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Optical Absorption Intensities of Rare-Earth Ions

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Electric dipole transitions within the $4f$ shell of a rare-earth ion are permitted if the surroundings of the ion are such that its nucleus is not situated at a center of inversion. An expression is found for the oscillator strength of a transition between two states of the ground configuration $4f^N$, on the assumption that the levels of each excited configuration of the type $4f^Nn'd$ or $4f^Nn'g$ extend over an energy range small as compared to the energy of the configuration above the ground configuration. On summing over all transitions between the components of the ground level ψ_J and those of an excited level $\psi'_{J'}$, both of $4f^N$, the oscillator strength P corresponding to the transition $\psi_J \rightarrow \psi'_{J'}$ of frequency ν is found to be given by

$$P=\sum T_\lambda \nu (\psi_J \| U^{(\lambda)} \| \psi'_{J'})^2,$$

where $\mathbf{U}^{(\lambda)}$ is a tensor operator of rank λ, and the sum runs over the three values 2, 4, and 6 of λ. Transitions that also involve changes in the vibrational modes of the complex comprising a rare-earth ion and its surroundings, provide a contribution to P of precisely similar form. It is shown that sets of parameters T_λ can be chosen to give a good fit with the experimental data on aqueous solutions of $NdCl_3$ and $ErCl_3$. A calculation on the basis of a model, in which the first hydration layer of the rare-earth ion does not possess a center of symmetry, leads to parameters T_λ that are smaller than those observed for Nd^{3+} and Er^{3+} by factors of 2 and 8, respectively. Reasons for the discrepancies are discussed.

I. INTRODUCTION

THE last decade has witnessed a remarkable growth in our knowledge of the spectroscopic properties of triply ionized rare-earth atoms. The interplay of experiment and theory has led to the elucidation of appreciable parts of the term schemes of many ions, and the splittings in the levels that arise when a rare earth ion is situated in a crystal lattice are now understood rather well. From the present vantage point, Van Vleck's classic paper on the puzzle of the rare earths[1] makes interesting reading, published as it was at a time when even the configurations involved in the spectral transitions had not been definitely established. The arguments remain essentially valid. The sharp absorption lines of rare-earth crystals in the visible and infrared regions of the spectrum do correspond to transitions within the configurations of the type $4f^N$, and the so-called extra levels have their origin in the interplay of electronic and vibrational effects.

Van Vleck's paper discusses the nature of the electronic transitions, that is, whether they can be classified as electric dipole, magnetic dipole, or electric quadrupole. His conclusion, that all three types play a role, was later criticized by Broer, Gorter, and Hoogschagen, who showed that the observed intensities of the transitions are in almost all cases too intense for magnetic dipole or electric quadrupole radiation to be important.[2] They also demonstrated that electric dipole transitions could be sufficiently strong to match the experimental intensities, but their calculations can at best be described as semiquantitative. The difficulty in estimating intensities of electric dipole transitions is that they arise from the admixture into $4f^N$ of configurations of opposite parity. To calculate such admixtures, not only must the energies and eigenfunctions of configurations such as $4f^{N-1}5d$ be known, but also that part of the crystal field potential responsible for the admixing. The problem of obtaining these data has proved complicated enough to restrain the performance of further theoretical work on the intensities of the absorption lines of the rare earths, though considerable advances have been made in the last few years on the similar problem of estimating the intensities of lines of transition-metal ions (see, for example, Griffith[3]). An added reason for the absence of a detailed theory may be the comparative lack of experimental data; for, apart from a few isolated cases,[4] the only oscillator strengths measured at present appear to be for solutions of rare-earth ions.[5,6] However, the situation will undoubtedly be remedied shortly. This expectation, taken with the information gained in the last decade on the properties, both experimental and theoretical, of the rare-earth ions, makes a fresh examination of the intensities of the absorption lines an attractive venture.

II. MATRIX ELEMENTS

The oscillator strength P' of a spectral line, corresponding to the electric dipole transition from the component i of the ground level of an ion to the component f of an excited level, is given by

$$P'=\chi[8\pi^2 m\nu/h]|(i|D_q^{(1)}|f)|^2. \qquad (1)$$

In this equation, m is the mass of an electron, h is

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[1] J. H. Van Vleck, J. Phys. Chem. **41**, 67 (1937).

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

[3] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, New York, 1961).

[4] A. Merz, Ann. Physik **28**, 569 (1937); H. Ewald, Z. Physik **110**, 428 (1938).

[5] J. Hoogschagen, *De Absorptiespectra van de zeldzame aarden* (N. V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, 1947). Most of the material in this thesis is summarized in J. Hoogschagen and C. J. Gorter, Physica **14**, 197 (1948)

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

Planck's constant, and ν is the frequency of the line. The factor χ makes allowance for the refractive index of the medium in which the ion is embedded; according to Broer *et al.*, for water $\chi=1.19$.[2] In terms of the polar coordinates (r_j,θ_j,ϕ_j) of electron j,

$$D_q^{(k)}=\sum_j r_j^k C_q^{(k)}(\theta_j,\phi_j),$$

where

$$C_q^{(k)}(\theta_j,\phi_j)=[4\pi/(2k+1)]^{1/2}Y_{kq}(\theta_j,\phi_j),$$

Y_{kq} being a spherical harmonic. The choice of q in Eq. (1) depends on the polarization of the incident light. Equation (1) can be regarded as a slight elaboration of Eq. (6-58) of Slater.[7]

In order to evaluate the matrix element of Eq. (1), we need detailed descriptions of the states i and f. Owing to the comparatively small splittings of the levels produced by the crystal field, it is usually a good approximation to assume at first that the quantum number J, corresponding to the total angular momentum of the electron system of the rare-earth ion, remains a good quantum number. Corresponding to the component i of the ground level of the configuration l^N, there exists, to the first approximation, a linear combination

$$(A|\equiv\sum_M (l^N\psi JM|\, a_M, \tag{2}$$

where M denotes the quantum number of the projection J_z of $\mathbf{J}$. The symbol ψ stands for the additional quantum numbers that may be necessary to define the level uniquely; if RS (Russell-Saunders) coupling were strictly followed, it would incorporate a definite S and L, the quantum numbers corresponding to the total spin and total orbit, respectively, of the electron system. However, it is unnecessary at this point to assume RS coupling. By analogy with Eq. (2), we may write

$$|A')\equiv\sum_{M'} a'_{M'}\, |l^N\psi'J'M') \tag{3}$$

for the first approximation to the upper state.

It might be thought that rare-earth ions in solution would be subject to rapidly fluctuating electric fields, and that the coefficients a_M and $a'_{M'}$ would therefore vary with time. While this may be true to a slight extent, it is now virtually certain that for aqueous solutions the immediate surroundings of the ions are rigidly locked in position. Evidence for this will be presented later; we mention it here to eliminate the possible misapprehension that the linear combinations (2) and (3) might have a well-defined significance only for ions embedded in crystal lattices.

The states $(A|$ and $|A')$, being constructed from the same configuration l^N, possess the same parity. However, under the replacement $\mathbf{r}_j\rightarrow-\mathbf{r}_j$, we find $\mathbf{D}^{(1)}\rightarrow-\mathbf{D}^{(1)}$. The equation

$$(A|D_q^{(1)}|A')=0$$

follows, and hence to the first approximation, no electric dipole transition occurs. This is merely a statement of the Laporte rule, of course. To obtain nonvanishing matrix elements of the components of $\mathbf{D}^{(1)}$, it is necessary to admix into $(A|$ and $|A')$ states built from configurations of opposite parity to l^N. For the moment, we consider only those configurations of the type $l^{N-1}l'$; these are certainly the most important. To distinguish such configurations, we augment l' with the principal quantum number n'; the symbol n is reserved for the analogous quantum number for the electrons of the ground configuration l^N, but we shall give it explicitly only when an ambiguity threatens.

The admixing of configurations of opposite parity can come about if the contribution V to the Hamiltonian arising from the interaction of the electrons of the ion with the electric field of the lattice, here assumed to be static, contains terms of odd parity. On making the expansion

$$V=\sum_{t,p} A_{tp}D_p^{(t)},$$

this condition becomes equivalent to the demand that not all A_{tp}, for which t is odd, vanish. The states (2) and (3) are now replaced by

$$\begin{aligned}(B|\equiv\sum_M\, &(l^N\psi JM|\,a_M\\ &+\sum_\kappa (l^{N-1}(n'l')\psi''J''M''|\,b(n'l',\psi''J''M''),\end{aligned}$$

and

$$\begin{aligned}|B')\equiv\sum_{M'}\, &a'_{M'}|l^N\psi'J'M')\\ &+\sum_\kappa b'(n'l',\psi''J''M'')\,|l^{N-1}(n'l')\psi''J''M''),\end{aligned}$$

where

$$\begin{aligned}b(n'l',\psi''J''M'')&\\ =\sum_M a_M&(l^N\psi JM|V|l^{N-1}(n'l')\psi''J''M'')\\ &\times[E(\psi J)-E(n'l',\psi''J'')]^{-1},\end{aligned} \tag{4}$$

and

$$\begin{aligned}b'(n'l',\psi''J''M'')&\\ =\sum_{M'} a'_{M'}&(l^{N-1}(n'l')\psi''J''M''|V|l^N\psi'J'M')\\ &\times[E(\psi'J')-E(n'l',\psi''J'')]^{-1}.\end{aligned} \tag{5}$$

The symbol $\sum_\kappa$ stands for the sum over ψ'', J'', M'', l' and over those values of n' for which $l^{N-1}(n'l')$ is an excited configuration. In Eqs. (4) and (5), $E(\psi J)$ and $E(\psi'J')$ denote the energies of the levels ψJ and $\psi'J'$ of l^N; similarly, $E(n'l',\psi''J'')$ stands for the energy of the level $\psi''J''$ of $l^{N-1}(n'l')$. It is now a simple matter to obtain the equation

$$\begin{aligned}(B|D_q^{(1)}|B')&\\ =\sum a_M\, a'_{M'}A_{tp}\{&(l^N\psi JM|D_q^{(1)}|l^{N-1}(n'l')\psi''J''M'')\\ &\times(l^{N-1}(n'l')\psi''J''M''|D_p^{(t)}|l^N\psi'J'M')\\ &\times[E(\psi'J')-E(n'l',\psi''J'')]^{-1}\\ &+(l^N\psi JM|D_p^{(t)}|l^{N-1}(n'l')\psi''J''M'')\\ &\times(l^{N-1}(n'l')\psi''J''M''|D_q^{(1)}|l^N\psi'J'M')\\ &\times[E(\psi J)-E(n'l',\psi''J'')]^{-1}\},\end{aligned} \tag{6}$$

the sum running over M, M', t, p, and those quantum numbers implied by the symbol κ.

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[7] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I.

III. APPROXIMATIONS

For all but the most trivial configurations, the ninefold sum of Eq. (6) is quite unwieldy. We must, therefore, search for approximate methods, taking care to make them as realistic as possible. The occurrence of the structure

$$|l^{N-1}(n'l')\psi''J''M'')\,(l^{N-1}(n'l')\psi''J''M''|$$

in Eq. (6) suggests that it might be possible to adapt the closure procedure in some way, thereby uniting $D_q^{(1)}$ and $D_p^{(t)}$ into a single operator that acts between states of l^N. For a description and analysis of this method, see Griffith.[8] The number of summations we wish to absorb into the closure depends on how far we are prepared to assume $E(n'l',\psi''J'')$ is invariant with respect to n', l', ψ'', or J''. For example, the mildest approximation we can make is to suppose that the splittings within multiplets of the excited configurations are negligible compared with the energies that the configurations as a whole lie above l^N. This amounts to supposing $E(n'l',\psi''J'')$ is independent of J''. If the states of l^N are expanded as linear combinations of perfect RS-coupled states of the type

$$(l^N\gamma SLJM|,$$

we can perform the sums over J'' and M'' in Eq. (6) by making use of equations such as

$$\sum_{J'',M''}(l^N\gamma SLJM|D_q^{(1)}|l^{N-1}l'\gamma''SL''J''M'')(l^{N-1}l'\gamma''SL''J''M|D_p^{(t)}|l^N\gamma'SL'J'M')$$
$$=\sum_\lambda(-1)^{p+q+L+L'}(2\lambda+1)\begin{pmatrix}1 & \lambda & t\\ q & -q-p & p\end{pmatrix}\begin{Bmatrix}1 & \lambda & t\\ L' & L'' & L\end{Bmatrix}(l^N\gamma SLJM|T_{p+q}^{(\lambda)}|l^N\gamma'SL'J'M'),\qquad(7)$$

where $\mathbf{T}^{(\lambda)}$ is a tensor whose amplitude is determined by

$$(L\|T^{(\lambda)}\|L')=(L\|D^{(1)}\|L'')(L''\|D^{(t)}\|L').\qquad(8)$$

The easiest way to verify Eq. (7) is to express all the matrix elements in terms of reduced matrix elements of the type involved in Eq. (8); it is then found that Eq. (7) is equivalent to the Biedenharn-Elliott sum rule (see Edmonds[9]).

It is at once evident that the simplifications afforded by using Eqs. (7) and (8) are very slight. The degree of closure must therefore be extended. The least severe extension is to suppose that $E(n'l',\psi''J'')$ is invariant with respect to ψ'' as well as to J''. This is equivalent to regarding the excited configuration $l^{N-1}(n'l')$ as completely degenerate. A glance at diagrams giving the approximate positions and extensions of low-lying configurations of the rare-earth ions, such as Figs. 4 and 5 of Dieke, Crosswhite and Dunn,[10] indicates at once that this assumption is only moderately fulfilled. It therefore constitutes a weak link in the theory. However, we may hope that the very complexity of configurations of the type $l^{N-1}(n'l')$ might reduce the possible error; for if there are a great many terms ψ'' in $l^{N-1}(n'l')$, it would not be unreasonable to expect that the entire sum over ψ'', if broken up into smaller sums over groups of closely lying terms, would decompose into a number of parts that, for various ψ' and J', were roughly proportional to one another.

Be this as it may, the approximation leads to a great simplification in the mathematics. The analog of Eq. (7) is

$$\sum_{J'',M'',\psi''}(l^N\psi JM|D_q^{(1)}|l^{N-1}(n'l')\psi''J''M'')(l^{N-1}(n'l')\psi''J''M''|D_p^{(t)}|l^N\psi'J'M')$$
$$=\sum_\lambda(-1)^{p+q}(2\lambda+1)\begin{pmatrix}1 & \lambda & t\\ q & -p-q & p\end{pmatrix}\begin{Bmatrix}1 & \lambda & t\\ l & l' & l\end{Bmatrix}(nl|r|n'l')(nl|r^t|n'l')(l\|C^{(1)}\|l')$$
$$\times(l'\|C^{(t)}\|l)(l^N\psi JM|U_{p+q}^{(\lambda)}|l^N\psi'J'M'),\qquad(9)$$

where $\mathbf{U}^{(\lambda)}$ is the sum over all the electrons of the single-electron tensors $\mathbf{u}^{(\lambda)}$, for which

$$(l\|u^{(\lambda)}\|l)=1.$$

In Eq. (9), the abbreviation

$$(nl|r^k|n'l')=\int_0^\infty \mathcal{R}(nl)r^k\mathcal{R}(n'l')dr\qquad(10)$$

is introduced, where $\mathcal{R}/r$ is the radial part of the appropriate single-electron eigenfunction. A straightforward way of deriving Eq. (9) is to expand the matrix elements of Eq. (7) by means of Eq. (27) of Racah,[11] to perform the sum over ψ'', and then to pass from RS to intermediate coupling. Alternatively, both Eqs. (7) and (9) can be obtained from Eq. (7.1.1) of Edmonds,[9] provided the symbol γ'' of that equation is interpreted judiciously.

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[8] J. S. Griffith, Mol. Phys. 3, 477 (1960).

[9] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

[10] G. H. Dieke, H. M. Crosswhite, and B. Dunn, J. Opt. Soc. Am. **51**, 820 (1961).

[11] G. Racah, Phys. Rev. **63**, 367 (1943).

Equation (9) is excellent for the purposes we have in mind; however, the closure procedure can be extended even further. If we assume $E(n'l';\psi''J'')$ to be invariant with respect to n' as well as to ψ'' and J'', and if the full description of the ground configuration contains no electrons with azimuthal quantum number l', then the fact that the radial functions $\mathcal{R}(n'l')$, for all n', form a complete set allows us to write

$$\textstyle\sum_{n'} (nl|r|n'l')(nl|r^t|n'l') = (nl|r^{t+1}|nl), \qquad (11)$$

and the problem of calculating interconfiguration radial integrals disappears. Since for rare-earth ions both the $3d$ and $4d$ shells are filled, this technique could not be used for $l'=2$; on the other hand, there is no objection to applying it to electrons for which $l'=4$, since no g orbital is occupied in the ground configuration. The possible occupation of l' orbitals precludes our extending the closure to all four quantum numbers n', l', ψ'', and J''.

Equation (9) can be used immediately to simplify the first product on the right-hand side of Eq. (6). A precisely similar substitution may be made for the second product; but owing to the relation

$$\begin{pmatrix} 1 & \lambda & t \\ q & -p-q & p \end{pmatrix} = (-1)^{1+\lambda+t} \begin{pmatrix} t & \lambda & 1 \\ p & -p-q & q \end{pmatrix}$$

the two parts cancel to a large extent if $1+\lambda+t$ is odd. For the right-hand side of Eq. (9) not to vanish, t must be odd; hence, the condition is fulfilled if λ is odd. The cancellation would be perfect if, or a given n' and l', the energy denominators

$$\begin{aligned} &E(\psi J) - E(n'l',\psi''J''), \\ &E(\psi'J') - E(n'l',\psi''J''), \end{aligned} \qquad (12)$$

which are supposed to be independent of ψ'' and J'', could be assumed equal. This is equivalent to the supposition that the configurations $l^{N-1}(n'l')$ lie far above the states involved in the optical transitions. Although the theory could no doubt be developed without making this assumption, a considerable simplification in the mathematics results if it is made. We therefore replace both differences (12) with the single expression $\Delta(n'l')$. Equation (6) can now be written as

$$\begin{aligned} (B|D_q^{(1)}|B') &= \sum_{p,t,\ \text{even}\ \lambda} (2\lambda+1)(-1)^{p+q} A_{tp} \begin{pmatrix} 1 & \lambda & t \\ q & -p-q & p \end{pmatrix} \\ &\qquad \times (A|U_{p+q}^{(\lambda)}|A')\Xi(t,\lambda), \end{aligned} \qquad (13)$$

where

$$\begin{aligned} \Xi(t,\lambda) = 2 \sum (2l+1)(2l'+1)(-1)^{l+l'} \\ \times \begin{Bmatrix} 1 & \lambda & t \\ l & l' & l \end{Bmatrix} \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & t & l \\ 0 & 0 & 0 \end{pmatrix} \\ \times (nl|r|n'l')(nl|r^t|n'l')/\Delta(n'l'). \end{aligned} \qquad (14)$$

The summation of Eq. (14) runs over all values of n' and l' consistent with $l^{N-1}(n'l')$ being an excited configuration. In Eq. (13), the operator $U_{p+q}^{(\lambda)}$ connects states of l^N; its matrix elements can therefore be calculated by standard tensor-operator techniques.

IV. SOLUTIONS OF RARE-EARTH IONS

If, for a rare-earth crystal, one wished to limit one's investigation of the intensities of the lines in some way, for example, to study the relative intensities of a group of lines corresponding to the transitions between the components of just a pair of levels, then no doubt Eq. (13) could be manipulated to throw the relevant quantum numbers into sharper relief. However, for general purposes, it seems unlikely that Eq. (13) could be simplified much further. In order, then, to calculate the oscillator strength of the transition from the component corresponding to $(A|$ to that corresponding to $|A')$, the radial integrals and crystal field parameters A_{pt} must be estimated, the sums of Eqs. (13) and (14) carried out, and the resulting matrix element

$$(B|D_q^{(1)}|B')$$

substituted for

$$(i|D_q^{(1)}|f)$$

in Eq. (1).

Apart from a few important exceptions, the fine structures of the absorption lines for rare-earth ions in solution, in contrast to those for ions in crystals, have not been resolved. Each broad absorption line corresponds to a transition from the ground level to an excited level. The measured oscillator strength of such a line is therefore the sum of the oscillator strengths of the various component lines, suitably weighted to allow for the differential probability of occupation of the components of the ground level. In the absence of detailed knowledge of the surroundings of a rare-earth ion in solution, the energies of the components of the ground level, and hence their probabilities of occupation, cannot be calculated. However, the splittings of the ground levels of rare-earth ions in crystals, such as have been observed[12] or calculated,[13] seldom exceed 250 cm^{-1}. For a level where this splitting obtains, the ratio of the probabilities of occupation of the highest to the lowest component is as high as 0.3 at room temperature; therefore, not too great an error should be introduced if we assume all the components of the ground level are equally likely to be occupied. Allowing for the arbitrary orientation of the rare-earth ions, Eq. (1) is replaced by

$$P = \chi[8\pi^2 m\nu/3h(2J+1)] \sum |(i|D_q^{(1)}|f)|^2, \qquad (15)$$

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[12] R. A. Satten, J. Chem. Phys. **21**, 637 (1953); H. Lammermann, Z. Physik **150**, 551 (1958); E. H. Carlson and G. H. Dieke, J. Chem. Phys. **34**, 1602 (1961).

[13] B. R. Judd, Proc. Roy. Soc. (London) **A241**, 414 (1957); M. J. D. Powell and R. Orbach, Proc. Phys. Soc. (London) **78**, 753 (1961).

where the sum runs over q and all components i and f of the ground and excited level. An equivalent formula has been given by Broer *et al.*[2] Using Eq. (13), we see that the sum over i and f reduces to a sum over certain states of the type $(A|$ and $|A')$. It is, of course, unnecessary to introduce the eigenfunctions of Eqs. (2) and (3); we can simply take the states $(l^N\psi JM|$ and $|l^N\psi'J'M')$ for the components of the ground and excited levels, respectively, and sum over M and M'. As is to be expected, all quantum numbers and suffixes that depend on a fixed direction in space disappear, and we obtain

$$P=\sum_{\text{even }\lambda} T_\lambda \nu (l^N\psi J\|U^{(\lambda)}\|l^N\psi'J')^2, \tag{16}$$

where

$$T_\lambda=\chi[8\pi^2 m/3h](2\lambda+1) \times\textstyle\sum_t (2t+1)B_t\Xi^2(t,\lambda)/(2J+1), \tag{17}$$

and

$$B_t=\textstyle\sum_p |A_{tp}|^2/(2t+1)^2. \tag{18}$$

V. OTHER CONTRIBUTIONS TO P

Before using Eq. (16) to make a direct comparison between experiment and theory, it is convenient to discuss briefly some effects that have so far been ignored. In the first place, no closed shells have been disturbed in the construction of the perturbing configurations; but it is clear that for Nd IV $4f^3$, for example, the tensors $\mathbf{D}^{(k)}$ can couple the ground configuration $4f^3$ to the configurations $3d^94f^4$ and $4d^94f^4$, as well as to configurations such as $4f^25d$ or $4f^25g$. However, owing to the symmetry about the double closed shell

$$(n''l'')^{4l''+2}(nl)^{4l+2},$$

all matrix elements of the type

$$((n''l'')^{4l''+2}(nl)^N\psi JM|D_q^{(k)}|(n''l'')^{4l''+1}(nl)^{N+1}\psi''J''M'')$$

can differ from the corresponding quantities

$$((nl)^{4l+2-N}\psi JM|D_q^{(k)}|(nl)^{4l+1-N}(n''l'')\psi''J''M'')$$

by a phase factor at most. In view of the relation

$$|(l^{4l+2-N}\psi J\|U^{(\lambda)}\|l^{4l+2-N}\psi'J')|^2=|(l^N\psi J\|U^{(\lambda)}\|l^N\psi'J')|^2,$$

Eq. (16) remains valid; but the sum over n' and l' of Eq. (14), which determines T_λ in virtue of Eq. (17), has to be augmented by those quantum numbers n'' and l'' corresponding to electrons in closed shells in the ground state of the ion. The large energy $\Delta(n''l'')$ required to remove an electron from a closed shell, together with the expectation that the radial integrals

$$(nl|r^k|n''l'')$$

for $k>0$ are small, leads us to anticipate that the required modifications to the coefficients T_λ are insignificant. It is interesting to observe that if we assume that all configurations of both types

$$(nl)^{N-1}(n'l')$$

and

$$(n''l'')^{4l''+1}(nl)^{N+1}$$

coalesce into a single highly degenerate level, the objection in Sec. III to extending the closure procedure to all quantum numbers disappears.

There exists a second and intrinsically more interesting mechanism that can contribute to the intensities of rare-earth ions in solution. So far, the electric field acting on an ion has been considered to be completely static. As mentioned in Sec. I, however, lines exist in the spectra of rare-earth crystals that correspond to the excitation of vibrational quanta. If the immediate surroundings of a rare-earth ion in solution form a stable complex, as seems likely, vibrational modes may exist, the excitation of which could contribute to the intensities of the broad absorption lines. To examine this idea in more detail, we follow Griffith and denote the normal co-ordinates of the vibrating complex by Q_i.[3] Further, let η stand for the totality of the vibrational quantum numbers. For our purposes, the basic eigenfunctions of the system are taken to be simple products of harmonic oscillator eigenfunctions with the electronic eigenfunctions of the rare-earth ion. If we suppose the parameters A_{tp} of Sec. II correspond to some equilibrium arrangement of the complex, then allowance for small vibrations can be made by replacing V by

$$V'=\sum_{t,p}\left[A_{tp}+\sum_i \frac{\partial A_{tp}}{\partial Q_i}Q_i\right]D_p^{(t)}.$$

For $\eta\neq\eta'$, it is a simple matter to obtain the equation

$$(B,\eta|D_q^{(1)}|B',\eta')=\sum_i (\eta|Q_i|\eta')\frac{\partial}{\partial Q_i}(B|D_q^{(1)}|B').$$

At a given temperature there is a certain probability that the vibrating complex is in the state defined by the set of quantum numbers η. If we denote this probability by $\rho(\eta)$, then the assumption made in Sec. IV regarding the population of the purely electronic components of the ground level leads in this case to a contribution P'' to P given by

$$P''=\sum_{\text{even }\lambda} T_\lambda'\nu(l^N\psi J\|U^{(\lambda)}\|l^N\psi'J')^2, \tag{19}$$

where

$$T_\lambda'=\chi[8\pi^2m/3h](2\lambda+1)\textstyle\sum_t (2t+1)B_t'\Xi^2(t,\lambda)/(2J+1),$$

and

$$B_t'=\sum_{p,i,\eta,\eta'}\left|\frac{\partial A_{tp}}{\partial Q_i}\right|^2|(\eta|Q_i|\eta')|^2\rho(\eta)/(2t+1)^2.$$

The importance for us of these results lies in the fact that Eq. (19) is of precisely the same form as Eq. (16).

TABLE I. Reduced matrix elements of $\mathbf{U}^{(\lambda)}$ for Nd^{3+}.

$S'L'J'$	Calculated energy (cm^{-1} above $^4I_{9/2}$)[a]	$(f^3[^4I_{9/2}]\|U^{(\lambda)}\|f^3[S'L'J'])$ $\lambda=2$	$\lambda=4$	$\lambda=6$
$^4D_{7/2}$	31 004	0.0004	0.0607	−0.0893
$^2L_{17/2}$	30 932	0	−0.0318	−0.0358
$^2I_{13/2}$	30 070	0.0123	0.0370	−0.0424
$^2L_{15/2}$	29 413	0	0.1612	0.1006
$^4D_{1/2}$	29 276	0	−0.5093	0
$^4D_{5/2}$	28 836	0.0111	−0.2390	0.1659
$^2I_{11/2}$	28 694	−0.0717	−0.1238	0.0594
$^4D_{3/2}$	28 641	0	0.4417	−0.1299
$^2P_{3/2}$	26 348	0	0.0345	−0.0271
$^2D_{5/2}$	23 880	−0.0002	0.0116	0.0479
$^2P_{1/2}$	23 147	0	−0.1884	0
$^4G_{11/2}$	21 826	0.0023	−0.0741	0.0906
$^2G_{9/2}$	21 255	−0.0358	0.1381	−0.1318
$^2D_{3/2}$	21 247	0	−0.1367	0.0121
$^2K_{15,2}$	21 027	0	−0.0747	−0.1228
$^4G_{9/2}$	19 720	−0.0662	0.2388	−0.1926
$^4G_{7/2}$	19 320	0.2529	−0.4257	0.2488
$^2K_{13/2}$	18 978	−0.0846	0.0157	0.1810
$^4G_{5/2}$	17 356	−0.9471	0.6399	−0.1885
$^2G_{7/2}$	17 354	−0.2580	0.4009	−0.1539
$^2H_{11/2}$	15 985	−0.0073	0.0515	−0.1020
$^4F_{9/2}$	14 903	0.0275	−0.0936	−0.2114
$^4F_{7/2}$	13 611	0.0337	0.2034	0.6525
$^4S_{3/2}$	13 454	0	0.0549	0.4862
$^2H_{9/2}$	12 612	0.0986	−0.0914	0.3392
$^4F_{5/2}$	12 607	0.0303	−0.4862	−0.6299
$^4F_{3/2}$	11 524	0	0.4778	0.2317

[a] See reference 14.

If, then, the T_λ are treated as parameters to be adjusted to fit the experimental data, a good fit is no guarantee that the lines are purely electronic in origin. Indeed, if the surroundings of a rare-earth ion in solution are such that all A_{tp} for odd t vanish, then P'' gives the sole contribution to P.

VI. COMPARISON WITH EXPERIMENT

The absorption data for aqueous solutions of rare-earth ions are too extensive to be analyzed completely within a reasonable length of time. It was therefore decided to limit the investigations to Nd^{3+} and Er^{3+}, corresponding to three $4f$ electrons and three holes in a complete $4f$ shell, respectively. Both ions exhibit a sufficiently complex absorption spectrum to provide a good test of the theory. Moreover, Wybourne has recently fitted the energies of the levels of these ions to a detailed and reasonably complete theory,[14] thereby providing extremely accurate eigenfunctions for us to work with. The availability of tables of reduced matrix elements of the type

$$(f^3\gamma SL\|U^{(\lambda)}\|f^3\gamma' SL')$$

is an added incentive for choosing these particular ions.[15]

The procedure for calculating the reduced matrix elements of Eq. (16) runs as follows:

(i) Carry out expansions of the type

$$(l^N\psi J| = \sum_{\gamma,S,L} h(\gamma SL)(l^N\gamma SLJ|.$$

The coefficients h of the RS-coupled states are given by Wybourne.[14]

(ii) Express every matrix element in Eq. (16) as a sum over reduced matrix elements involving RS-coupled states.

(iii) Evaluate the new matrix elements by means of the formula

$$(l^N\gamma SLJ\|U^{(\lambda)}\|l^N\gamma' S'L'J')$$
$$=\delta(S,S')(-1)^{S+L'+J+\lambda}[(2J+1)(2J'+1)]^{1/2}$$
$$\times\begin{Bmatrix} L & \lambda & L' \\ J' & S & J \end{Bmatrix}(l^N\gamma SL\|U^{(\lambda)}\|l^N\gamma' SL'), \quad (20)$$

which can easily be obtained from Eq. (7.1.8) of Edmonds.[9]

(iv) Use the tables of 6-j symbols[16] and the tables of reduced matrix elements[15] to calculate the right-hand side of Eq. (20).

The results of the calculations are given in Table I for Nd^{3+} and in Table II for Er^{3+}. The levels are labeled by their principal components; the spectroscopic symbols are enclosed in square brackets to emphasize that the SL designations are not exact. All the levels listed in Tables I and II, with the exceptions of $^4D_{7/2}$, $^2L_{17/2}$, $^2I_{13/2}$, $^2L_{15/2}$, $^4D_{1/2}$, $^4D_{5/2}$, and $^2I_{11/2}$ of Nd^{3+}, have been identified with levels observed experimentally; the seven exceptions are included because their energies correspond closely to two broad bands measured by Hoogschagen.[5]

Since all reduced matrix elements of $\mathbf{U}^{(\lambda)}$ for $\lambda>6$ vanish between f-electron states, the oscillator strengths

TABLE II. Reduced matrix elements of $\mathbf{U}^{(\lambda)}$ for Er^{3+}.

$S'L'J'$	Calculated energy (cm^{-1} above $^4I_{15/2}$)[a]	$(f^{11}[^4I_{15/2}]\|U^{(\lambda)}\|f^{11}[S'L'J'])$ $\lambda=2$	$\lambda=4$	$\lambda=6$
$^2G_{9/2}$	24 893	0	0.1314	0.4809
$^4F_{3/2}$	22 701	0	0	−0.3658
$^4F_{5/2}$	22 321	0	0	−0.4712
$^4F_{7/2}$	20 717	0	−0.3816	−0.7909
$^2H_{11/2}$	19 407	0.8456	−0.6420	0.3127
$^4S_{3/2}$	18 525	0	0	0.4624
$^4F_{9/2}$	15 449	0	−0.7107	−0.6717
$^4I_{9/2}$	12 496	0	−0.4567	−0.1302
$^4I_{11/2}$	10 415	0.1856	−0.0290	−0.6259

[a] See reference 14.

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[14] B. G. Wybourne, J. Chem. Phys. **32**, 639 (1960); **34**, 279 (1961). Orthogonality checks brought to light a number of errors in the eigenfunctions tabulated in the second paper. In the $J=1/2$ part of his Table II, 0.2426 should be −0.2426; 0.9760 should be 0.9701; and 0.2178 should be 0.2426. The entry +0.0076 in the first line of the $J=7/2$ part of Table II should be −0.0076. No checks have been made in his Table III for levels other than those actually observed, but it is clear from inspection that the entries of the $J=1/2$ part are inconsistent.

[15] B. R. Judd, Proc. Roy. Soc. (London) **A250**, 562 (1959).

[16] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooton, *The 3-j and 6-j Symbols* (Technology Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1959).

TABLE III. Oscillator strengths for Nd^{3+}.

Spectral region (cm^{-1})	Upper levels involved in transition	$P\times10^6$ $NdCl_3$ Theory	 $NdCl_3$ Expt[a]	 $Nd(NO_3)_3$ Expt[a]	 $Nd(ClO_4)_3$ Theory	 $Nd(ClO_4)_3$ Expt[b]
29 600–31 250	$^4D_{7/2}$, $^2I_{13/2}$, $^2L_{17/2}$	0.46	2.36		0.40	1.7
26 750–29 600	$^4D_{3/2}$, $^2I_{11/2}$, $^4D_{5/2}$, $^4D_{1/2}$, $^2L_{15/2}$	10.13	9.52		10.16	9.8
25 750–26 750	$^2P_{3/2}$	0.04	0.05	0.05	0.03	0.02
24 250–25 750	[c]		0.03	0.03		
23 500–24 250	$^2D_{5/2}$	0.06	0.08	0.08	0.05	0.06
22 750–23 500	$^2P_{1/2}$	0.43	0.38	0.38	0.45	0.30
20 250–22 750	$^2K_{15/2}$, $^2D_{3/2}$, $^2G_{9/2}$, $^4G_{11/2}$	1.47	2.31	2.35	1.32	1.9
18 250–20 250	$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	5.48	6.58	6.78	4.92	5.8
16 250–18 250	$^2G_{7/2}$, $^4G_{5/2}$	10.6	10.5	11.7	8.38	8.3
15 250–16 250	$^2H_{11/2}$	0.20	0.39	0.39	0.17	0.14
14 250–15 250	$^4F_{9/2}$	0.78	0.83	0.83	0.65	0.51
13 000–14 250	$^4F_{7/2}$, $^4S_{3/2}$	9.84	8.88	8.78	8.17	7.6
11 900–13 000	$^4F_{5/2}$, $^2H_{9/2}$	8.48	9.22	9.17	7.32	7.7
11 000–11 900	$^4F_{3/2}$	2.02	3.02	2.93	1.96	2.3

[a] From reference 5.
[b] From reference 6.
[c] The line in this region reported by Hoogschagen has not been observed by Stewart, and no corresponding level occurs in the theoretical scheme. It is certainly spurious.

P depend only on the three parameters T_2, T_4, and T_6. It is a simple matter to take the experimental data for a given solution and choose the three parameters that give the best fit with experiment. This has been done for Hoogschagen's data for aqueous solutions of $NdCl_3$ and $ErCl_3$, and also for the analogous data of Stewart on aqueous solutions of $Nd(ClO_4)_3$. A least-squares procedure is used in all three cases, although the variation of P over almost three orders of magnitude suggests that some other scheme might be more appropriate. The results are set out in Tables III, IV, and V. Hoogschagen found that for quite concentrated solutions (about $0.1M$), the oscillator strengths for the chloride and nitrate solutions of a given rare-earth ion vary only very slightly; the nitrate data are included in Tables III and IV, but additional fitting procedures have not been carried out for them. The excellence of the agreement can be taken in at a glance by referring to Figs. 1 and 2, where the experimental and theoretical data for the solutions of $NdCl_3$ and $ErCl_3$, given in the second and third columns of Tables III and IV, are drawn out. For Nd^{3+}, even the feeble transitions $^4I_{9/2}\rightarrow {}^2P_{3/2}$, $^4I_{9/2}\rightarrow {}^2D_{5/2}$, and $^4I_{9/2}\rightarrow {}^2P_{1/2}$ are well accounted for. Only the band in the region 29 600–31 250 cm^{-1} is in significant disagreement with the theory, perhaps indicating that the assumed level assignments are incorrect.

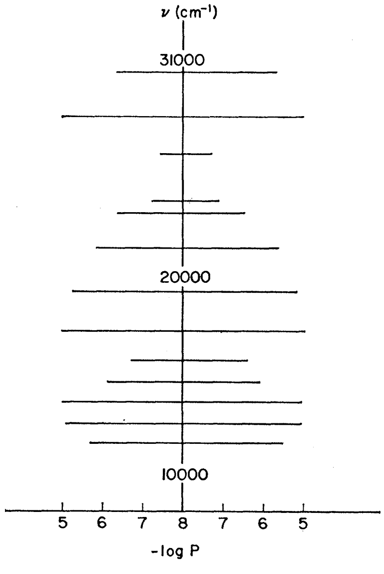

FIG. 1. A comparison between experimental and theoretical oscillator strengths of transitions in aqueous solutions of $NdCl_3$. The lengths of the horizontal lines running from the central vertical line give a measure of $-\log P$; theoretical values are given on the left, experimental values on the right. The ordinate of a horizontal line gives the approximate energy of the corresponding transition, in cm^{-1}.

In addition to the data given in Table III, Stewart has recorded the oscillator strengths of a number of weak lines in the ultraviolet range for solutions of neodymium perchlorate. These have not been included in the analysis, partly because of the difficulty of identifying the upper levels, and partly because these levels are quite close to the lower levels of $4f^25d$, thus vitiating the assumptions made in the derivation of Eq. (13).

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

Spectral region (cm^{-1})	Upper level involved in transition	$P\times10^6$ $ErCl_3$ Theory	 $ErCl_3$ Expt[a]	 $Er(NO_3)_3$ Expt[a]
23 900–25 100	$^2G_{9/2}$	0.89	0.74	0.74
21 500–23 100	$^4F_{5/2}$, $^4F_{3/2}$	1.15	1.31	1.31
20 000–21 500	$^4F_{7/2}$	2.34	2.22	2.22
18 700–20 000	$^2H_{11/2}$	2.91	2.91	3.14
17 500–18 700	$^4S_{3/2}$	0.57	0.83	0.83
14 600–16 400	$^4F_{9/2}$	2.27	2.37	2.37
12 000–12 900	$^4I_{9/2}$	0.47	0.34	0.34
9900–10 400	$^4I_{11/2}$	0.63	0.50	0.50

[a] From reference 5.

TABLE V. Observed values of the parameters T_λ (in units of 10^{-21} sec).

Solute	T_2	T_4	T_6
$NdCl_3$	8.7	17.3	35.3
$Nd(ClO_4)_3$	4.2	18.0	29.1
$ErCl_3$	3.2	5.6	4.8

VII. VARIATION OF T_2

Owing to the selection rules

$$\Delta L, \Delta J \leq 2$$

on the matrix elements of $\mathbf{U}^{(2)}$, the parameter T_2 often plays only a minor roll in determining the oscillator strengths P. Bearing in mind that P depends on the squares of the reduced matrix elements, we see from Table II that only the transition ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$ in erbium salts is at all sensitive to T_2. Curiously enough, it is only this transition that exhibits an intensity difference between the chloride and the nitrate solutions (see Table IV).

If we now turn to the data for solutions of $NdCl_3$ and $Nd(NO_3)_3$, we find very similar effects. The largest difference in intensity between the corresponding lines in the two solutions occurs for the transition to the two virtually coincident levels ${}^4G_{5/2}$ and ${}^2G_{7/2}$; and a glance at Table I reveals that of all the matrix elements

$$(f^3[{}^4I_{9/2}]\|U^{(2)}\|f^3[S'L'J']),$$

the ones for

$$[S'L'J'] \equiv [{}^4G_{5/2}]$$

and for

$$[S'L'J'] \equiv [{}^2G_{7/2}]$$

are the two largest in magnitude. Again, the second-largest difference occurs for transitions to the group of levels ${}^2K_{13/2}$, ${}^4G_{7/2}$, and ${}^4G_{9/2}$; and the matrix elements for which

$$[S'L'J'] \equiv [{}^4G_{7/2}]$$

is the third largest in magnitude. Lesser differences do not appear to be simply related to matrix elements of $\mathbf{U}^{(2)}$; but in spite of this, the evidence is sufficiently strong to leave little doubt that of the three parameters, T_2 is peculiarly sensitive to changes in the anion. Of course, Stewart's work with the perchlorate provides a third set of data to compare with the chloride and the nitrate; but it is felt that the differences between the fourth and seventh columns of Table III, and hence also between the first two rows of Table V, are to be ascribed mainly to differences in experimental technique rather than to any real change in the parameters T_λ.

VIII. ENVIRONMENT OF A RARE-EARTH ION IN SOLUTION

So far, the quantities T_λ have been treated purely as variable parameters, to be adjusted to fit experiment. To account for their values, we must construct a model for at least the immediate surroundings of a rare-earth ion. Unfortunately, little is known about the form such a model should take. That the nearest neighbors of a rare-earth ion occupy well defined positions is clear from the mere existence of fine structure in the spectra of solutions of europium salts.[17] The occurrence of an identical fine structure in aqueous solutions of europium chloride and very dilute europium nitrate indicates that in these two cases the nearest neighbors, and probably the next-nearest neighbors too, are water molecules. Examination of the lines corresponding to the transitions ${}^7F_0 \rightarrow {}^5D_1$, ${}^7F_0 \rightarrow {}^5D_2$, ${}^5D_0 \rightarrow {}^7F_1$, and ${}^5D_0 \rightarrow {}^7F_2$ reveals that all the degeneracies of the levels involved are lifted; the point symmetry at a rare-earth ion must therefore be quite low. Several lines show a marked increase of intensity when alcohol is used in place of water as a solvent, and Sayre, Miller, and Freed regarded this as demonstrating that the complex comprising a rare-earth ion and its immediate surroundings possesses a center of inversion, in contrast to the situation for alcoholic solvents.[18] Taken with the splittings of the levels, this interpretation limits the immediate point symmetry at a rare-earth ion in aqueous solution to D_{2h}. Miller subsequently proposed a model possessing this symmetry, using the criterion that the water molecules around the rare-earth ion should be arranged as in a fragment of a high-pressure ice.[19] He chose a configuration in which the eight water molecules nearest the ion lie at the vertices of two rectangles, whose planes are perpendicular and whose centers coincide with the nucleus of the rare-earth ion. This arrangement was consistent with the structure of ice III derived by McFarlan.[20]

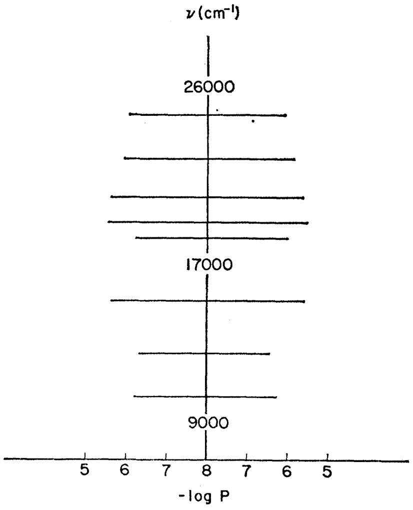

FIG. 2. A comparison between experimental and theoretical oscillator strengths of transitions in aqueous solutions of $ErCl_3$. The design of the figure is the same as that of Fig. 1.

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[17] S. Freed, Revs. Modern Phys. **14**, 105 (1942).

[18] E. V. Sayre, D. G. Miller, and S. Freed, J. Chem. Phys. **26**, 109 (1957).

[19] D. G. Miller, J. Am. Chem. Soc. **80**, 3576 (1958).

[20] R. L. McFarlan, J. Chem. Phys. **4**, 253 (1936).

A different configuration was proposed later by Brady, who carried out x-ray diffraction experiments on aqueous solutions of $ErCl_3$.[21] He found that six or possibly seven water molecules cluster around the rare-earth ion, the distance between the erbium nucleus and the nuclei of the oxygen atoms being about 2.3 Å. He interpreted the finer points of the diffraction pattern in terms of a model in which the rare-earth ion is at the center of an octahedron of water molecules. Two chlorine atoms are supposed to be on opposite sides of the octahedron such that their nuclei are coplanar with four oxygen nuclei and the erbium nucleus.

Objections can be raised to both Miller's and Brady's models. As Miller himself pointed out to the writer, a recent reexamination of the structure of ice III has shown that there are no fragments with D_{2h} symmetry[22]; also, there appears to be no position where a rare-earth ion can be placed interstitially and have six or seven oxygen atoms as close as the diffraction data demand. Until the structures of denser forms of ice become known, no further progress along the lines suggested by Miller seems possible.

Turning now to Brady's model, we note first that the superposition of an axial and an octahedral field splits a level for which $J=1$ into only two components, in disagreement with experiment. Secondly, since the splittings of levels are largely determined by the nearest neighbors of the rare-earth ion, and since an octahedral field leaves all levels for which $J=1$ degenerate, we should expect the splitting of such a level to be extremely small. However, the splittings of $^7F_1$ and $^5D_1$ in aqueous solutions of $EuCl_3$ are as large as those of the corresponding levels of $EuCl_3 \cdot 6H_2O$, a crystal where the immediate point symmetry at a europium ion is as low as C_2.

In the absence of a satisfactory model for the surroundings of a rare-earth ion, we must modify the project of calculating accurate values of the parameters T_λ. Now, the structures are known of several types of hydrated rare-earth crystals. It would, therefore, be possible to calculate T_λ in these cases, taking, say, the complex comprising the rare-earth ion and its adjacent water molecules. Such a structure may differ considerably from the actual complex existing in dilute aqueous solutions: the water molecules in solution should be slightly closer to the central ion, and their angular positions cannot be expected to correspond exactly to a crystalline arrangement. Nevertheless, the similarities are sufficiently marked to make such a calculation worthwhile, and a comparison between the theoretical and experimental values of T_λ should throw some light on the actual structure of the complex in solution.

From the various models of the rare-earth ion and its surroundings that we might construct, it seems proper to choose one that reproduces, approximately at any rate, the observed splittings of the levels $^5D_1$, $^5D_2$, $^7F_1$, and $^7F_2$ of Eu^{3+} in aqueous solutions. The striking similarity of these splittings to those of the corresponding levels of Eu^{3+} in $EuCl_3 \cdot 6H_2O$ has already been remarked. The detailed analysis of the isomorphic crystal $GdCl_3 \cdot 6H_2O$ indicates that the europium ion is surrounded by six water molecules and two chlorine ions.[23] If we remove the latter without disturbing the former, the crystal splittings of the levels should not be greatly affected; moreover, the number of water molecules is consistent with the x-ray diffraction data. The resulting complex $Eu(OH_2)_6{}^{3+}$ does not possess a center of inversion; hence we can apply the theory of Sec. IV to calculate the quantities T_λ. We stress at this point that it is not suggested that the actual configuration of water molecules in aqueous solutions is the same as that is crystals of $EuCl_3 \cdot 6H_2O$. Our model is chosen simply to provide a basis with which the experimental values of T_λ can be compared.

IX. CALCULATION OF THE PARAMETERS T_λ

The configuration of water molecules surrounding a rare-earth ion influences the parameters T_λ through the quantities B_t, defined in Eq. (18). For a configuration of charges q_i at coordinates (R_i,Θ_i,Φ_i), the crystal field parameters A_{tp} are given by

$$A_{tp}=(-1)^{p+1}\sum_i eq_iR_i^{-t-1}C_{-p}^{(t)}(\Theta_i,\Phi_i), \quad (21)$$

provided it is assumed that the electrons on the rare-earth ion spend a negligible time at radial distances greater than the smallest R_i. If each charge q_i is replaced by a dipole of strength μ, directed in the same sense towards the origin, and lying a distance R from it, the substitution

$$eq_iR_i^{-t-1}\rightarrow \mu e(t+1)R^{-t-2}$$

should be made in Eq. (21). If we use the spherical harmonic addition theorem (for example, see Edmonds[9]) we find

$$B_t=[\mu e(t+1)/(2t+1)R^{t+2}]^2\sum_{i,j}P_t(\cos\omega_{ij}), \quad (22)$$

where ω_{ij} denotes the angle between the radial vectors leading to dipoles i and j. Terms for which $i=j$ in the sum must be included.

For the proposed model of the rare-earth complex, the angles ω_{ij} can be easily calculated from the known positions of the oxygen atoms in $GdCl_3 \cdot 6H_2O$. In doing this, it is to be noted that Marezio *et al.* use an oblique coordinate scheme.[23] The only values of t of interest to us are 1, 3, 5, and 7; for all other values, the 3-j symbols in Eq. (14) vanish on putting $l=3$. We find that

$$\sum_{i,j}P_t(\cos\omega_{ij})$$

assumes the values 1.671, 14.44, and 1.726 for $t=3$, 5, and 7, respectively. The analogous sum for $t=1$ is also nonzero, implying that there is a finite electric field at

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[21] G. W. Brady, J. Chem. Phys. **33**, 1079 (1960).

[22] W. B. Kamb and S. K. Datta, Nature **187**, 140 (1960).

[23] M. Marezio, H. A. Plettinger, and W. H. Zachariasen, Acta. Cryst. **14**, 234 (1961).

the origin, and hence that the rare-earth ion is not in a position of equilibrium. This blemish in our model is not serious, however. Our aim is solely to obtain approximate values for the quantities B_t, and not to construct a perfectly self-consistent model. In any case, we could easily take advantage of the much lower power of $1/R$ associated with P_1 in Eq. (22) to pass the responsibility of ensuring that B_1 is zero to the second hydration layer of a more elaborate model, while only slightly affecting B_3, B_5, and B_7.

The next step is to estimate the dipole moment μ. For $Gd(OH_2)_6^{3+}$, the average distance R' of the six oxygen nuclei from the nucleus of the ion Gd^{3+} is 2.412 Å. Accepting the atomic radii given by Templeton and Dauben,[24] we find this distance should be increased to 2.469 Å for Nd^{3+}, and decreased to 2.355 Å for Er^{3+}. These distances are not the distances R to the centers of the water dipoles, of course. If we make the simplifying assumption that the negative charge of a water molecule in the complex coincides with the oxygen nucleus, then with a knowledge of the polarizability α and the ordinary dipole moment μ' of the water molecule, we can calculate μ by solving the equations

$$\mu=\mu'+3|e|\alpha/R^2,$$

$$\mu=4|e|x,$$

and

$$R=R'+x.$$

Taking $\mu'=1.85\times10^{-10}$ esu, and $\alpha=1.48\times10^{-24}$,[25] we obtain

$$\mu=4.72\times10^{-18}\text{ esu},$$

and

$$R=2.716\text{ Å}$$

for Nd^{3+}, and

$$\mu=4.95\times10^{-18}\text{ esu},$$

and

$$R=2.615\text{ Å}$$

for Er^{3+}. The calculation of B_3, B_5, and B_7 may now be readily completed.

The remaining factor in Eq. (17) involves $\Xi(t,\lambda)$. As can be seen from a glance at Eq. (14), the calculation of quantities of this type entails the estimation of some radial integrals and energy denominators. It is to be expected that the term in the sum of Eq. (14) for which $l'=2$ and $n'=5$ predominates; partly because $\Delta(5d)$ is the smallest of all energy denominators, as can be seen from Fig. 5 of Dieke *et al.*,[10] and partly because the smaller degree of overlap between a $4f$ eigenfunction and other orbitals of the type $n'd$ for which $n'\geq6$ should result in greatly reduced radial integrals. Let us therefore concentrate on excited configurations of the type $4f^{N-1}5d$ and, for the moment, neglect all others.

TABLE VI. Radial integrals (in atomic units).

Integral	Pr^{3+}	Nd^{3+}	Er^{3+}	Tm^{3+}
$(4f\|r\|5d)$	0.900	0.869	0.615	0.583
$(4f\|r^3\|5d)$	5.47	5.17	2.75	2.45
$(4f\|r^5\|5d)$	50.5	47.1	19.9	16.5
$(4f\|r^2\|4f)$	1.464	1.394	0.831	0.761
$(4f\|r^4\|4f)$	5.34	4.96	1.95	1.57
$(4f\|r^6\|4f)$	39.6	36.4	10.5	7.31
$(4f\|r^8\|4f)$	500	450	100	62

Dieke *et al.* have found that for Ce^{3+} the configuration $5d$ lies about 50 000 cm^{-1} above $4f$, whereas for Yb^{3+}, $4f^{12}5d$ lies about 100 000 cm^{-1} above $4f^{13}$. A linear interpolation gives the values 58 000 cm^{-1} and 92 000 cm^{-1} for Nd^{3+} and Er^{3+}, respectively. It seems reasonable to take one of these values, appropriate to the ion under investigation, for the denominator $\Delta(5d)$.

The radial integrals would be difficult to estimate were it not for the work of Rajnak, who has recently calculated $5d$ eigenfunctions for Pr^{3+} and Tm^{3+}.[26] She made the assumption that the central field that the $5d$ electron moves in is the same as that for a $4f$ electron; the latter can be obtained from a self-consistent calculation carried out by Ridley for the ground states of these two ions.[27] The radial integrals and their interpolated values are set out in the first three rows of Table VI. Strictly, the use of Eq. (10) to calculate all the radial integrals is not consistent with the assumption $r<R$; but the errors introduced in doing so are sufficiently small to be neglected.

It is now a straightforward matter to collect the various parts of the calculation together. The values of T_λ, thus obtained, are given in the third column of Table VII. Some of the entries of Table V are included so that a direct comparison between experiment and theory can be made. We see that T_4 and T_6 for Nd^{3+} agree to within a factor of 3. However, the theoretical parameter T_2 for Nd^{3+}, and all three for Er^{3+}, are smaller than the corresponding experimental values by

TABLE VII. Theoretical and selected experimental values of the parameters T_λ (in units of 10^{-21} sec).

		Calculated		Observed in chloride solutions
Ion	Parameter	$(n'l')\equiv(5d)$ only	$(n'l')\equiv(5d)$ and all $(n'g)$	(from Table V)
Nd^{3+}	T_2	0.94	3.62	8.7
	T_4	6.73	9.96	17.3
	T_6	16.4	17.2	35.3
Er^{3+}	T_2	0.05	0.28	3.2
	T_4	0.38	0.59	5.6
	T_6	0.68	0.72	4.8

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[24] D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc. **76**, 5237 (1954).

[25] D. Polder, Physica **9**, 709 (1942).

[26] K Rajnak, Lawrence Radiation Laboratory Report UCRL-10134, J Chem. Phys. (to be published).

[27] E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

an order of magnitude. It might be thought that the neglect of configurations of the type $4f^{N-1}n'd$, where $n' \geq 6$, is largely responsible for the discrepancies. However, this is unlikely.

In the first place, it can be seen from Table VI that the products

$$(4f|r^t|5d)(4f|r|5d)$$

are almost equal to the corresponding quantities

$$(4f|r^{t+1}|4f).$$

Hence, even if we used Eq. (11) to perform a closure over all configurations of the type $4f^{N-1}n'd$, $3d^94f^{N+1}$, and $4d^94f^{N+1}$ (for a fixed N), placing them as low as $4f^{N-1}5d$ in energy, our results would differ insignificantly from those already obtained.

The irrelevance of higher configurations of the type $4f^{N-1}n'd$ can be seen in another way. If $l'=2$, then T_2, T_4, and T_6 depend on B_3 and B_5 only. The linear relationship between the parameters T_λ that this implies is

$$T_2/8 = T_4/55 - T_6/3575.$$

Since we have $T_\lambda > 0$, the inequality $T_2/T_4 < 8/55$ follows. The observed ratios are much larger than 8/55, and hence they cannot be accounted for by including the effects of $4f^{N-1}6d$, $4f^{N-1}7d$, $4d^94f^{N+1}$, etc.

Configurations of the type $4f^{N-1}n'g$ remain to be considered. Their comparative proximity to the ionizing limit suggests the validity of a closure procedure over all n'; but the large radial extension of the g eigenfunctions makes it difficult to decide where the ionizing limit is for an ion in a complex. For the free ion Pr^{3+}, even the nodeless eigenfunction $\mathcal{R}(5g)$ attains its maximum value as far as 3.3 Å from the nucleus; it follows that the eigenfunctions for ions in complexes are determined by conditions beyond the first hydration layer. If the six dipoles of this layer are replaced by an equivalent uniform dipole shell, the classical electrostatic potential difference between points inside and just outside is $6\mu/R^2$, which is equivalent to approximately 100 000 cm^{-1}. Presumably, the ionizing limit of a free rare-earth ion should be reduced by at least this amount for an ion in a complex. Interpolating between Ridley's energies ϵ for Pr^{3+} and Tm^{3+},[27] and assuming the energies of the configurations $4f^{N-1}n'g$ coincide at the corrected ionizing limit, we find $\Delta(n'g)$ to be 167 000 cm^{-1} for Nd^{3+} and 207 000 cm^{-1} for Er^{3+}. Terms in Eq. (17) that involve B_7 are negligible, and the new values of $\Xi(t,\lambda)$, for which $(n'l')$ runs over $(5d)$ and all pairs of the type $(n'g)$, can be obtained from the old by multiplication by

$$1+\frac{(t+7)!(6-t)!}{(\lambda+7)!(6-\lambda)!}\,\frac{(4f|r^{t+1}|4f)}{(4f|r|5d)(4f|r^t|5d)}\,\frac{\Delta(5d)}{\Delta(n'g)}.$$

The results of the calculation are given in the fourth column of Table VII. The parameters T_λ are in all cases increased, but they are still differ by factors of 2 and 8 from the experimental values for Nd^{3+} and Er^{3+}, respectively.

X. DISCUSSION

In searching for the reasons underlying the differences between experiment and theory, we should not lose sight of the fact that, for Nd^{3+}, the agreement is perhaps better than we might reasonably have anticipated. No vibrational structure of the kind typical of crystals has been seen in aqueous solutions of $EuCl_3$,[18] suggesting that the observed absorption bands in solutions of other rare-earth ions correspond to pure electronic transitions. It is natural to conclude that the model on which the calculations of Sec. IX are based is in essence correct: this implies that, in solution, the complex comprising the rare-earth ion and the first hydration layer does not possess a center of inversion. If the opposite were true, we should have to rely on the absence of a center of inversion in the second hydration layer to give rise to pure electronic transitions. If we set the dipoles of this layer 3.7 Å from the nucleus of the rare-earth ion, then, ignoring angular effects, T_6 would be smaller than the previously calculated value by a factor of at most

$$(2.7/3.7)^{14} = 0.012,$$

even supposing the strengths of the dipoles were comparable to those of the first layer. Instead of being too small by a factor of 2, the parameter T_6 for Nd^{3+} would be too small by a factor of over 100.

It is not difficult to find possible explanations for a discrepancy of a factor of 2. As was mentioned in Sec. VIII, it is to be expected that the water molecules surrounding a rare-earth ion in solution are closer to it than those in a crystal. Owing to the dependence of T_λ on R^{-10} or R^{-14}, it would only be necessary to reduce R by 0.1 Å to account for the difference. The tendency of the negative charge on the oxygen atoms to be drawn towards the tripositive rare-earth ion will also tend to increase the parameters T_λ. Of course, errors are introduced by assuming free-ion eigenfunctions in the calculation of the radial integrals. Following the arguments of Marshall and Stuart,[28] the eigenfunctions of the electrons of the water molecules have nonvanishing amplitudes inside the orbits of the $4f$ and $5d$ electrons of the rare-earth ion; consequently, the effective nuclear charge seen by these electrons is reduced, and the orbits expand. This implies that the radial integrals of Table VI are too small. As in the two previous cases, we find that the calculated values of T_λ should be increased. The combined effect of these mechanisms might possibly depend sharply enough on the radius of the rare-earth ion to account for the greater discrepancy factor for Er^{3+}, though changes in the angular positions of the water molecules could be important.

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[28] W. Marshall and R. Stuart, Phys. Rev. **123**, 2048 (1961).

The factors of 2 and 8 by which the experimental and theoretical values of T_λ differ for Nd^{3+} and Er^{3+} can plausibly be accounted for. However, the chance seems extremely remote that an additional factor of 100 or so could be accommodated along similar lines. The analysis strongly suggests that the first hydration layer of a rare-earth ion in aqueous solution does not possess a center of inversion. This is, of course, in conflict with the models of Miller and of Brady, discussed in Sec. VIII. The deduction of Sayre *et al.* that a center of inversion exists was based on the feebleness of certain lines in the spectrum of aqueous solutions of $EuCl_3$ compared to the corresponding ones in alcoholic solutions.[18] One of these lines, corresponding to the transition ${}^7F_0 \rightarrow {}^5D_2$, has been measured by Hoogschagen, and has an oscillator strength of 9×10^{-9}.[5] Small as this number is, it is consistent with the absence of a center of inversion. To demonstrate this, we use perturbation theory and calculate the appropriate matrix elements of $\mathbf{U}^{(\lambda)}$ by means of the formula

$$\begin{aligned}([{}^7F_0]\|U^{(\lambda)}\|[{}^5D_2]) &= ({}^7F_0|\Lambda|{}^5D_0)({}^5D_0\|U^{(\lambda)}\|{}^5D_2)[E({}^7F_0)-E({}^5D_0)]^{-1}\\ &\quad+({}^7F_0\|U^{(\lambda)}\|{}^7F_2)({}^7F_2|\Lambda|{}^5D_2)[E({}^7F_2)-E({}^5D_2)]^{-1},\end{aligned}$$

where Λ is the spin-orbit interaction. The matrix elements can be evaluated by the methods of Elliott *et al.*[29] The oscillator strength P depends solely on T_2, which can be obtained by linearly interpolating the observed values for aqueous solutions of $NdCl_3$ and $ErCl_3$. The result, $P=6\times10^{-9}$, is in satisfactory agreement with experiment.

We are now left with the problem of explaining why certain lines in the spectrum of alcoholic solutions of $EuCl_3$ are anomalously strong. We shall not explore this problem in detail here; it is worth noting, however, that the transitions that are much more intense in alcoholic solvents, such as ${}^7F_0 \rightarrow {}^5D_2$ of Eu^{3+}, and what appear to be transitions of the type ${}^8S_{7/2} \rightarrow {}^6D_J$ of Pr^{3+},[30] depend solely on T_2. On the other hand, the transitions that do not undergo striking changes of intensity, such as ${}^3H_4 \rightarrow {}^3P_J$ of Pr^{3+},[30] depend on T_4 and T_6 only, at least in the lowest order of perturbation theory. Since both T_2 and T_4 depend strongly on B_3, an apparent increase of T_2 in alcoholic solutions without a corresponding increase of T_4 could occur only through the excitation of vibrational modes, which might be undetected as such if sufficiently low in frequency. Only T_2' of Eq. (19) depends on B_1'; hence, in fitting experiment to the parameters T_2, T_4 and T_6, a large value of B_1' would make itself felt through T_2 alone. It is possible that the peculiar variation of T_2 described in Sec. VI has its origin in a mechanism of this sort; but, from what is known of the relative intensities of electronic lines and their accompanying vibrational structures, it seems hard to account for a change of T_2 by an order of magnitude in this way.

The sensitivity of T_2 to the environment of a rare-earth ion can be demonstrated for other environments; Moeller and Ulrich, for example, find that in benzene solutions of neodymium and erbium chelates, one line of Nd^{3+} (at 5745 Å) and two lines of Er^{3+} (at 5228 and 3792 Å) are very much enhanced relative to aqueous solutions of the ions.[31] From Tables I and II, we see that the matrix elements of $\mathbf{U}^{(2)}$ linking the states corresponding to the first two of these lines are the only ones exceeding 0.3 in magnitude; for the third line, which lies beyond the range covered in Table II, we find

$$(f^{11}[{}^4I_{15/2}]\|U^{(2)}\|f^{11}[{}^4G_{11/2}])=0.9533.$$

Thus, within the spectral ranges considered, the three lines showing the greatest variations of intensity correspond exactly to the three largest reduced matrix elements of $\mathbf{U}^{(2)}$.

XI. CONCLUSION

Although the theory of Secs. II and III is applicable to a rare-earth ion in a crystalline environment, the absence of experimental data on the oscillator strengths of lines in rare-earth crystals has obliged us to discuss the theory in terms of solutions of rare-earth ions. The difficulty of distinguishing between the pure electronic parts of the line intensities from contributions coming from transitions in which vibrational modes are simultaneously excited is not present for the spectra of rare-earth crystals, or at least for those spectra that have been analyzed. Data for crystals, when available, will therefore permit more rigorous tests of the theory to be carried out.[32]

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[30] D. G. Miller, E. V. Sayre, and S. Freed, J. Chem. Phys. **29**, 454 (1958).

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[32] *Note added in proof.* Oscillator strengths for a number of infrared absorption lines in several rare-earth trichlorides have been recently reported by F. Varsanyi and G. H. Dieke [J. Chem. Phys. **36**, 835 (1962)]. Calculations on the relative intensities of the polarized components of these lines are being carried out by J. D. Axe (private communication).