethyl acetate and LiNO₃-KNO₃ than in aqueous solutions. The appreciable increase in the intensity of the two bands identified as due to transitions from the ground state $^4I_{15/2}$ to $^2H_{11/2}$ and to $^4G_{11/2}$ is accounted for solely by the increase in \mathfrak{J}_2 .

Although several reasonably intense bands are found in the ultraviolet in Er³⁺, the tail from a large band with a maximum >50 000 cm⁻¹ again interferes. In addition, a weak band near 29 700 cm⁻¹, found in Er³⁺ in HClO₄, does not fit the energy-level scheme adopted. At this point we can only surmise that it is either a component of one of the other bands or it

originates from a transition to a level that is perturbed by interaction with higher configurations.

The existence of a sharp, relatively intense band of Er³⁺ at 39 200 cm⁻¹ in the HClO₄-DClO₄ system, not observed in nitrate solutions because of the absorption by NO₃⁻ itself in this region of the spectrum, suggested a possible further check of the energy fit to the ultraviolet region. The only calculated energy level in this region which has matrix elements large enough to make an appreciable contribution to the observed oscillator strength ($P=9.4 \times 10^{-6}$), is the $^4D_{7/2}$ level. Using the values of \mathfrak{J}_λ established in the visible-infrared range, together with the matrix elements given in Table X for $^4D_{7/2}$, we calculate a value of $P=4.87 \times 10^{-6}$. This level will lie rather close to the lower states of the $4f^{10}5d$ configuration, making the assumptions of the Judd-

TABLE IX. Oscillator strengths for Er³⁺.

Spectral region ^a (cm ⁻¹)	HClO ₄ -DClO ₄		$P \times 10^6$ LiNO ₃ -KNO ₃		Ethyl acetate	
	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.
6 140- 7 090	1.76	1.52	1.74	1.44	2.55	1.97
9 670-10 660	0.54	0.64	0.95	0.90	1.01	1.05
11 490-13 160	0.30	0.33	0.28	0.39	0.36	0.37
14 680-15 870	2.24	2.14	2.00	2.14	2.43	2.48
17 890-18 700	0.74	0.61				
			{18.4	21.0	{15.0	16.8
18 700-19 900	2.57	2.80				
19 900-21 300	2.03	2.32	2.46	2.04	2.83	2.79
21 700-23 000	1.34	1.16	1.23	0.94	1.57	1.42
23 800-25 300	0.74	0.89	0.98	0.74	1.20	1.08
25 840-27 230	4.87	4.73	36.3	34.7	28.2	27.1
rms deviation ^b	2.06×10 ⁻⁷		1.28×10 ⁻⁶		8.66×10 ⁻⁷	

^a The range indicated is approximately the same in each solvent.^b Root-mean-square deviation calculated from Eq. (14).

TABLE X. Matrix elements for Er^{3+} .

$S' L' J'$	Calculated energy (cm^{-1})	$[\mathbf{U}^{(2)}]^2$	$[\mathbf{U}^{(4)}]^2$	$[\mathbf{U}^{(6)}]^2$
$^4I_{13/2}$	6 547	0.0195	0.1173	1.4299
$^4I_{11/2}$	10 177	0.0291	0.0004	0.3969
$^4I_{9/2}$	12 325	0	0.1856	0.0122
$^4F_{9/2}$	15 144	0	0.5275	0.4612
$^4S_{3/2}$	18 305	0	0	0.2230
$^2H_{11/2}$	19 211	0.7326	0.4222	0.0927
$^4F_{7/2}$	20 300	0	0.1467	0.6280
$^4F_{5/2}$	21 950	0	0	0.2237
$^4F_{3/2}$	22 308	0	0	0.1256
$^2G_{9/2}$	24 478	0	0.0157	0.2278
$^4G_{11/2}$	26 434	0.8970	0.5123	0.1172
$^2K_{15/2}$	27 226	0.0229	0.0043	0.0794
$^4G_{9/2}$	27 412	0	0.2436	0.1190
$^2G_{7/2}$	27 952	0	0.0186	0.1153
$^4D_{7/2}$	39 028	0	0.8917	0.0292

Ofelt theory less valid. This, together with the experimental problem of accurately evaluating the oscillator strength of the particular band would suggest the agreement between the experimental and calculated oscillator strengths is as good as could be expected. It appears that the intensity calculations confirm the

assignment of the $^4D_{7/2}$ level, calculated to be at 39 028 cm^{-1} , to the observed band at 39 200 cm^{-1} .

$\text{Yb}^{3+}(4f^{13})$

Since there is only one excited f level in Yb^{3+} , the observation of the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition yields insufficient data to evaluate the \mathfrak{J}_λ parameters. From Eq. (4), we have

$$P = (\sigma/196)[3\mathfrak{J}_2 + 10\mathfrak{J}_4 + 21\mathfrak{J}_6]. \quad (15)$$

Extrapolating from the data for Er^{3+} and Tm^{3+} , we obtain values of \mathfrak{J}_λ for an aqueous solution as shown in Table XI. These values result in a calculated oscillator strength of 4.0×10^{-6} . This transition will have some magnetic-dipole character, since $P_{\text{MD}} = 2.36 \times 10^{-7}$ (from Table II). Combining these two results the total calculated oscillator strength is $P = 4.2 \times 10^{-6}$, which may be compared with our experimental value of 3.33×10^{-6} . Similarly, for Yb^{3+} in $\text{LiNO}_3\text{-KNO}_3$ we calculate a total oscillator strength, $P = 7.13 \times 10^{-6}$ based on \mathfrak{J}_λ values given in Table XI, whereas experimentally we find $P = 7.99 \times 10^{-6}$.

The fact that \mathfrak{J}_2 was not well defined for Tm^{3+} in $\text{HClO}_4\text{-DClO}_4$ had a minor effect on the calculation of P for Yb^{3+} since according to Eq. (15) the term involving \mathfrak{J}_2 is appreciably less than those involving \mathfrak{J}_4 and \mathfrak{J}_6 . While \mathfrak{J}_4 was also subject to a rather large sta-

TABLE XI. Values of \mathfrak{J}_λ .

		$\text{HClO}_4\text{-DClO}_4$	$\text{LiNO}_3\text{-KNO}_3$	Ethyl acetate
Pr^{3+}	\mathfrak{J}_2	$-0.27 \pm 4.47 \times 10^{-8}$	$1.19 \pm 0.52 \times 10^{-8}$	$0.24 \pm 1.35 \times 10^{-8}$
	\mathfrak{J}_4	$2.08 \pm 0.16 \times 10^{-8}$	$8.69 \pm 1.54 \times 10^{-9}$	$1.12 \pm 0.41 \times 10^{-8}$
	\mathfrak{J}_6	$2.74 \pm 0.28 \times 10^{-8}$	$8.94 \pm 2.05 \times 10^{-9}$	$1.81 \pm 0.55 \times 10^{-8}$
Nd^{3+}	\mathfrak{J}_2	$1.58 \pm 0.57 \times 10^{-9}$	$1.54 \pm 0.04 \times 10^{-8}$	$1.22 \pm 0.05 \times 10^{-8}$
	\mathfrak{J}_4	$5.48 \pm 0.51 \times 10^{-9}$	$3.62 \pm 0.39 \times 10^{-9}$	$7.21 \pm 0.42 \times 10^{-9}$
	\mathfrak{J}_6	$1.02 \pm 0.07 \times 10^{-8}$	$5.59 \pm 0.55 \times 10^{-9}$	$1.02 \pm 0.06 \times 10^{-8}$
Nd^{3+a}	\mathfrak{J}_2	$2.36 \pm 0.68 \times 10^{-9}$		
	\mathfrak{J}_4	$5.23 \pm 0.61 \times 10^{-9}$		
	\mathfrak{J}_6	$1.07 \pm 0.09 \times 10^{-8}$		
Er^{3+}	\mathfrak{J}_2	$1.59 \pm 0.22 \times 10^{-9}$	$2.18 \pm 0.16 \times 10^{-8}$	$1.60 \pm 0.09 \times 10^{-8}$
	\mathfrak{J}_4	$2.26 \pm 0.36 \times 10^{-9}$	$2.54 \pm 2.76 \times 10^{-9}$	$3.28 \pm 1.53 \times 10^{-9}$
	\mathfrak{J}_6	$2.38 \pm 0.18 \times 10^{-9}$	$1.92 \pm 1.20 \times 10^{-9}$	$2.83 \pm 0.79 \times 10^{-9}$
Er^{3+a}	\mathfrak{J}_2	$1.53 \pm 0.28 \times 10^{-9}$		
	\mathfrak{J}_4	$2.53 \pm 0.37 \times 10^{-9}$		
	\mathfrak{J}_6	$2.29 \pm 0.18 \times 10^{-9}$		
Tm^{3+}	\mathfrak{J}_2	$7.68 \pm 8.80 \times 10^{-10}$	$1.44 \pm 0.25 \times 10^{-8}$	$1.06 \pm 0.20 \times 10^{-8}$
	\mathfrak{J}_4	$2.36 \pm 0.39 \times 10^{-9}$	$3.85 \pm 1.05 \times 10^{-9}$	$3.48 \pm 0.60 \times 10^{-9}$
	\mathfrak{J}_6	$2.48 \pm 0.23 \times 10^{-9}$	$2.36 \pm 0.62 \times 10^{-9}$	$2.63 \pm 0.44 \times 10^{-9}$
Yb^{3+}	\mathfrak{J}_2	1.20×10^{-9}	1.81×10^{-8}	1.33×10^{-8}
	\mathfrak{J}_4	2.26×10^{-9}	3.20×10^{-9}	3.35×10^{-9}
	\mathfrak{J}_6	2.43×10^{-9}	2.14×10^{-9}	2.73×10^{-9}

^a These values of \mathfrak{J}_λ were calculated from data in Ref. 22, as were the values reported by Judd (Ref. 10); however, the matrix elements used were those generated in the course of the present investigation.

tistical error for Er^{3+} in $\text{LiNO}_3\text{--KNO}_3$, as may be seen from Table XI, the value obtained would seem to be reasonable in view of good agreement between P_{calc} and P_{exptl} for Yb^{3+} .

5. INTERPRETATION OF RESULTS

The results we have obtained show that the experimental oscillator strengths of the lanthanides studied may be interpreted in terms of three parameters \mathfrak{J}_2 , \mathfrak{J}_4 , and \mathfrak{J}_6 using Eq. (4). This equation was derived by Judd and independently by Ofelt by assuming that the observed intensities of the transitions are the result of mixing into the states of the f^N configuration some of the character of states of the opposite parity configurations $f^{N+1}d^{-1}$, $f^{N-1}d$, and $f^{N-1}g$ by the *odd* terms in the electrostatic ligand field. The success of our phenomenological application of Eq. (4) might lead us to conclude that the electrostatic description of the ligand field is indeed justified. Such a conclusion would, however, be premature. The Judd-Ofelt theory provides a successful phenomenological description of the experimental oscillator strengths for the same reasons that the ligand-field theory of crystal splittings has been so successful.

In both ligand-field theory and theories of intensities, we must be very careful to distinguish those parts of the theory that depend purely upon symmetry arguments from those that depend on the explicit features of individual models. The electrostatic model has only been successful to the extent that it has used group theoretical properties that are common to both ligand-field theory and molecular orbital theory. The distinction between different models will only be apparent when the parameters are evaluated in terms of the specific assumptions of the models. At the present stage of development it is probably too early to attempt detailed calculations for specific models. These calculations will be of considerable complexity and it is probably best at this time to attempt an examination of the properties of the parameters \mathfrak{J}_λ with a preliminary aim at establishing those features that a successful model must be able to encompass.

Within a given media the parameters \mathfrak{J}_λ do not appear to change by more than an order of magnitude in going from the light to the heavy members of the lanthanide series. This behavior is consistent with the nature of the $4f^N$ shell of the lanthanides. For a given lanthanide ion in aqueous solution the \mathfrak{J}_λ parameters are of approximately the same order of magnitude, with \mathfrak{J}_2 being slightly smaller than \mathfrak{J}_4 and \mathfrak{J}_6 . From the point of view of an electrostatic model of the ligand fields this similarity is indeed surprising. The electrostatic model predicts the proportionality¹⁰

$$\mathfrak{J}_\lambda \propto \langle r^{t+1} \rangle^2 / R^{2t+2}, \quad (16)$$

where $t=3$ for \mathfrak{J}_2 , 3 and 5 for \mathfrak{J}_4 , and 5 and 7 for \mathfrak{J}_6 ; $\langle r^{t+1} \rangle$ is the radial expectation value for the f electron, and R is the radial distance of the ligand ions from the

central ion of interest. Equation (16) would lead us to anticipate marked dissimilarities in the relative magnitudes of \mathfrak{J}_2 , \mathfrak{J}_4 , and \mathfrak{J}_6 , which is contrary to our observations. Furthermore, this model would predict that \mathfrak{J}_4 and \mathfrak{J}_6 would be extremely sensitive to changes in the environment of the central ion whereas in fact, these two parameters do not appear to undergo any dramatic changes in spite of quite radical changes in the environment. This is in marked contrast to the tenfold increase in \mathfrak{J}_2 in going from aqueous solutions to the $\text{LiNO}_3\text{--KNO}_3$ eutectic or to ethyl acetate solutions.

It has been known for some time that certain absorption bands in the lanthanides^{19,24-27} and the actinides²⁸ are unusually sensitive to changes in the ligands. Furthermore, it has been found on occasion that absorption spectra will show an over-all appearance, upon changing ligands, of *decreased* extinction coefficients while at the same time certain bands show a relative *increase* in their extinction coefficients.²⁹ These changes may be correlated with a marked *increase* in the magnitude of \mathfrak{J}_2 relative to \mathfrak{J}_4 and \mathfrak{J}_6 . This is consistent with the observations of Judd¹⁰ and Jørgensen and Judd¹³ that the sensitive bands usually involve transitions with $\Delta J \leq 2$ which is a necessary condition for the matrix elements of $\mathbf{U}^{(2)}$ to be nonzero.

Jørgensen and Judd¹³ have made a detailed study of the origin of the remarkable sensitivity of \mathfrak{J}_2 , with respect to changes in the ligands. They have carefully examined several possible sources for this sensitivity and concluded that it owes its origin to the inhomogeneity of the dielectric. According to their mechanism there is an asymmetric distribution of the dipoles induced by the electromagnetic field in the medium surrounding the lanthanide or actinide ion. The variation of the electric vector across the ion is then very much greater than for the case of a homogeneous dielectric with the result that the intensities of the electric-quadrupole transitions, which are normally exceedingly weak, are enormously enhanced and become at least comparable to those of the more usual induced electric-dipole transitions. Jørgensen and Judd have called these enhanced transitions pseudoquadrupole transitions in recognition of the fact that their intensity is proportional to the first power of the transition energy and not to the cube as for pure electric-quadrupole transitions.

Since the pseudoquadrupole transitions will give contributions to the oscillator strength having the same energy and angular dependence as the $\lambda=2$ term

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in the induced electric-dipole expression, their effect will be entirely accommodated by the parameter \mathfrak{J}_2 .

It is interesting to note that \mathfrak{J}_2 is practically the same in the LiNO_3 - KNO_3 melts and in the ethyl acetate solutions of the anhydrous lanthanide nitrates. Whereas in the aqueous solutions the first coordination sphere contains only water molecules, in the other two media the first coordination sphere will contain the nitrate group and hence we might well expect the values of \mathfrak{J}_2 to be similar in these two media but dissimilar to those in the aqueous solution.

6. CONCLUDING REMARKS

The results we have obtained are in substantial agreement with the theories of Judd and Ofelt. Furthermore, the suggestion of Jørgensen and Judd that the hypersensitive transitions are of the pseudoquadrupole type are consistent with the results reported here. We

intend to extend the measurements and calculations to cover the light actinides and the entire lanthanide series.

In spite of the apparent success of the Judd-Ofelt theory further development is required and the limitations of the model must be clearly recognized. The interpretation of the \mathfrak{J}_λ parameters remains the fundamental problem and additional experimental data could greatly assist in the development of more sophisticated models and in distinguishing between competing models.

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Nuclear Magnetic Resonance in RbMnF_3

RICHARD E. PAYNE,* RICHARD A. FORMAN, AND ARNOLD H. KAHN

National Bureau of Standards, Washington, D. C.

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A nuclear magnetic resonance study of ^{85}Rb , ^{87}Rb , and ^{19}F in paramagnetic RbMnF_3 is reported. The measured shifts of the rubidium nuclear resonances are the first reported for the case of an alkali nucleus in the paramagnetic XMF_3 perovskite compounds ($\text{X}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$; $\text{M}=\text{Mn}, \text{Ni}, \text{Co}$). The shift for rubidium is in the opposite direction from that expected from a $5s$ contact hyperfine interaction. The isotropic hyperfine interaction of the fluorine indicates the presence of 0.51% unpaired $2s$ spins in the F^- orbitals from each Mn^{++} neighbor; this result is in good agreement with previous work for the F^- resonances in these paramagnetic materials. The anisotropic shift of the F^- resonance was examined in a powder sample and a $2p$ hyperfine coupling coefficient obtained.

I. INTRODUCTION

WORK on magnetic fluorides by Shulman and Jaccarino,¹ Shulman and Knox,² Lee, Portis, and Witt,³ and others has brought attention to the compounds XMnF_3 , where X represents $\text{Na}, \text{K}, \text{Rb}$, and Cs .

RbMnF_3 is a particularly interesting member of this group because it is cubic and remains cubic⁴⁻⁶ below its Néel temperature of 82.6°K .⁷ We have chosen to ex-

amine the shifts of the nuclear magnetic resonances of the rubidium and fluorine nuclei. The crystal structure of RbMnF_3 is given in Fig. 1. The unit cell has the Mn^{++} ion at its center, Rb^+ ions at its corners, and F^- ions at its face centers. The lattice parameter is 4.234 \AA at room temperature.⁸ The Rb^+ ions are located at sites with cubic point symmetry, while the point symmetry of the F^- sites is tetragonal.

II. APPARATUS AND SAMPLE

Two samples were used: one which was believed to be a single-crystal chip, and the other a finely ground powder packed into a spherical glass shell which had an inside diameter of about 8 mm. The powder sample results were used for all calculations.

* Present address: Woods Hole Oceanographic Institution, Woods Hole, Massachusetts.

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