Theory of Electric Shifts of the Optical and Magnetic Resonance Properties of Paramagnetic Ions in Crystals

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A theory of electric-field-induced energy shifts and g shifts in paramagnetic crystals is presented. This theory is based on the modern tensor-operator techniques. An "equivalent even interaction" is introduced which operates only among the states of the ground manifold. Using this method the g shift of Yb^{3+} in $CaWO_4$ tungstate is treated in detail with good results. We also consider the effects of odd fields on the observed crystal-field parameters, optical shifts in external electric fields, and field-induced transition probabilities.

I. INTRODUCTION

In a paramagnetic crystal in which the ionic sites are not inversion symmetric, an external electric field may induce energy shifts which are linear in the applied field. These shifts can be described as linear shifts of the g tensor or D tensor of the paramagnetic ground states or by additional crystal-field terms in the excited states. The linear electric shifts arise from the combined effect of the internal odd fields within the crystal and the externally applied field. It is therefore possible to use experiments on electric shifts to learn more about the influence of odd crystal fields on the properties of paramagnetic crystals and to connect these results with other odd-field effects such as oscillator strengths, Faraday rotations, etc.

In the past several years, there have been a number of interesting experiments on the effects of electric fields on crystals. These include the work of Bloembergen's group on electric shifts in quadrupole resonance,[1] the magnetoelectric effects of Folen *et al.*,[2] and the pseudo-Stark effect in the R_1 state of ruby by Kaiser *et al.*[3] Since this group of pioneering experiments there has been the important work of Ludwig, Woodbury, and Ham[4] on g and D shifts in a variety of transition elements and S ground-state rare earths, of Mims[5] on g shifts in a number of rare earths with Kramer's doublet ground states and Royce and Bloembergen,[6] Artman and Murphy,[7] and Krebs[8] on Cr^{3+} and Fe^{3+} in Al_2O_3. Quadratic effects have been studied by Weger and Feher.[9]

Until the present, no quantitative theory unifying the various electric effects has been presented. It is the purpose of this paper to take a step in this direction through the application of some tensor operator techniques. Section II is devoted to a general theory of electric shifts in paramagnetic crystals. This is based on the method developed by Judd[10] and by Ofelt[11] for calculating oscillator strengths in crystals and is primarily applicable to rare earths although it may be of some use in iron-series elements as well. In Sec. III we consider the case of Yb^{3+} in $CaWO_4$. In Sec. IV we consider a number of applications of the general theory including the effects of odd fields on the observed empirical crystal-field parameters, optical shifts, quadratic effects, and the possibility of induced electric optical transitions.

II. GENERAL THEORY

In most considerations of the rare earths we can picture the low-lying levels ($<30\,000$ cm^{-1}) to be of pure f-electron character. Even crystal-field terms, $A_{2k}{}^q Y_{2k}{}^q(\theta,\varphi)$, which are generally weak compared to the spin-orbit interaction, break the spherical symmetry and produce the crystal field splittings. If the crystal-field parameters $A_{2k}{}^q$ are treated as empirical, one can usually obtain good fits to the energy levels and g values. The Hamiltonian for this system can then be written as

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_e + V_{\text{ev}}, \\ \mathcal{H}_e &= \mathcal{H}(\text{electrostatic}) + \lambda L\cdot S, \\ V_{\text{ev}} &= \sum_{k,q} A_{2k}{}^q Y_{2k}{}^q(\theta,\varphi), \end{aligned} \tag{1}$$

where $\mathcal{H}$ is assumed to act only within the manifold of states of f^n, that is, a pure f-electron system, and V_{ev} is the even crystal-field potential.

In a crystal in which the rare-earth ion is not at a center of symmetry, the crystal field contains odd terms as well, so that states of the opposite parity must be mixed into the f^n manifold, e.g., $\psi = a\Phi(4f^n)$

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

$+b\Phi(4f^{n-1}5d)$. In fact, the d-state mixing is essential to the explanation of the observed oscillator strength, since in noninversion-symmetric crystals most optical transitions within the (nominal) f^n manifolds are found to be of electric-dipole character. Judd[10] and Ofelt[11] have developed a theory for the determination of optical-dipole moments in such crystals using tensor operator methods. By a slight generalization of this method we shall see how the linear electric shifts as well as quadratic effects in the odd fields or in the external electric fields may be analyzed.

A. The Equivalent Even Field

Consider the Hamiltonian

$$\mathcal{H}=\mathcal{H}_e+V_{\text{ev}}+V_{\text{odd}}^{(1)}+V_{\text{odd}}^{(2)}.$$

In this expression V_{ev} is the internal even field which exists independent of the odd terms (in the simplest form it is pure electrostatic in nature) and $V_{\text{odd}}^{(1)}$ is the odd crystal field while $V_{\text{odd}}^{(2)}$ is the odd potential energy arising from an external electric field. The proper functions of the even part of this crystal field are given by[12]

$$(\mathcal{H}_e+V_{\text{ev}})\psi_{\text{ev}}=E\psi_{\text{ev}}. \tag{2}$$

The odd crystal-field terms mix the ground manifold with the higher, opposite-parity manifolds. For an arbitrary odd interaction V_{odd} the two lowest order terms are given by

$$\sum_{\psi_0}\frac{\langle\psi_{\text{ev}}|V_{\text{odd}}|\psi_0\rangle\langle\psi_0|V_{\text{odd}}|\psi_{\text{ev}}'\rangle}{(E_{\text{ev}}-E_{\text{odd}})}, \tag{3}$$

and

$$\sum_{\psi_0,\psi_0'}\frac{\langle\psi_{\text{ev}}|V_{\text{odd}}|\psi_0\rangle\langle\psi_0|V_{\text{ev}}|\psi_0'\rangle\langle\psi_0'|V_{\text{odd}}|\psi_{\text{ev}}'\rangle}{(E_{\text{ev}}-E_{\text{odd}})(E_{\text{ev}}-E_{\text{odd}}')}. \tag{4}$$

Equation (3) represents a shift in the energy levels of the ground manifold without explicit consideration of the odd state mixing in the ground states, while (4) involves the splittings due to the even fields through the small odd-state composition of the ground manifold caused by the odd fields. The ratio of the magnitude of the terms in (4) relative to (3) is given by

$$\frac{\langle\psi_{\text{odd}}|V_{\text{ev}}|\psi_{\text{odd}}\rangle}{(E_{\text{ev}}-E_{\text{odd}})}.$$

This term we will see is generally negligible for all the cases we shall consider.

Now the term (3) can always be expressed as an effective Hamiltonian acting only within the states ψ_{ev} of the ground manifold, e.g., pure f states.

$$V_{\text{eqv}}=\sum_{\psi_{\text{odd}}}V_{\text{odd}}\frac{|\psi_{\text{odd}}\rangle\langle\psi_{\text{odd}}|}{E_{\text{odd}}-E_{\text{ev}}}V_{\text{odd}}, \tag{5}$$

where V_{eqv} is now an equivalent even crystal field term which operates only within the *ground manifold*. Our problem is now reduced to that of evaluating this "equivalent even operator."

Let us, without loss of generality, express V_{odd} as a sum of spherical harmonics:

$$V_{\text{odd}}=\sum A_k{}^qY_k{}^q(\theta,\varphi),\quad (k=2p+1).$$

If it is recognized that the $Y_k{}^q$ are irreducible tensor operators, the full power of modern operator techniques may be applied. From an inspection of Eq. (5) and the expression for V_{odd} we see that the evaluation of V_{eqv} is essentially the problem of determination of the tensor product of spherical harmonics:

$$Y_{2k+1}{}^qY_{2p+1}{}^r=\sum_n a_{2n}{}^{q+r}Y_{2n}{}^{q+r}.$$

In our case the problem is greatly complicated by the vast number of opposite parity states to be summed over. The problem is greatly simplified by applying arguments similar to those used in Ref. 10. We make a fairly trivial extension of the two basic equations in Ref. 10 to make them apply to the present case, the computation of V_{eqv}.

Suppose the ground configuration is (nl^N) and an opposite parity configuration is $(nl^{N-1}n'l')$, where the l are the angular momentum of single electrons (e.g., d, f electrons), the superscripts are the number of electrons of type l, and the n are the principal quantum numbers. We must further specify the states by introducing quantum number ψ_i, J_i, M_i, where J_i, M_i refer to the total angular momentum and ψ includes all the other quantum numbers necessary to describe uniquely any given state, i.e., S, L, γ. The energy separation configurations is then

$$E(n'l',\psi_i'J_i')-E(nl,\psi_jJ_j).$$

If the multiplet splittings in the primed states are very small compared to the separation of the even and odd manifolds, we can take the energy difference to be essentially independent of J'. Performing sums of J', M' one obtains for the product of spherical harmonics [for conciseness we omit the energy denominator $\Delta E(n'l'\psi',nl\psi)$ as well as the crystal-field parameters which appear in Eq. (5); they will be introduced when necessary below, in Eq. (7) and after].

$$\sum_{J',M'}\langle l^N\gamma_iS_iL_iJ_iM_i|Y_k{}^q|l^{N-1}l'\gamma'SL'J'M'\rangle\langle l^{N-1}l'\gamma'SL'J'M'|Y_p{}^r|l^N\gamma SL_jJ_jM_j\rangle$$
$$=\sum_k(-)^{p+k+L_iL_j}\frac{(2k+1)^{1/2}(2k'+1)^{1/2}}{4\pi}(2K+1)\begin{pmatrix}k & K & p\\ q & -q-r & r\end{pmatrix}\begin{Bmatrix}p & k & k\\ L_j & L' & L_i\end{Bmatrix}\langle l^N\gamma SL_iJ_iM_i|T_{q+r}{}^k|l^N\gamma'SL_jJ_jM_j\rangle.$$

The $3j$ and $6j$ symbols have been used in the above equation.

[12] In Eq. (2) it is immaterial whether a proper function ψ is even or odd so long as it is of definite parity. Here we shall always designate the ground manifold as even in spite of the fact that we will occasionally refer to f electrons.

Even though the closure procedure has produced an operator acting only with the ground manifold, it is still much too complicated to use. We will not digress further with this equation. Following Judd,[10] we extend the closure procedure by demanding that ΔE be invariant with respect to ψ' (only a fair approximation) which enables us to dispose of S' and L'. We obtain

$$\sum_{J',M',\psi'} \langle l^N\psi_i J_i M_i | Y_k{}^q | l^{N-1}(n'l')\psi' J' M'\rangle\langle l^{N-1}(n'l')\psi' J' M' | Y_p{}^r | l^N\psi_j J_j M_j\rangle$$

$$=\left[\sum -(2l+1)(2l'+1)\frac{[(2k+1)(2p+1)]^{1/2}}{4}\begin{Bmatrix} k & K & p \\ l & l' & l \end{Bmatrix}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & p & l \\ 0 & 0 & 0 \end{pmatrix}\right]$$

$$\times(2K+1)(-)^{q+r}\begin{pmatrix} k & K & p \\ q & -q-r & r \end{pmatrix}\langle i | U_K{}^Q | j\rangle$$

$$\equiv\beta(ll',kpK)(2K+1)(-)^{q-r}\begin{pmatrix} k & K & p \\ q & -q-r & r \end{pmatrix}, \tag{6}$$

where

$$\langle i | U_K{}^Q(\theta,\varphi) | j\rangle=\langle l^N\psi_i J_i M_i | Y_k{}^q | l^N\psi_j J_j M\rangle(4\pi)^{1/2}\Big/(2l+1)(2K+1)^{1/2}\begin{pmatrix} l & K & l \\ 0 & 0 & 0 \end{pmatrix},\quad Q=q+r.$$

In obtaining Eq. (6) it is assumed that the energy difference between the states i and j of the ground manifold is very small compared with the separation between the ground and opposite parity manifold. We have, therefore, that the equivalent operator [Eq. (5)] arising from the tensor product of the odd harmonics $A_p{}^q A_p{}^r Y_k{}^q(\theta,\varphi)Y_p{}^r(\theta,\varphi)$ is given by

$$V_{\text{eqv}}(ll',kqprKQ)=\gamma(ll',kqprKQ)Y_K{}^Q(\theta,\varphi)$$

$$=\frac{\alpha(ll',kpK)A_k{}^q A_p{}^r}{E(n'l')-E(nl)}(-)^{q-r}\begin{pmatrix} k & K & p \\ q & Q & r \end{pmatrix}\times Y_K{}^Q(\theta,\varphi), \tag{7}$$

where

$$\alpha(ll',kpK)=\beta(ll',kpK)[4\pi(2K+1)]^{1/2}\Big/(2l+1)\begin{pmatrix} l & K & l \\ 0 & 0 & 0 \end{pmatrix}.$$

Before completing the computation of the equivalent even operators one must sum over all the relevant k, q and p, r as well as l'. In general there are only a small number of spherical harmonics to be summed over so that this portion of the problem is not too difficult. It is also possible that only one or two of the $n'l'$ are significant (owing to the size of the radial integrals and progressively larger energy denominators) so that the over-all method is not impractical.

Some very important aspects of Eqs. (6) and (7) can be discussed immediately. First, within our approximation that Eq. (4) is negligible and that the energy separation of states within the ground manifold are far less than the even-odd energy separation, the equivalent even interaction $\gamma Y_K{}^Q$ is constant for all states of the ground manifold. In the $3d$ and $4f$ elements, for example, Eqs. (6) and (7) should hold quite well for all states within about 20 000 cm^{-1} of the lowest state. Moreover, (6) and (7) do not depend on N (the number of $4f$ or $3d$ electrons in the ion) except in the matrix element of $U_k{}^q$ or $Y_k{}^q$ within the ground manifold, that is $\alpha(ll',kpK)$ is independent of N. Of course the odd fields and/or the radial integral may vary for different rare earths, and the energy of the opposite parity states differs from ion to ion, but the basic tensor reduction is identical for all ions in a given series.

B. Effects of Odd Fields (Including Applied Fields)

Let us express V_{odd} as a sum of an odd crystal field and an externally applied electric field:

$$V_{\text{odd}}=V_c(\text{odd})+V_{\text{ap}}.$$

In the tensor product $V_{\text{odd}}|\rangle\langle|V_{\text{odd}}/\Delta E$ we get terms like

$$[V_c(\text{odd})|\rangle\langle|V_c(\text{odd})]/\Delta E, \tag{8a}$$

$$[V_c(\text{odd})|\rangle\langle|V_{\text{ap}}]/\Delta E, \tag{8b}$$

$$[V_{\text{ap}}|\rangle\langle|V_{\text{ap}}]/\Delta E. \tag{8c}$$

Each of these gives rise to terms in the equivalent Hamiltonian which may be easily interpreted. The first term is just a correction to the even crystal field arising from the odd crystal field. This may influence the energy and g values of the states in the ground manifold. The second term gives rise to the linear electric effects with which we are primarily concerned here. Finally the last term leads to an equivalent interaction quadratic in the applied field.

For each of the terms in Eq. (8), the corresponding equivalent even field may be obtained through the direct application of Eqs. (6) and (7). Let us consider

(8a) first:

$$V_{\mathrm{eqv}}^{(1)}=\sum_{\mathrm{odd}}\frac{V_c(\mathrm{odd})\,|\psi_{\mathrm{odd}}\rangle\langle\psi_{\mathrm{odd}}|\,V_c(\mathrm{odd})}{\Delta E}.$$

If we assume

$$V_c(\mathrm{odd})=\sum A_k{}^q(\theta,\varphi)Y_k{}^q(\theta,\varphi),$$

then

$$V_{\mathrm{eqv}}^{(1)}=\sum_{l'Q,}\sum_{K=|k-k'|}^{|k+k'|}\gamma(ll',kqk'q'KQ)Y_K{}^Q(\theta,\varphi).$$

This term can cause deviations of the energies and g values from those one would predict assuming the even "electrostatic" field was known.

It is important to note that $V_{\mathrm{eqv}}^{(1)}$ must be identical in form to the electrostatic even field V_{ev}, since the odd field belongs to the identity representation of the symmetry group just as the even field does. No new crystal-field terms can arise from this tensor product.

Calculation of $V_{\mathrm{eqv}}^{(1)}$ in a specific instance [using the results of Eqs. (5)–(7) to be described later] shows that it is not necessarily negligible. This fact has been recognized by Artman and Murphy.[7] In actual practice the even crystal-field parameters are always determined empirically rather than theoretically. Since $V_{\mathrm{eqv}}^{(1)}$ is identical for all states of the ground manifold, it is additive with the electrostatic part of V_{ev}. *The effective field of the sum is indistinguishable from the usual* V_{ev} in any parametrization procedure. Hence, to within the approximations leading to Eq. (6), one cannot attribute a breakdown of the parametrization method of determining g, D and crystal field splittings to the presence of odd crystal fields. It is true that the equivalent operator method is somewhat questionable for the upper states of the ground manifold (i.e., $>25\,000\ \mathrm{cm}^{-1}$) and for extremely large odd fields. However, in practical cases the levels being fit in crystals are rarely that high and the odd field rarely so large that any significant departure from the crystal-field theory could result. For the cause of any failure of the parametrization method (if indeed, such failure exists) one must look for effects of interactions other than those of the odd field. In Sec. III we will calculate $V_{\mathrm{eqv}}^{(1)}$ for Yb^{3+} in $CaWO_4$.

When an electric field is applied to a crystal which has no center of symmetry, the expression (8b) becomes important. The external field gives rise to the internal potential

$$e\mathbf{E}(i)\cdot\mathbf{r}=(\tfrac{4}{3}\pi)^{1/2}er[E_z(i)Y_1{}^0-E_x(i)(Y_1{}^1-Y_1{}^{-1})/\sqrt{2}+iE_y(i)(Y_1{}^1+Y_1{}^{-1})/\sqrt{2}].$$

The odd field is taken as $A_k{}^q(Y_k{}^q+Y_k{}^{-q})$. For a rare earth k can be 1, 3, 5, 7, while for a $3d$ element $k=1$, 3, or 5. For simplicity here we take a single k and q and also a single l'. Then for the case of $4f$ electrons with $n'l'=5d$, we have for the case of E along the z axis

$$V_{\mathrm{eqv}}^{(2)}=(\tfrac{4}{3}\pi)^{1/2}eE(i)\frac{\langle 3d|r|rf\rangle}{E(5d)-E(4f)}A_k{}^q\times[\gamma(32,kq10k-1q)Y_{k-1}{}^q(\theta,\varphi)+\gamma(32,kq10k+1q)Y_{k+1}{}^q(\theta,\varphi)].\quad(9)$$

The γ are given in Eq. (7). The generalization of Eq. (9) to include other electric field orientations should be obvious.[13]

$V_{\mathrm{eqv}}^{(2)}$ operating within the ground manifold (i.e., the pure f or d states) can now produce changes in the energies (D shifts and optical shifts) and g changes which are linear in the applied field. These effects will be discussed in the next section and thereafter.

The question of the relation between the local applied electric field at a paramagnetic ion and the external field is very complex. We shall use the correction formula given in Ref. 14, which is based on the Clausius-Mosotti theory.

There is also the question of the importance of ionic motion in determining the electric shifts. The general expression for the equivalent even field can easily be extended to include this case. However, the bulk movement giving rise to the dielectric constant need not produce much change in higher order odd terms at an impurity site, which are determined by its close neighbors. At any rate, we find that the g shifts in rare-earth tungstates can be well explained by the pure electronic effect described in Eq. (9). (Sec. III.)

There is, finally, the last term in Eq. (8), the "direct" quadratic terms $V_{\mathrm{eqv}}^{(3)}$. We must distinguish between this term and the *second-order* effects of the linear term $V_{\mathrm{eqv}}^{(2)}$, which are also quadratic in the electric field, since, as we shall see, their symmetry properties are very different. For an electric field in the x-z plane, $\theta=45°$, $\varphi=0$,

$$V_{\mathrm{eqv}}^{(3)}=(2\pi/3\sqrt{2})[e^2r^2E^2(i)/\Delta E]\gamma(ll',101121)\times[Y_2{}^1(\theta,\varphi)-Y_2{}^{-1}(\theta,\varphi)].\quad(10)$$

The expression for $V_{\mathrm{eqv}}^{(3)}$ for an arbitrary direction of electric field may be easily determined.

If the crystal has a center of symmetry, $V_{\mathrm{eqv}}^{(3)}$ will be the only electric-field terms of any importance. In the absence of inversion symmetry, the linear electric term occurs. Even when symmetry forbids a first-order linear shift, the second-order linear effects can in some cases be comparable to the direct quadratic effect. We will postpone any consideration of this to Sec. IID.

[13] It may be noted that potential terms such as $Y_1{}^0$ and $Y_1{}^{\pm1}$ have nonzero derivatives at the origin and thus one might suppose there is a nonzero force on the nucleus. However it must be kept in mind that the electron cloud will become polarized by such a potential term thus shielding the nucleus from the applied field. This polarization is described by the mixing of states of opposite parity.

[14] J. O. Artman and J. Murphy, Phys. Rev. **135**, A1622 (1964).

C. Linear D and g Shifts

In the case of rare earths we are not usually dealing with orbitally quenched states. Then we need only find the matrix elements of $\mathcal{H}_{eq}$ within some J manifold to determine the additional splitting induced by the external electric field. For example, if $q=0$, $k=1$ and we take the $J=\frac{5}{2}$ state of Ce^{3+}, which we assume to be diagonal in the internal crystal field, we obtain the following potential for $E\|c$:

$$V_{eqv}\approx\gamma Y_2^0.$$

The matrix of the interaction is

$$\begin{pmatrix} D_1+a_1 & 0 & a_4 \\ 0 & D_2+a_2 & 0 \\ a_4 & 0 & D_3+a_3 \end{pmatrix},$$

where the D are the energy of each level, which consists of a Kramers doublet, and where the a_i are the matrix elements of V_{eqv}. The a_i terms give rise to a shift of the energy levels in the applied field. These are difficult to observe since the D diagonal elements correspond to far-infrared wavelengths. In the matrix above, all the a_i are expected to be much smaller than the energy differences in zero field. Therefore the effects of a_4, the off-diagonal term, will be negligible compared to the shifts induced by the a_1, a_2, a_3. The a_4 will produce what we called the second-order linear effect which is important only if the a terms along the diagonal are zero (this occurs for certain crystal symmetries and for some electric field orientations).

The third-rank tensor for the electric D shift is well known and indeed is identical to the piezoelectric tensors. It is interesting to note that the form of this tensor can be derived quite trivially by expressing the crystal fields and the applied electric field as spherical harmonics and writing out their products. This holds true for any crystal symmetry. Hence in this method we automatically compute all the elements of the electric shift tensor.

In iron-series ions and in Eu^{2+}, Gd^{3+} the ground state is generally "orbitally quenched." Only through intermediate coupling effects of the spin-orbit interaction can the orbital degeneracy be removed. For example, within an orbitally quenched, "effective" spin-$\frac{3}{2}$ state such as Cr^{3+}

$$A_2^0Y_2^0\rightarrow D[S_z^2-\tfrac{1}{3}S(S+1)].$$

Now it is easy to see that the ratio D/A_2^0 is exactly the same as the ratio between γ and D' in $\mathcal{H}_{eq}\simeq\gamma Y_2^0\rightarrow D'[S_z^2-\frac{1}{3}S(S+1)]$; the "quenching" of the crystal field is the same for all spherical harmonics of the same order. To be explicit, if $m=D/A_2^0$ then

$$\gamma Y_2^Q\rightarrow m\gamma f(S_Q),$$

where $f(S_Q)$ is the appropriate Stevens harmonic. The same rule of course holds true when considering higher order spherical harmonics and their associated Stevens harmonics.

The D-shift tensor (second-order in S) may be written R_{ijk} where $\mathcal{H}_{eff}$ is (axial crystals)

$$\mathcal{H}_{eff}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+D[S_E^2-\tfrac{1}{3}S(S+1)]+\sum_{ijk}R_{ijk}E_iS_jS_k. \quad (11)$$

It is clear that the E_iR_{ijk} are just equal to the quenched form of the spherical harmonic products discussed above. It is quite trivial to write out the explicit form for any particular one of them (we are still dealing, however, with the pure electronic polarizability case).

A number of interesting observations can be made now which do not require a detailed discussion. First it is easy to see that any state which is not orbitally quenched (e.g., certain ions in cubic symmetry or some non-Kramers systems in axial symmetry), will be very sensitive to an applied electric field. In this case the R-tensor component will be expected to be large compared to a quenched system. If the normal D tensor is large, the R tensor may be expected to be *correspondingly large* since the quenching affects both operators in an identical way. If D is nonzero for the state under consideration, then unless V_{eqv} *belongs to the identity representation of the site symmetry group* (i.e., $Y_1^qV_{odd}$ produces a term identical to the even crystal field), all the matrix elements of V_{eqv} will be *off-diagonal.* This means that since $V_{eqv}/D\ll1$, all energy shifts will be $\approx(V_{eqv})^2/D$.

Degenerate states in systems with an even number of electrons would be expected to have a large shift if the electric field produces an equivalent field with off-diagonal matrix elements [e.g., $a'(S_x^2-S_Y^2)$, etc.]. $a'S_z^2$ would remove part of the degeneracy of the three-dimensional representations in cubic symmetry, again leading to exceptionally large shifts. The four-dimensional Γ_8 states (cubic symmetry, odd number of electrons) may also be split by an external electric field.

g Shifts

It is also possible to obtain a g shift which is linear in the applied electric field. In most cases of interest the g shift is only an apparent change of the effective g which occurs when we mix higher states into an isolated Kramers doublet. Consider a case such as Ce^{3+} with a $J=\frac{5}{2}$ ground state. In a paramagnetic-resonance experiment, only one doublet will generally be observable since the crystal-field splittings are usually $\gg kT$. Although the equivalent Hamiltonian V_{eqv} never couples Kramers conjugate states, it can mix the lowest doublet with the other states of the $J=\frac{5}{2}$ manifold. It is this additional mixing induced by the electric field which leads to an effective change in the g of the spin-Hamiltonian. This type of effect can occur in all rare earths with a Kramer's doublet ground state as well as in cases

where the ground doublet arises from a state which is not quenched in a pure cubic field. Ti^{3+}, "strong-field" Fe^{3+}, and their isoelectronic counterparts are a few of the possibilities for very large electric g shifts. The electric field *does not change the gyromagnetic ratio* but instead changes the *state composition* within the manifold in which $(L+2S)$ operates. In the spin-Hamiltonian formalism, this is expressed as a change in the g of an effective spin-$\frac{1}{2}$ state.

The method for dealing with the g shift in unquenched states is to set up the matrix for the *entire J manifold* (or its equivalent for $3d$ cases like Ti^{3+}) of

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{J}+V_{\mathrm{eqv}}.$$

One must then diagonalize the resulting matrix and determine the energy (hence the effective g shift) for various values of H and E.

In the principal-axis system of the unperturbed crystal we can write the previous equation in a form applying only to the lowest doublet (to first order in V_{eqv}) as

$$\begin{aligned}\mathcal{H}&=\beta\sum_i g_iH_iJ_i+\beta\sum_i H_i\times(g_iJ_iV_{\mathrm{eqv}})\\&=\beta g_iH_iJ_i+E_kT_{kij}(g_jJ_jH_i+g_iJ_iH_j).\end{aligned}\tag{12}$$

In this expression T_{kij} is a constant of proportionality arising from the tensor product of J_i and V_{eqv}. From a practical point of view the T_{kij} in the spin-Hamiltonian is most conveniently calculated by directly diagonalizing the full matrix expression of the complete manifold. This question will be considered more explicitly when we discuss the g shift in Yb^{3+} later in this paper.

D. Direct Quadratic Effect

We saw in Sec. IIC that the second-order linear terms are proportional to $[V_{\mathrm{eqv}}^{(2)}]^2/D$ while the energy shift due to the direct quadratic term is proportional to $V_{\mathrm{eqv}}^{(3)}$. Using Eqs. (8) and (7) but ignoring coupling coefficients, the ratio of the second-order to direct quadratic terms is very roughly

$$V_c^2(\mathrm{odd})/(\Delta E\times D),$$

where ΔE is the energy separation of even and odd manifolds. For $V_c(\mathrm{odd})$ large ($\sim$5000 cm^{-1}) and D small ($<$300 cm^{-1}) we see that the ratio is near unity. However, taking the exact expressions including all the coupling coefficients we find that the direct effect will generally be dominant for $\mathbf{E}\|c$ while the second-order linear effect dominates for $\mathbf{E}\|x$. In calculating the direct quadratic effect it is interesting to note that Eq. (10) does not involve the crystal symmetry at all. By taking the tensor product of the electric-field terms we can derive the fourth-rank direct quadratic tensor in a straightforward way. The following analysis is intimately connected with our closure method since it is this procedure which eliminates the dependence of the tensor on the explicit crystal structure. As a result there is a vast decrease in the number of independent components in the quadratic electric tensor. Taking all possible products of first-rank spherical tensors [each may be taken as $z\rightarrow Y_1^0$, $-y\rightarrow(Y_1^1+Y_1^{-1})/\sqrt{2}i$, $-x\rightarrow(Y_1^1-Y_1^{-1})/\sqrt{2}$] and interpreting the resulting second-rank tensor in usual way we obtain components *xxzz, yyzz, zzzz, xxxx, xxyy, yyxx, yyyy, xyxy, xzxz, yzyz.*

These are not independent since they are all related by $3j$ symbols. In terms of the internal electric field, we can express the quadratic electric tensor as

$$\mathcal{H}_Q=A_{ijkl}'E_iE_jx_kx_l/r^2.$$

In this form (which is equivalent to using the Y_2^Q effective operator) A_{ijkl}' can be determined directly from (8c) and (7). In spin-Hamiltonian form

$$\mathcal{H}_Q=B_{ijkl}'E_iE_jS_kS_l.$$

In either form we find the following relation among all the tensor components B_{ijkl} or A_{ijkl}':

$$\begin{aligned}&xxzz=yyzz=\tfrac{1}{2}zzzz,\\&xyxy=(\sqrt{\tfrac{3}{2}})zzzz,\\&xxxx=-yyxx=-xxyy=yyyy=(\sqrt{\tfrac{3}{2}})zzzz,\\&xzxz=yzyz=(1/2\sqrt{3})zzzz.\end{aligned}\tag{13}$$

Let us define a second-rank tensor ϵ which relates the internal to the external fields. Therefore $E_i=\epsilon_{ip}E_p^e$, where E_p^e is the applied electric field. ϵ is of course related to the polarizibility tensor. If the principal axes of ϵ are the same as that of the paramagnetic system, we can write $\mathcal{H}$ in this system as

$$\mathcal{H}=B_{ijkl}E_i^eE_j^eS_kS_l,\tag{14a}$$

$$B_{ijkl}=\epsilon_{ii}\epsilon_{jj}B_{ijkl}'.\tag{14b}$$

There are now as many independent components of B as there are independent ϵ.

In crystals which do not have unique x and y axes, a complication arises. For in such crystals there is no reason to suppose that the principal axes of the polarizability will coincide with the principal axes of D or of g. In an axial crystal this is unimportant since the projection of the α or D ellipsoids in the x, y plane are circles. For lower symmetries which are neither dihedral nor contain vertical reflection plane which specify x and y directions, ϵ_{ij} cannot be used in diagonal form. In this case

$$B_{ijkl}=\sum_{p,q}\epsilon_{ip}\epsilon_{jq}B_{pqkl}'.\tag{14c}$$

Of course if we do not use the closure procedure these simple answers do not occur and the inherent crystal symmetry arises in B' as well as in B. For the general case the terms in B' are not all related and several additional terms may occur. The tensor will become identical in form to the piezoresistive tensor. A careful

check of the quadratic electric effect could provide a good check of the validity of the closure method.

E. Relation of the Various Odd-Field Effects

We have seen that the linear D shift and g shift depend on the size of the odd crystal fields. This is also true of the oscillator strength of the optical transitions. Indeed, the equivalent fields which cause the optical transitions are derived in exactly the same way as those resulting from the static electric field. That is $erE_0e^{i\omega t}V_{\text{odd}} = \gamma_k{}^Q Y_k{}^Q(\theta,\varphi)e^{i\omega t}$ where the methods of IIA are used for the computation of $\gamma_k{}^Q$. Ordinary time-dependent perturbation theory is then applied using the above equivalent fields. Obviously, the oscillator strength depends on $(\gamma_k{}^Q)^2$ and hence on $V_{\text{odd}}{}^2$. The linear g and D shifts depend linearly on $\gamma_k{}^Q$ and V_{odd}. The latter experiments may therefore be expected to be more sensitive to the effect of the odd fields. Kiss and Weakliem, Ref. 15, have used a relation between f numbers and electric energy shifts to analyze their observation (the first in rare earths) of optical shifts. In this paper, I have taken a slightly different approach in that I always assume the rare-earth wave functions are exactly known. In this way the spin-orbit interaction does not enter into the expressions given for the electric effects. This is partly based on an earlier paper (Ref. 16) where I predicted large optical shifts in rare earths.

The static electric field experiments may depend on the ionic polarizability as well as on the electronic effect. If the former dominates, the values for the odd crystal fields computed from the electric effect would be in error. It should be possible to sort the ionic and electronic contributions by comparing the odd fields determined from the optical f numbers (where the ionic effect should be negligible) and the odd fields required by the g, D-shift experiments. We shall do just this for the case of $CaWO_4$ in the next section.

III. g SHIFT IN $CaWO_4$

Recently Mims has reported an extensive set of experiments on g shifts in four rare-earth ions in $CaWO_4$. Because of its relative simplicity and the fact that the optical spectrum of the Yb^{3+} is known in $CaWO_4$, we will concentrate on Yb^{3+} and to some extent on Ce^{3+}. In $CaWO_4$, there are four terms in the electric tensor. In usual notation for a third-rank tensor (first index represents electric-field direction, $x\to 1$, $y\to 2$, $z\to 3$) these are $T_{131}=T_{232}$, $T_{132}=-T_{231}$, $T_{311}=-T_{322}$ and T_{312} with the added provision that the tensor is symmetric in the last two indices. The Hamiltonian is best described by the expression

$$\begin{aligned}\mathcal{H}&=V_{\text{eqv}}+g_i\beta H_iJ_i\,,\\ V_{\text{eqv}}&=\sum A_k{}^2[Y_k{}^2(\theta,\varphi)+Y_k{}^{-2}(\theta,\varphi)]eErY_1{}^q(\theta,\varphi)\\ &\quad+B_k{}^2[Y_k{}^2(\theta,\varphi)-Y_k{}^{-2}(\theta,\varphi)]eErY_1{}^q(\theta,\varphi)\,,\end{aligned}\tag{15}$$

where the products in V_{eqv} are evaluated through the use of Eqs. (6) and (7). For our cases, the lowest state is an isolated Kramers doublet. The effective Hamiltonian is

$$\mathcal{H}=\beta g_iH_iJ_i+\beta E_kT_{kij}(g_jH_iJ_j+g_iH_jJ_i)\,.$$

Mims[5] has shown that the g shift of the lowest Kramers doublet can best be described by the tensor representing the quantity δg^2:

$$\begin{aligned}\delta g^2&=\hat{r}\cdot\delta\hat{A}\cdot\hat{r}\\ &=\sum_k E_k[B_{k11}l^2+B_{k22}m^2+B_{k33}n^2\\ &\qquad+2B_{k23}mn+2B_{k13}lm+2B_{k12}ln]\,,\end{aligned}\tag{16}$$

where l, m, n are direction cosines,

$$B_{kij}=(1/\beta)(g_{iq}T_{kqj}+T_{kiq}g_{qj})\,.$$

Only in this form does the expression for the g shifts have a simple geometric form. For example, for E along z, H along the x direction,

$$\begin{aligned}\delta g^2&=E_3(B_{311}{}^2+B_{312}{}^2)^{1/2}\sin(2\varphi-2\varphi_3)\,,\\ \tan 2\varphi_3&=-B_{31}/B_{36}\,,\end{aligned}\tag{17}$$

and in the principal axis system (axial case)

$$\begin{aligned}B_{311}&=(2/\beta)g_1T_{311}\,,\\ B_{312}&=(1/\beta)(g_1T_{312}+g_2T_{312})=(2/\beta)(g_1T_{312})\,.\end{aligned}$$

For E along a, H at an angle θ, φ relative to the a, b, c set of axes,

$$\begin{aligned}\delta g^2&=E_x(B_{123}{}^2+B_{113}{}^2)^{1/2}\sin 2\theta\sin(\varphi-\varphi_1)\,,\\ \tan\varphi_1&=-B_{113}/B_{123}\,,\\ B_{113}&=(1/\beta)(g_\perp+g_\parallel)T_{113}\,,\\ B_{123}&=(1/\beta)(g_\perp+g_\parallel)T_{123}\,.\end{aligned}$$

In S_4 symmetry, the g tensor has arbitrary orientation in the x-y plane. This, of course, is of no consequence in usual resonance experiments since the axial symmetry requires $g_1=g_2=g_x=g_y$ for any mutually orthogonal directions in the a-b plane. In the electric g-shift case, this is not the case since the changes in the g tensor will be relative to directions of the principal axes. Even for identical crystal fields the principal directions in the a-b plane will vary from ion to ion (i.e., will differ for Ce^{3+}, Nd^{3+}, etc.) in an arbitrary, though in principle calculable, manner.

The effect of this is that given the orientation of the principal axes, the orientation of the effective field (and the odd field) is arbitrary relative to this set of axes. For this reason in an S_4 symmetry, the zeros in the g-shift

[15] Z. J. Kiss and H. A. Weakliem, Phys. Rev. Letters **15**, 457 (1965).

[16] A. Kiel, in *Proceedings of the International Conference on Magnetism* (The Institute of Physics and the Physical Society, London, 1965), p. 465.

expression may lie almost anywhere in the a-b plane and will vary from ion to ion almost arbitrarily. In addition, φ_1 in general will not equal φ_3 [see Eq. (17)] and the difference between them will vary from ion to ion. We will give some examples below.

First we return to the equivalent field method and we thus evaluate the actual tensor elements in a simplified case.

Pappalardo[17] has investigated the optical spectra of Yb^{3+} in $CaWO_4$. From his data and some additional calculations, we find the energy and wave functions for the $^2F_{7/2}$ state given in Table I. In that paper, the optical oscillator strengths are also given for the several transitions $[(1\text{–}8)\times10^{-5}]$. The oscillator strength is given by the expression

$$f_{ij}=\frac{8\pi^2 m\nu}{h}\langle r^2\rangle_{\mathrm{av}}\frac{4\pi}{3}\left|\frac{\langle i|V_{\mathrm{odd}}Y_1{}^q|j\rangle}{\Delta E}\right|^2. \tag{18}$$

For Yb^{3+} it is a moderately good assumption that the $A_3{}^2Y_3{}^2$ term in the crystal-field expansion dominates since the $|\bar{r}|^n$ terms are particularly small in this case. Using the strongest transition of Ref. 17 and Eqs. (18) and (7) gives

$$A_3{}^2\simeq 7500\ \mathrm{cm}^{-1}.$$

We can now use these parameters to calculate the effective-field terms.[18]

In units of inverse cm per 1000 V/cm we obtain for Yb^{3+} in $CaWO_4$ the following equivalent even fields (we discuss the choice of the imaginary form below):

$$\begin{aligned}&\gamma_2{}^2(Y_2{}^2-Y_2{}^{-2})=-0.00033(Y_2{}^2-Y_2{}^{-2}),\\ &\qquad\qquad\gamma_4{}^2=-0.00055,\\ &\gamma_2{}^1(Y_2{}^1+Y_2{}^{-1})=0.00033(Y_2{}^1-Y_2{}^{-1}),\\ &\qquad\qquad\gamma_4{}^1=0.0021,\\ &\gamma_4{}^3=-0.00028\ \mathrm{cm}^{-1}.\end{aligned} \tag{19}$$

The electric g shift depends intimately on the composition and energy of all states in the $J=\frac{7}{2}$ manifold. Specifically, we must diagonalize the term $V_{\mathrm{eq}}+\beta H(L+2S)$ within this ground manifold. Clearly the $J=\frac{5}{2}$ manifold centered about an energy of 10 000 cm^{-1} will give a negligible contribution to this effect.

TABLE I. Proper functions and energy of Kramer pairs in $J=\frac{7}{2}$ manifold; Yb^{3+} in $CaWO_4$ ($H=0$).

Function	Energy (cm^{-1})
$\psi_1(\pm)=-0.70\lvert\frac{7}{2}\mp\frac{5}{2}\rangle+0.713\lvert\frac{7}{2},\pm\frac{3}{2}\rangle$	0
$\psi_2(\pm)=0.392\lvert\frac{7}{2},\mp\frac{1}{2}\rangle+0.92\lvert\frac{7}{2},\pm\frac{7}{2}\rangle$	220
$\psi_3(\pm)=0.713\lvert\frac{7}{2},\mp\frac{5}{2}\rangle+0.70\lvert\frac{7}{2},\pm\frac{3}{2}\rangle$	350
$\psi_4(\pm)=0.92\lvert\frac{7}{2},\mp\frac{1}{2}\rangle-0.392\lvert\frac{7}{2},\pm\frac{7}{2}\rangle$	600

[17] R. Pappalardo and D. L. Wood, J. Mol. Spectry. **10**, 81 (1963).

[18] It is clear that we could have used the f numbers to calculate the effective field directly. However, we will use the $A_3{}^2$ in another application later so we have chosen to find it directly.

The calculation of g shifts requires the manipulation of an 8×8 matrix for Yb^{3+} (and up to 16×16 for Er^{3+}). Instead the entire problem was programmed for a computer by the author. Given the state functions and energies of the ground manifold and the equivalent fields, all components of the g-shift tensor could be computed. Complex wave functions and fields could be handled by this program but required doubling the dimensions of all matrices. Subsidiary programs were written to find the wave functions to be used in the main computation. The same programs can be used for determining D shifts, optical energy shifts, oscillator strengths, and quadratic effects in a fairly routine manner.

Two points should be mentioned before presenting the results of these calculations. First, we have assumed up till now that the electric field was the internal field. In $CaWO_4$, the "average" dielectric (it is slightly anisotropic in this case) constant is 10. We use the correction formula derived by Artman and Murphy[14] to relate the external to internal fields in $CaWO_4$.[19] We present all results in terms of the measured laboratory field (V/cm). The second point involves the fact that we have chosen the imaginary forms for the equivalent fields which implies that the $A_3{}^2$ odd field is also imaginary. We have done this arbitrarily to obtain approximate agreement with the orientation of the tensor observed by Mims.

We obtain finally for the δg^2 tensor

$$\begin{aligned}&(B_{123}{}^2+B_{123}{}^2)^{1/2}=171\times10^{-9}/(\mathrm{V/cm}),\\ &(B_{311}{}^2+B_{312}{}^2)^{1/2}=71\times10^{-9}/\mathrm{V/cm}),\\ &\qquad\varphi_1=90^\circ,\quad\varphi_2=45^\circ.\end{aligned}$$

This compares with Mims' results

$$\begin{aligned}&(B_{123}{}^2+B_{113}{}^2)^{1/2}=212\times10^{-9}/(\mathrm{V/cm}),\\ &(B_{311}{}^2+B_{312}{}^2)^{1/2}=81\times10^{-9}/(\mathrm{V/cm}),\\ &\qquad\varphi_1=106^\circ,\quad\varphi_2=47^\circ.\end{aligned}$$

These results, which obtained only for pure real wave functions and the mentioned assignment of the odd field, give no "twist" of g tensor for $\mathbf{E}\|c$ and $\mathbf{E}\perp c$ (i.e., $2\varphi_2=\varphi_1=90^\circ$). This corresponds to a case of pseudo D_{2d} symmetry, the g tensor ($E=0$) having been rotated by 45° from its position in real D_{2d} symmetry.

By rotating V_{odd} by another 15° [that is if we set the ratio of the real component of $V_c(\mathrm{odd})$ to the imaginary part equal to tan 15°] we get

$$\varphi_1=103.7^\circ,\quad\varphi_2=50.1^\circ.$$

The over-all agreement for this case seems quite acceptable and strongly indicates that the electronic effect is sufficient to account for the observed g shifts without recourse to ionic effects. In a later paper we will consider the cases of Nd^{3+} and Er^{3+} and Mn^{3+} in some

[19] Using the correction formula given in Ref. 14, which includes the Lorentz correction and some additional corrections, we find that the internal field is 3.5 times the applied field.

detail and go into greater detail in the angular dependence.

The Yb^{3+} results can be used to predict the approximate size of the g shift in Ce^{3+}. Unfortunately, in this case, we do not have any optical data to guide us. The ground state in Ce^{3+} has a form $0.895|\frac{5}{2},\frac{5}{2}\rangle+0.44|\frac{5}{2},-\frac{3}{2}\rangle$. $g_{\parallel}=2.93$, $g_{\perp}=1.48$. Extrapolating from Yb^{3+} data, the $\mu=\frac{1}{2}$ state should be at about 180 cm^{-1} with the other $\mu=\frac{3}{2}$ state perhaps another 200 cm^{-1} above $\mu=\frac{1}{2}$. $\langle\bar{r}\rangle$ in Ce is about 1 atomic unit (au) compared with some 0.55 au in Yb^{3+}, and $\Delta(f-d)$ is about 45 000 cm^{-1} compared with 90 000 cm^{-1}. If we assume that A_3^2 is the same for both, the Ce^{3+} effective field should be about four times as large as for Yb^{3+}. Actually A_3^2 should be about four times as great in Ce since $\langle f|r^3|d\rangle$ is larger, but this large a variation in the crystal-field components is not observed in the even field components, nor in the oscillator strength analysis.[10] We therefore assume A_3^2 in Ce is 25% greater so that overall the effective fields in Ce will be five times as great.

We get then

$$(B_{123}^2+B_{113}^2)^{1/2}=171\times10^{-9}\ (\mathrm{V/cm}),$$
$$(B_{311}^2+B_{312}^2)^{1/2}\simeq60\times10^{-9}/(\mathrm{V/cm}).$$

This compares with values of 170×10^{-9} and 87×10^{-9} obtained in experiment.

IV. MISCELLANEOUS COMPUTATIONS

A. Optical Energy Shifts

Using the equivalent field values for Yb^{3+} given in Eq. (19), we have calculated the energy shifts of all the $4f$ states of Yb^{3+}. For an external field of 100 000 V/cm and effective dielectric constant of 3.5, we tabulate the results in Table II. The states of the $J=\frac{7}{2}$ manifold were given in Table I.

The largest possible optical shift for this case is about 3.1×10^{-3} cm^{-1} per 100 000 V/cm. If the electric field is taken along the c axis, the shifts are all about $\frac{1}{10}$ of those obtained for $\mathbf{E}\|x$. In view of the rather large linewidth observed in the tungstates these shifts would be extremely difficult to observe. The reason for the smallness of these shifts in comparison with the very large g shifts obtained is due to the fact, mentioned earlier, that in S_4 symmetry the effective field cannot have any diagonal elements [see Eq. (19)]. This property occurs whenever there is a horizontal reflection plane. For other rare-earth ions in $CaWO_4$, the optical shifts will be as small or smaller. These shifts are examples of the second-order linear effect. They will be compared to the direct quadratic effect in IVC.

TABLE II. Energy shift in effective field (100 000 V/cm, $\epsilon_{\mathrm{eff}}=3.5$).

Level	J	Unperturbed energy (cm^{-1})	Energy shift (cm^{-1}) $E\|x$	Energy shift $E\|c$
1	$\frac{7}{2}$	0	-1.5×10^{-3}	-1.4×10^{-4}
2	$\frac{7}{2}$	220	3.7×10^{-4}	-3.8×10^{-5}
3	$\frac{7}{2}$	350	3.8×10^{-4}	8.0×10^{-6}
4	$\frac{7}{2}$	600	7.6×10^{-4}	1.6×10^{-4}
5	$\frac{5}{2}$	10 000	1.6×10^{-3}	2.2×10^{-4}
6	$\frac{5}{2}$	10 000	-1.3×10^{-3}	-1.7×10^{-4}
7	$\frac{5}{2}$	10 400	-2.9×10^{-4}	-5.6×10^{-5}

If we consider a case such as that for garnets where an odd field of the form Y_3^0 occurs, one finds that for $\mathbf{E}\|(c$ axis), the effective field has a form identical to that of the even crystal field. For about the same magnitude of the crystal fields, one obtains optical shifts ranging up to 1 cm^{-1} for Yb^{3+} for very large external fields ($\sim$100 kV/cm) along the c axis. A shift of this magnitude should be easily observable. In other rare earths such as Nd^{3+} or Sm^{3+}, the shifts generally will be somewhat smaller than this but it should be quite large in Pr^{3+}.

It should be noted that it is not necessary for the f number of a given pair of levels to be large for a large electric shift to occur (and vice versa as in Yb^{3+} in $CaWO_4$). The electric shift with $\mathbf{E}\|c$ will arise chiefly from the *diagonal terms* in V_{eff} and whatever off-diagonal contribution may arise will come from *within the J manifolds* of the individual states. The oscillator strength arises from the matrix element of the oscillating effective field between the two states in question. It is therefore possible to have very small oscillator strength because of the smallness of the matrix element and still have large shifts. The opposite case is somewhat less likely, except when σ_h occurs, since two states must each have very small or nearly equal diagonal elements.

B. Effect of Odd-Fields on the Empirical Crystal Field

In Sec. IIA we interpreted Eq. (8a) as an effective Hamiltonian which is a correction to the even crystal field. Using the value of A_3^2 determined in Sec. IIIA, we can now calculate the size of this correction term to the even field. Using Eq. (7) we obtain

$$\gamma_4^0Y_4^0=\gamma(32\,323-32\,240)Y_4^0=-\frac{1}{3(\sqrt{\pi})}\frac{(A_3^2)^2}{\Delta}Y_4^0,$$

$$\gamma_6^0Y_6^0=\gamma(32\,323-32\,260)Y_6^0=\frac{5(\sqrt{13})}{16\times21(\sqrt{\pi})}\frac{(A_3^2)^2}{\Delta}Y_6^0.$$

For our value of $A_3^2=7500$ cm^{-1}, $\Delta=90\,000$ cm^{-1} we find the coefficient of Y_4^0 to be -110 cm^{-1} and that of Y_6^0 to be -18.4 cm^{-1}. In addition $\gamma_4^4=-(10/7)^{1/2}\gamma_4^0=+132$ cm^{-1} and $\gamma_6^4=(14)^{1/2}\gamma_6^0=-69$ cm^{-1}. Some of these effective field parameters, especially γ_4^0 and γ_4^4, form a substantial part of the observed empirical even crystal field parameter ($A_4^0\simeq700$ cm^{-1}, $A_4^4\simeq800$ cm^{-1}). In cerium, where the $5d$ states are much closer and the A_3^2 terms probably are considerably larger, the contribution of the effective field may be almost comparable to the "electrostatic contribution." As discussed in Sec. IIC, this does not lead to a breakdown in the para-

metrization procedure since the effective field and "electrostatic" even fields are simply additive so long as the effective field may be taken as constant over the $4f$ manifold. However, in some of the upper states of the $4f$ manifold ($E>30\,000$ cm^{-1}), some of the closure approximations may be invalid which could then lead to breakdown of the parametrization.

C. Magnitude of the Quadratic Effect

We will now calculate the size of the quadratic electric interaction. Using Eqs. (7) and (8c)

$$\begin{aligned}\gamma_2{}^0Y_2{}^0&=\gamma(32\,101020)Y_2{}^0\\&=\frac{(eE\bar{r})^2}{\Delta}20(2\pi)^{1/2}(-1)^{q+q'}\begin{pmatrix}2&1&1\\0&0&0\end{pmatrix}\begin{Bmatrix}1&2&1\\3&2&3\end{Bmatrix}\\&\qquad\times\left[\begin{pmatrix}3&2&1\\0&0&0\end{pmatrix}^2\Big/\begin{pmatrix}3&3&2\\0&0&0\end{pmatrix}\right]Y_2{}^0(\theta,\varphi)\\&=\frac{(eE\bar{r})^2}{\Delta}\times1.35Y_2{}^0.\end{aligned}$$

We obtain finally ($\bar{r}=0.55$ au, $\Delta=90\,000$ cm^{-1})

$$(\gamma_2{}^0/\epsilon_{\text{eff}}{}^2)=6\times10^{-15}\ (\text{cm}^{-1}\text{ per }(\text{V/cm})^2)E^2Y_2{}^0(\theta,\varphi).$$

For $\epsilon_{\text{eff}}=5$, $E=30\,000$ V/cm, the quadratic potential is about 1.3×10^{-4} cm^{-1}. This compares with the linear tungstate potentials for this field ranging between 0.04 cm^{-1} and 0.3 cm^{-1}. Thus at this fairly high field, the quadratic potential effects are expected to be $\sim1/100$ of the linear effects. The procedure for determining the g and D shifts, once the quadratic potential is known, is identical to that for the linear case.

The quadratic shifts, although small, are still within the range of possible observation. Unfortunately, the observation of relative shifts of inversion image sites as used by Mims in his spin-echo technique is not applicable to this case. It might be noted that the quadratic optical shifts can be larger than optical shifts owing to the linear (but off-diagonal) terms in crystals with horizontal reflection planes.

If we express $Y_2{}^0$ as $a(S_z{}^2-\frac{1}{3}S^2)$, then from IIC,

$$\begin{aligned}B_{zzzz}'&=6\times10^{-15}\times a\ \text{cm}^{-1}\text{ per }(\text{V/cm})^2\\&=B_{zzzz}/\epsilon_{\text{eff}}{}^2.\end{aligned}$$

The other terms in the quadratic electric tensor may be derived simply by using the relations given in Sec. IIC. In rare earths as previously it is more convenient to leave the effective potential in spherical-harmonic form rather than to convert to spin-Hamiltonian form.

D. Induced Electric Transitions

Let us consider the possibility of inducing electric transitions by applying an external electric field. This is a possible method for inducing electric transitions in centrosymmetric crystals or for cases where selection rules forbid electric-dipole transitions. In this case we want the effective interaction of [see Eq. (7)]

$$\begin{aligned}(\tfrac{4}{3}\pi)^{1/2}(Y_1{}^qe^{i\omega t})(eE\bar{r}Y_1{}^{q'})&\\=e^{i\omega t}(eE\bar{r}/\Delta)\eta(32,1q1q'2Q)Y_2{}^Q,&\end{aligned}$$

$$\eta=(-)^{q-q'}\begin{pmatrix}2&1&1\\-Q&q&q'\end{pmatrix}\alpha(32\,112).$$

The oscillator strength therefore becomes

$$f=\frac{8\pi^2m\nu\bar{r}^2}{h}\frac{4\pi}{3}\left(\frac{eE\bar{r}\eta}{\Delta}\right)^2|\langle i|Y_2{}^Q|j\rangle|^2.$$

In fields of 100 000 V/cm and for the most favorable cases, we find that the induced f due to an external electric field is less than 5×10^{-10} and usually very much less than this in cases like Nd^{3+}, Sm^{3+}. Hence we conclude that the application of external field is not a practical method for enhancing the transition probability.

V. DISCUSSION

We have seen that if an effective-field approach is taken, virtually all types of electric shifts may be described within a single, consistent formalism. Furthermore, it is quite feasible to calculate the size of any of the electric shifts and to relate these to oscillator strengths, etc. One can also make an *a priori* estimate of the size of the electric effects if the energy level scheme of any system is known. For example, in g shifts one can see from the formalism that the existence of a close-lying excited state will lead to large shifts. This in part causes the large g shifts in Er^{3+} in $CaWO_4$. Furthermore, we know that the effective field is inversely proportional to the separation of the odd- and even-parity state. Hence in divalent rare earths, where the d bands are depressed, one may expect especially large electric effects. Similarly in states with incomplete quenching of the orbital momentum one expects large electric shifts; indeed whenever D is large or g deviates substantially from 2 the corresponding electric shifts should be especially large unless forbidden by symmetry considerations.

In a succeeding paper, we shall consider the case of electric shifts in a quenched system, Mn^{2+} in $CaWO_4$ as well as other rare earths in the tungstate.

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