and in each case the B value and the corresponding slope agreed within the quoted uncertainty.

III. DISCUSSION

The results presented in the previous section indicate that the specific heats of KDP and KH_2AsO_4, as measured by Stephenson and co-workers, possess a logarithmic singularity at the respective transition temperatures. Now a thermodynamic analysis of the properties of ferroelectric crystals shows that[10]:

(a) The value obtained from a specific-heat measurement on the crystal in the ferroelectric phase may depend critically on the electrical constraint and to a lesser extent on the mechanical constraints applied to the crystal.

(b) The *differences* between the specific heats for different constraints undergo at most *finite* discontinuities at the transition temperature.

We may thus conclude that evidence for a singularity in any one of the specific-heat functions of a ferroelectric can be taken as evidence for the same singularity appearing in the others. Hence, while we do not know the constraints relevant to the unplated polycrystalline specimens[11] used by Stephenson and

co-workers, we may still deduce that the specific heat at constant displacement (D) and constant strain (S), $C_{D,S}$, of KH_2PO_4 and of KH_2AsO_4 possesses a logarithmic singularity at the transition temperature.

In general, the specific heat $C_{D,S}$ is of interest in the comparison between theory and experiment; the present case is of particular interest since these two ferroelectrics are examples of order-disorder systems in which the dipole-dipole forces play a significant role in the phase transition.

We conclude by pointing out that a measurement of the clamped transition entropy and transition energy associated with the proton distribution requires: (a) specific-heat measurements on specimens subject to known constraints and (b) careful measurements of the dielectric properties of the ferroelectric phase. Such data are not available in the literature.

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[10] J. Grindlay (to be published).
[11] The agreement between the anomalous entropies $\int_0^\infty C^a (d\theta/\theta)$ obtained by Stephenson and co-workers and the theoretical clamped transition entropy [J. C. Slater, J. Chem. Phys. 9, 16 (1941)] $\int_0^\infty C_E, s^a (E=0) (d\theta/\theta) = R \ln\frac{3}{2}$, associated with the proton distribution suggests that the constraint was constant (zero) electric field. The values of the anomalous entropies are 0.74 ± 0.06 cal/mole deg for KDP and 0.90 ± 0.05 cal/mole deg for KH_2AsO_4; $R \ln\frac{3}{2} = 0.81$ cal/mole deg.

Nonlinear and Linear Shielding of Rare-Earth Crystal-Field Interactions

A. J. Freeman

National Magnetic Laboratory,* Massachusetts Institute of Technology, Cambridge, Massachusetts

AND

R. E. Watson†

Bell Telephone Laboratories, Murray Hill, New Jersey

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It was shown previously that significant nonlinear shielding of the rare-earth electrostatic crystalline-field interactions may occur, and hence that the standard parametrization scheme used to determine the crystal-field parameters, $V_L^M = A_L^M \langle r^L \rangle$, was questionable. These nonlinear effects arise from the same distortions of the closed shells in rare-earth ions which produce the (larger) linear shielding of the crystal field V_c. In this paper, both nonlinear and linear shielding effects have been investigated for the rare-earth ions Ce^{3+}, and Tb^{3+} through Yb^{3+} inclusive. The method of single substituted configurations is employed and is shown to avoid the difficulties associated with the traditional single-determinant perturbation-theory approach previously used exclusively by various authors. Results based on both methods are given and compared; significant differences in linear-shielding predictions are found to be introduced by the inexact traditional approach. Calculations for the nonlinear $5p \rightarrow 4f$ effects have been done, and results displayed, as a function of the strength of V_c (based on the point-charge model). The relevance of these effects to experiment is examined qualitatively.

I. INTRODUCTION

THE electrostatic crystal-field model has been used in numerous studies of the optical and magnetic properties of rare-earth ions in solids. A key role is played in these investigations by the parameters V_L^M

$= \mathcal{U}_L^M \langle r^L \rangle$ determined experimentally to represent appropriate matrix elements of the crystal-field operator

$$V_c = \sum_{L,M} A_L^M r^L Y_L^M (\theta, \varphi)$$

$$\equiv \sum_{L,M} \left(\frac{4\pi}{2L+1} \right)^{1/2} \mathcal{U}_L^M r^L Y_L^M (\theta, \varphi) \quad (1)$$

acting on the open shell of $4f$ electrons alone. While this method has been thought to be too crude a representation to have much meaning as an *ab initio* theory, its successes as a semiempirical theory have led to an increasing number of applications. For example, in recent years, studies of the magnetic ordering in rare-earth metals[1] has relied heavily on the electrostatic model to describe the anisotropy energy as arising mainly from the electrostatic interaction between the $4f$ electrons and the crystalline field produced by the surrounding charge distribution. A knowledge of the parameters $V_L{}^M$ is essential to the predictions of this and other effects.

We have recently shown, using Ce^{3+} as an example, that significant nonlinear effects may occur, associated with the distortion of the closed shells in the rare-earth ion, and hence that the standard parametrization schemes used to determine the $V_L{}^M$ parameters are at best questionable.[2] These nonlinear effects arise in addition to the large linear shielding of V_c also produced by the distortions of the closed shells.[2-5]

In this paper, we deal with linear shielding, by comparing the traditional single-determinant perturbation-theory approach followed in I and elsewhere[3-5] with the proper perturbation theory based on intermediate states of exact free-ion symmetry. The predictions of the two methods are found to differ significantly in several cases. For estimates of the nonlinear shielding effects, reliance is placed on single-substitution configuration-interaction theory. This is, in principle, an exact method and as such, represents an improvement over the crude estimates in I (although we shall see that problems of maintaining numerical accuracy do enter). Only $p \rightarrow 4f$ contributions are considered here. These are important for $V_2{}^0$ and dominate for $V_4{}^0$ fields. Results are reported for Ce^{3+} and for heavy rare-earth ions and their relevance to experiment is discussed.

II. LINEAR AND NONLINEAR SHIELDING

To determine how distortions in the closed shells of a rare-earth ion affect the ion's electrostatic crystal-field energy, we first inspect the "bare"-$4f$-shell crystal-field terms. The matrix element of $V_L{}^M$ between two one-electron functions, which have the same spin m_s, but in general different orbital quantum numbers (l and m and l' and m', respectively), is from Eq. (1)

$$\langle lm | V_L{}^M | l'm' \rangle = C^L(lm; l'm') \mathcal{V}_L{}^M \langle r^L \rangle_{ll'}. \quad (2)$$

Here C^L is a Condon and Shortley C^k coefficient[6] and

$$\langle r^L \rangle_{ll'} = \int_0^\infty U_l(r) r^L U_{l'}(r) dr, \quad (3)$$

where the U_l are one-electron radial functions. Expressed in terms of the familiar $3j$ coefficients,[7] Eq. (2) becomes

$$\langle lm | V_L{}^M | l'm' \rangle = (-1)^m [(2l+1)(2l'+1)]^{1/2}$$

$$\times \begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & L & l' \\ -m & M & m' \end{pmatrix} \mathcal{V}_L{}^M \langle r^L \rangle_{ll'}. \quad (4)$$

For a single determinant Ψ_o, representing an open $4f$-shell rare-earth ion in which all orbitals of a given shell have common radial behavior, the diagonal $V_L{}^0$ energy is

$$\langle \Psi_o | V_L{}^0 | \Psi_o \rangle = 7 \mathcal{V}_L{}^0 \langle r^L \rangle_{4f,4f} \begin{pmatrix} 3 & L & 3 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{m''} (-1)^{m''} \begin{pmatrix} 3 & L & 3 \\ -m'' & 0 & m'' \end{pmatrix}, \quad (5)$$

where the sum spans all occupied $4f$ m_l values. It is the "shielding" of such an energy term by distortions of the ion's closed shells which we consider now. We will not consider off-diagonal $V_L{}^M$ matrix elements.

A. Linear Shielding

The electrostatic energy effects associated with closed-shell distortions can in large part be incorporated in a factor R^L such that the crystal-field energy becomes

$$\langle \Psi_o | V_L{}^0 (1 - R^L) | \Psi_o \rangle.$$

Such effects are known as *linear shielding* since they act simply as a scale factor on the crystal field strength $V_L{}^0$. There are two approaches to estimating the contributions to R_L which we may refer to as the single-determinant and the singly-substituted configuration methods. The first has been used exclusively to date in crystal field shielding estimates[2-5] and it has also been applied to other rare-earth shielding problems.[8] The second approach makes more rigorous use of perturbation theory and has the advantage of always being exact (though involving increased computational labor). The two methods yield results which differ significantly.

Single-Determinant Perturbation Theory

Here, second-order perturbation theory is used to estimate the single substitution configuration mixing

[1] T. A. Kaplan, Phys. Rev. **124**, 329 (1961); R. J. Elliott, *ibid.* **124**, 346 (1961); H. Miwa and K. Yosida, Progr. Theoret. Phys. (Kyoto) **26**, 693 (1961); for a review see T. Nagamiya, J. Appl. Phys. **33**, 1029S (1962).

[2] R. E. Watson and A. J. Freeman, Phys. Rev. **133**, A1571 (1964), henceforth referred to as I.

[3] G. Burns, Phys. Rev. **128**, 2121 (1962).

[4] C. J. Lenander and E. Y. Wong, J. Chem. Phys. **38**, 2750 (1963).

[5] D. K. Ray, Proc. Phys. Soc. (London) **82**, 47 (1963).

[6] See, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), Chap. VI, in particular pp. 176–179.

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

[8] For example, B. R. Judd, Proc. Phys. Soc. (London) **82**, 874 (1963).

energy associated with excited determinantal functions Ψ_k, where one (n,l,m) one-electron orbital of a closed shell of Ψ_o has been replaced by another n', l', m' orbital having the same spin. This type of configuration mixing has been discussed in detail in I.[9]

Linear-shielding energy then arises from second-order terms which are, of necessity, linear in $V_L{}^0$,

$$\Delta E_{l \to l',m}{}^{(1)} = \frac{2\langle \Psi_o | V_L{}^0 | \Psi_{l \to l',m}\rangle\langle \Psi_{l \to l',m} | H_o | \Psi_o\rangle}{E_o - E_{l \to l',m}}, \quad (6)$$

where Ψ_k is specified by the $lm \to l'm$ substitution involved (m' must equal m for nonzero mixing) and where H_o is the free ion many-electron Hamiltonian.[10] The numerator of $\Delta E^{(1)}$ can be rewritten in terms of one-electron matrix elements giving

$$\Delta E_{l \to l',m}{}^{(1)} = \frac{2\langle lm | V_L{}^0 | l'm\rangle\langle l'm | h | lm\rangle}{E_o - E_{l \to l',m}}, \quad (7)$$

where h is the one-electron free ion, Hartree-Fock Hamiltonian defined for Ψ_o. It should be noted that h consists of spherical contributions, h_{spher}, [coming from the kinetic and nuclear potential energy terms and from both closed and 4f-shell Coulomb and exchange potentials], and of aspherical 4f-shell terms.

The standard linear shielding term is obtained by summing Eq. (7) over the m_l and m_s values common to the l and l' shells. Doing this, and anticipating that we will be interested only in cases where $L \neq 0$ (hence we need consider only the aspherical h terms), one obtains

$$^L\Delta E_{l \to l'}{}^{(1)} = \sum_{m,m_s} \Delta E_{l \to l',m}{}^{(1)},$$

$$= \sum_{\substack{m''m_s'' \\ m\, m_s}} \frac{2\langle lm | V_L{}^0 | l'm\rangle}{E_o - E_{l \to l'm}}$$

$$\times \sum_k \{ C^k(lm; l'm)C^k(4fm'',4fm'')\mathcal{F}^k(l,4f; l'4f) - \delta(m_s m_s'')C^k(4fm'',lm)C^k(l'm,4fm'')\mathcal{G}^k(l,4f; 4fl') \}, \quad (8)$$

where[11] the m'', m_s'' sums are over occupied 4f-shell orbitals, the m_s sum covers $\pm\tfrac{1}{2}$ and the m summation spans all positive and negative values which are smaller in magnitude than l and l'. The allowed k values are determined by the properties of the C^k coefficients, by L and by the m summation. The $\mathcal{F}^k$ and $\mathcal{G}^k$ are radial Coulomb and exchange interelectronic integrals of the form

$$\mathcal{F}^k(ab; cb) \equiv \int_0^\infty \int_0^\infty U_a(r_1)U_c(r_1)(r_<{}^k/r_>{}^{k+1})$$
$$\times [U_b(r_2)]^2 dr_1 dr_2 \quad (9)$$

and

$$\mathcal{G}^k(ab; bc) \equiv \int_0^\infty \int_0^\infty U_a(r_1)U_b(r_1)(r_<{}^k/r_>{}^{k+1})$$
$$\times U_b(r_2)U_c(r_2) dr_1 dr_2. \quad (10)$$

The sum over m and m_s is commonly done in Eq. (8) by assuming the energy denominator to be a constant, δE. Using Eq. (4) and expressing the C^k in terms of 3j coefficients,[12] Eq. (8) becomes

$$^L\Delta E_{l \to l'}{}^{(1)}$$

$$= \frac{14 \mathcal{V}_L{}^0\langle r^L\rangle_{ll'}[(2l+1)(2l'+1)]^{1/2}}{\delta E}\begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \left[\frac{2}{2L+1}\begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 3 & L & 3 \\ 0 & 0 & 0 \end{pmatrix}\mathcal{F}^L(l4f; l'4f) \right.$$

$$\left. - \sum_k \begin{Bmatrix} 3 & L & 3 \\ l' & k & l \end{Bmatrix}\begin{pmatrix} l & k & 3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 3 & k & l' \\ 0 & 0 & 0 \end{pmatrix}\mathcal{G}^k(l4f; 4fl') \right]$$

$$\times \left[\sum_{m''}(-1)^{m''}\begin{pmatrix} 3 & L & 3 \\ -m'' & 0 & m'' \end{pmatrix} \right], \quad (11)$$

where $\{\ \}$ denotes a Racah 6j symbol[7] and the m'' sum is over the m_l values of all occupied 4f orbitals. A linear shielding factor $R^L_{l \to l'}$ can be obtained by dividing this

[9] See, R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955) for a more general coverage of configuration interaction theory.

[10] For simplicity in this paper, H_o will be limited to kinetic and electrostatic terms, yielding a LSM_LM_S coupling scheme. The omission of spin-orbit coupling is an obvious shortcoming for a rare-earth investigation but the complications attendant with its inclusion are not warranted in the present investigation.

[11] In Eq. (8) we have anticipated that we will wish to evaluate it for $L>0$ and have omitted the h_{spher} contributions of Eq. (7).

The $\langle lm | h_{\mathrm{spher}} | l'm\rangle$ matrix elements are zero valued if $l \neq l'$ and while not necessarily zero if $l = l'$, the m summation causes these to make a zero valued contribution to $^L\Delta E$ if $L \neq 0$.

[12] The C^k and 3j coefficients are related by

$$C^k(lm; l'm') = (-1)^m[(2l+1)(2l'+1)]^{1/2}$$
$$\times \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k & l' \\ -m & m-m' & m' \end{pmatrix}.$$

result by Eq. (5) yielding

$$R_{l \to l'}{}^L \equiv -{}^L\Delta E_{l \to l'}{}^{(1)}/\langle \Psi_o | V_L{}^0 | \Psi_o \rangle$$

$$= \frac{-2[(2l+1)(2l'+1)]^{1/2}\langle r^L \rangle_{ll'}}{\delta E \langle r^L \rangle_{4f4f}} \left[\frac{2}{2L+1} \begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \mathfrak{F}^L(l4f; l'4f) - \sum_k \begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 3 & k & l' \\ 0 & 0 & 0 \end{pmatrix} \Big/ \begin{pmatrix} 3 & L & 3 \\ 0 & 0 & 0 \end{pmatrix} \right.$$

$$\left. \times \begin{Bmatrix} 3 & L & 3 \\ l' & k & l \end{Bmatrix} \mathcal{G}^k(l4f; 4fl') \right]. \quad (12)$$

This expression, being independent of the M_L and M_S values of Ψ_o, is a linear shielding factor. It is equivalent to the more general tensor operator expression obtained by Judd.[8] It holds whether Ψ_o is a single or multideterminant function. In the latter case, Eqs. (11) and (12) would have an additional summation over fractional parentage coefficients. This, taken with the m'' sum, would cancel in the numerator and denominator of Eq. (12) as did the m'' sum here. Finally, it should be emphasized that Eq. (12) and that of Judd do not hold for the (uninteresting) case of $L=0$ since h_{spher} was dropped in the derivation.

Our experience in I indicates that Eq. (12) supplies an inaccurate estimate of the linear shielding arising from the $5p \to 4f$ (i.e., $l=p$ and $l'=f$) terms, which represent our main concern in this paper. There are two reasons for this: First, the energy denominators of Eq. (8) vary by as much as 20% among the different contributing m values, suggesting that the assumed constancy of δE in Eqs. (11) and (12) is not altogether appropriate. Second, and more serious, the $4f$ shell is already partially filled, meaning that not all $4f$ m_l and m_s values are available for the sum over intermediate $\Psi_{5p \to 4f}$ determinants. This requirement of the exclusion principle means that one will, in general, not be able to complete the m and m_s summations of Eq. (8) which are essential to Eqs. (11) and (12).[13] In addition, the $4f$ m_l and m_s values, not available to these summations, will be a function of the M_L and M_S values of Ψ_o. This means that (1) $R^L{}_{5p \to 4f}$ is an inaccurate indication of $5p \to 4f$ linear shielding *and* (2) that simply correcting the sums in Eq. (8) for the requirements of the exclusion principle will not produce a linear shielding term.

While the linear shielding calculations of Burns,[3] Lenander and Wong,[4] and Ray[5] considered only the Coulomb $\mathfrak{F}^k$ term of Eq. (12), we saw in I that the exchange $\mathcal{G}^k$ terms make substantial linear shielding contributions. [These same exchange terms appeared very important to nonlinear effects.] Unfortunately, as we have just indicated, even the complete Eq. (12) does not always supply an adequate description of linear shielding.

The Singly Substituted Configuration Approach

Consider now a second approach to linear shielding which is always exact. Instead of dealing with a set of intermediate states which are single determinants as in Eq. (6), we construct a set of singly substituted *configuration* functions $\Psi_{i,nl \to n'l'}$, which are eigenfunctions of L^2, S^2, L_z, and S_z, by removing a one-electron orbital with principle quantum numbers n and l from our ground state Ψ_o and replacing it with one of $n'l'$. A $\Psi_{i,nl \to n'l'}$ has quantum numbers $L'S'M_L'$ and M_S' which need not be in common with those of Ψ_o and in general it will be a multideterminant function. Normally some of its constituent determinants will differ with Ψ_o, or with a constituent determinant of a multideterminant Ψ_o, by one orbital while others will differ by two or more orbitals due to m_l and m_s assignments. In other words, a singly substituted configuration in general involves singly *and* more highly substituted determinants. Consider now the second-order perturbation energy which is linear in $V_L{}^0$, namely

$$\Delta E_{i,nl \to n'l'}$$

$$= \frac{2\langle 0, L''S''M_L''M_S'' | H_o | i, nl \to n'l', L'S'M_L'M_S' \rangle \langle i, nl \to n'l', L'S'M_L'M_S' | V_L{}^0 | 0, L''S''M_L''M_S'' \rangle}{E_o - E_{i,nl \to n'l'}}. \quad (13)$$

Only the singly substituted Ψ_i determinants contribute to the $V_L{}^0$ matrix element while both single and double substitutions contribute[9] to that of H_o. Since H_o commutes with $L^2S^2L_z$ and S_z, nonzero H_o matrix elements only occur when the $\Psi_i L'S'M_L'$ and M_S' values are identical to those of Ψ_o. In addition, the H_o matrix element and the energy denominator are independent of M_L'' and M_S'' so ΔE becomes

$$\Delta E_{i,nl \to n'l'} = C_{o,i}\langle inl \to n'l', L''S''M_L''M_S'' | V_L{}^0 | 0, L''S''M_L''M_S'' \rangle, \quad (14)$$

[13] It is this requirement on the m and m_s summations which causes Eq. (13) of I to differ with Eq. (8) here.

where $C_{o,i}$ is a function of Ψ_o and Ψ_i but not of their M_L and M_S values. Let us define a shielding factor, $S^L{}_{i,nl\to n'l'}$ by dividing ΔE by Eq. (5);

$$S^L{}_{i,nl\to n'l'} = -\frac{C_{o,i}\langle inl \to n'l', L''S''M_L''M_S'' \,|\, V_L^0 \,|\, 0, L''S''M_L''M_S''\rangle}{\langle 0, L''S''M_L''M_S'' \,|\, V_L^0 \,|\, 0, L''S''M_L''M_S''\rangle}. \tag{15}$$

Expressing the V_L^0 matrix elements in terms of reduced matrix elements [e.g., Eq. (5.4.1) of Edmonds[7]], we discover that $S^L{}_{i,nln'l'}$ is independent of M_L'' and M_S'', i.e.,

$$S^L{}_{i,nl\to n'l'}$$
$$= -\frac{C_{o,i}\langle i, nl \to n'l', L''S''\|V_L^0\|0, L''S''\rangle}{\langle 0, L''S''\|V_L^0\|0, L''S''\rangle}. \tag{16}$$

Finally, for any given Ψ_o, there will often be more than one Ψ_i of given $nl \to n'l'$ and the same L'' and S''. A list[14] of the number of these intermediate $np \to 4f$ Ψ_i's is given for the trivalent rare-earth ground states in Table I. The number is in some cases substantial.

A linear shielding factor can be defined for the $nl \to n'l'$ configuration mixing by simply summing over the Ψ_i

$$S^L{}_{nl\to n'l'} = \sum S^L{}_{i,nl\to n'l'}. \tag{17}$$

We will call this linear shielding of the second kind to differentiate it from the $R^L{}_{l\to l'}$ of Eq. (12). It involves no averaging of energy denominators and it does not run afoul of the exclusion principle for the $nl \to 4f$ case. Equation (17), incidentally, requires more work to evaluate than does $R^L{}_{l\to l'}$. We will see the two types of linear shielding to differ noticeably for the $5p \to 4f$ case. For example, $R^L{}_{5p\to 4f}$ is nonzero for Tm^{3+}, Gd^{3+} and Yb^{3+} while Table I indicates that $S^L{}_{5p\to 4f}$ is zero-valued for these ions owing to the lack of intermediate Ψ_i states having the required ground-state L'' and S'' symmetry.

Some ambiguity can arise in the evaluation of an equation such as (17) owing to there being a choice allowed in the set of $\Psi_{i,nl\to n'l'}$ states, if more than one such state of appropriate symmetry exists. In such a case one should use the set of intermediate states among which our many-electron free-ion Hamiltonian H_o is diagonalized. Except for perturbed-function normalization terms, this choice leads to but one type of higher order perturbation energy term which is linear in V_L^0. It is

$$2\frac{\langle 0|H_o|i\rangle\langle i|V_L^0|j\rangle\langle j|H_o|0\rangle}{(E_o-E_i)(E_o-E_j)}, \tag{18}$$

and contributions from such terms should be added to the S^L of Eq. (17). Of the ions we will consider, such occur for Ce^{3+} and Dy^{3+} and have been found to be insignificant.

B. Nonlinear Shielding

When one inspects the $5p \to 4f$ matrix elements appropriate to an equation such as (6) or (13) one discovers that the V_L matrix elements can be of the same order as the off-diagonal H_o terms. This fact suggests that if linear shielding is of experimental significance, then mixing effects, which are of higher order in V_L^0, can be significant as well. Such terms are, of necessity, nonlinear, i.e., they cannot be incorporated into a shielding factor such as S^L or R^L which merely scales the crystal-field interactions. Instead, they contribute to the deviation in position of one crystal field level with respect to others[15] and to a common energy shift of all the crystal field levels of the ground configuration. To the extent that the latter is the case, we are of course not interested, since experimentally it is energy differences which one observes. The fact that V_L^0 and H_o matrix elements are of the same order does not, therefore, necessarily mean that nonlinear effects are as significant as their linear counterparts.

Since V_L^0 matrix elements can be nonzero between states of differing L, nonlinear effects rely on a larger array of intermediate states than may their linear counterparts. Among other things, this leads to situations where nonlinear shielding occurs and linear effects cannot. For example, there is $5p \to 4f$ shielding of the V_2^0 and V_4^0 crystal field levels of the Tm^{3+} ground ^3H state despite the fact that $S^L{}_{5p\to4f}$ is zero valued (see Table I).

Before leaving this section and going on to consider

TABLE I. The number of $(np)^5(4f)^{n+1}$ states with L and S in common with the ground $(np)^6 4f^n$ states of the rare-earth ions.

Ion	Ground state	Number of $(np)^5 4f^{n+1}$ states
Ce^{3+}	$(4f)^1$ ^2F	3
Pr^{3+}	$(4f)^2$ ^3H	7
Nd^{3+}	$(4f)^3$ ^4I	9
Pm^{3+}	$(4f)^4$ ^5I	9
Sa^{3+}	$(4f)^5$ ^6H	7
Eu^{3+}	$(4r)^6$ ^7F	3
Gd^{3+}	$(4f)^7$ ^8S	0
Tb^{3+}	$(4r)^8$ ^7F	1
Dy^{3+}	$(4f)^9$ ^6H	2
Ho^{3+}	$(4f)^{10}$ ^5I	1
Er^{3+}	$(4f)^{11}$ ^4I	1
Tm^{3+}	$(4f)^{12}$ ^3H	0
Yb^{3+}	$(4f)^{13}$ ^2F	0

[14] We are grateful to Dr. A. Rotenberg for a computer program which was instrumental in obtaining this list.

[15] For a simple example of second-order effects see Fig. 1 of I.

the calculations which have been done, we might note the feature of the $5p \to 4f$ configuration mixing which has led to our preoccupation with it in the present paper. As already noted, this mixing makes a significant V_2^0 and a dominant V_4^0 linear shielding contribution. Normally the strongest of such shielding is associated with the largest numerators in equations such as (6) and (13). This is not the case for the $5p-4f$ mixing. The off-diagonal V_L^0 and H_o matrix elements are of the same order and are not particularly large. The energy denominators, on the other hand, are the smallest encountered in closed shell $nl \to n'l'$ configuration mixing. It is these small denominators which cause the linear $5p \to 4f$ shielding to be important and (when coupled with H_o and V_L^0 matrix elements of the same magnitude) which lead to significant nonlinear effects as well.

III. THE CALCULATIONS

As indicated, our concern in this paper is entirely with the $p \to 4f$ shielding contributions. The R^L and S^L appropriate to such terms have been evaluated using Eqs. (12) and (16), respectively. The radial integrals necessary to both cases were obtained with nonrelativistic Hartree-Fock functions.[16] The Ψ_o and Ψ_i necessary for estimating the S^L were obtained by diagonalizing H_o among the allowed $4f^n p^6$ and the $4f^{n+1}p^5$ sets of determinants, respectively. Convenience dictated the evaluation of Eq. (15) rather than (16), and was done for Ψ_o states where $L = M_L$ and $S = M_S$.

The calculations were done for the Hund's rule ground states of Ce^{3+} and Tb^{3+} through Yb^{3+} inclusive. This choice avoids spherical Gd^{3+}, which has no diagonal crystal field energy to shield, and the $4f^2$ through $4f^6$ ions for which S^L estimates are formidable and nonlinear calculations are worse. The $4f^2-4f^6$ ion difficulties are hinted at by the count of intermediate states given in Table I.

The nonlinear $5p \to 4f$ shielding has been estimated by diagonalizing $H_o + V_L^0$ (for given V_L^0) between the full set of $4f^n 5p^6$ and $4f^{n+1} 5p^5$ single determinants of given M_L and M_S yielding an unperturbed ground-state energy $\langle \Psi_o | H_o + V_L^0 | \Psi_o \rangle$ plus linear and nonlinear crystal field shielding contributions,[17] denoted by $E(V_L^0, M_L, M_S)$. The results for differing M_L and M_S, yield a set of $E(V_L^0, M_L, M_S)$ energy levels which may be compared with the bare crystal field level scheme of Eq. (5). This process introduces nonlinear shielding effects arising from within the $4f^n 5p^6$ configuration (i.e., mixing in of states of differing L). These effects can be separated out by diagonalizing $H_o + V_L^0$ within that configuration alone and will be inspected when they arise. In order to keep the number of calculations

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[16] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[17] There will also be some H_o correlation energy arising from mixing the configurations but this neither interests us nor complicates matters since it is independent of M_L and M_S.

within bounds, only states for which $S = M_S$ have been considered.

Essential to nonlinear shielding is its dependence on field strength. A definition of the crystal fields in terms of which the calculations are done is therefore necessary. We will speak of potentials of strength Z due to a $+Ze$ point charge, 5 atomic units away from the rare-earth nucleus along the z axis. This gives

$$V_{L,z^0}(\mathbf{r}) \equiv -Z \left(\frac{4\pi}{2L+1} \right)^{1/2} (5)^{-L-1} Y_L^0(\theta\varphi) r^L \quad (19)$$

or

$$\mathcal{V}_{L,z^0} = -Z(5)^{-L-1}. \quad (20)$$

In this notation, the calculations reported in I involved potentials with $Z = 4$, which represents the extreme strong field limit appropriate to actual crystals for V_2^0. However, as L increases so does the Z appropriate to that limit, with a Z of perhaps 8 providing an equivalent limit for V_6^0.

A potential of the form of Eq. (19) arises from assuming its source to be electrostatic charge situated *external* to the ion. This assumption may have justification when obtaining matrix elements involving the $4f$ shell alone [e.g., Eq. (5)] but its use is more than doubtful when the outer $5s$ and $5p$ shells of a rare-earth ion are involved. Overlap and orthogonality effects between these shells and the ion's environment are significant and these shells will be involved in covalent effects once they are opened up by a distortion such as the $5p \to 4f$ considered here. We believe that the inclusion of these effects would have severe repercussions on one's conclusions concerning the interaction of a rare-earth ion with its environment, and that their omission is the most serious shortcoming of the present and other investigations. We should note that the linear shielding estimates assumed [e.g., see Eq. (12)] an external electrostatic potential and therefore join the nonlinear estimates in this shortcoming. A treatment which rigorously accounts for the above matters would at best be formidable.

IV. LINEAR-SHIELDING RESULTS

Estimates of the $5p \to 4f$ contributions to the linear shielding of a V_2^0 field appear in Table II. Listed are the R^2 and S^2 values as well as the individual $\mathfrak{F}^2$, $\mathfrak{G}^2$,

TABLE II. The $5p \to 4f$ contributions to the linear shielding of a V_2^0 field.

Ion	R^2				S^2
	$\mathfrak{F}^2$ term	$\mathfrak{G}^2$ term	$\mathfrak{G}^4$ term	Total	
Ce$^{3+}4f^1$	+0.206	−0.029	−0.022	+0.154	+0.150
Tb$^{3+}4f^8$	+0.102	−0.015	−0.007	+0.080	+0.003
Dy$^{3+}4f^9$	+0.229	−0.033	−0.015	+0.181	+0.066
Ho$^{3+}4f^{10}$	+0.098	−0.014	−0.006	+0.078	0
Er$^{3+}4f^{11}$	+0.091	−0.013	−0.005	+0.073	+0.026
Tm$^{3+}4f^{12}$	+0.092	−0.013	−0.005	+0.074	0
Yb$^{3+}4f^{13}$	+0.092	−0.012	−0.004	+0.067	0

and $\mathcal{G}^4$ terms contributing to R^2. All the results are shielding (i.e., are >0). Their most significant feature is the difference between R^2 and S^2 for all ions but Ce^{3+}. The zero-valued S^2 factors for Ho^{3+}, Tm^{3+}, and Tb^{3+} follow from symmetry[18] whereas experimentally significant shielding is predicted for the same ions by the R^2 terms. In the case of the R^2 shielding where the relative roles of Coulomb, $\mathcal{F}^k$, and exchange, $\mathcal{G}^k$, shielding may be assessed, we see the exchange terms contribute a 20 to 25% reduction in the shielding. When inspecting Table II, we should remember that there are other $V_2{}^0$ shielding contributions (e.g., $5s \rightarrow d$ and $p \rightarrow p'$) which are, we believe, more amenable to an estimate by means of Eq. (12). From these terms, one would obtain (see I) approximately a 25% shielding contribution which will vary relatively little from ion to ion.

The $5p \rightarrow 4f$ contributions to the shielding of a $V_4{}^0$ field appear in Table III. Here the $\mathcal{G}^2$ exchange overpowers the $\mathcal{F}^4$ direct terms and cause a net *antishielding* (i.e., S^L and R^L are <0). Again the differences between S^L and R^L predictions are of almost the order of the shielding terms themselves with the more exact S^L predictions yielding the stronger antishielding. This is consistent with the $V_2{}^0$ case where they yielded the weaker shielding. There are, of course, additional $V_4{}^0$ shielding terms whose net effect should be a shielding of one or a few percent, implying that most rare-earth ions undergo a mild linear $V_4{}^0$ enhancement.

When they have arisen, the third-order terms of Eq. (18) have been but 0.1% of the S^L contributions coming from Eqs. (15)–(17). When dealing with an ion, such as Nd^{3+} or Pm^{3+}, where there are a large number of intermediate states (see Table I), these third-order terms might become significant.

Before leaving linear shielding let us briefly inspect the $p \rightarrow 4f$ shielding of the inner p shells. It will be zero-valued for Ho^{3+}, Tm^{3+}, and Yb^{3+}, as was the case for the $5p \rightarrow 4f$ terms, and for the same reason. Results for the $3p$ and $4p$ shells of Ce^{3+} and Tb^{3+} are listed in Table IV. For computational simplicity these are R^L estimates. The $3p$ shell terms are insignificant but the

$4p$ R^2 terms are not. The $4p$ energy denominators are an order of magnitude larger than their $5p$ counterparts but so, also, are the $\mathcal{F}^L$ integrals. The two trends compensate and the final shielding is determined by $\langle r^L \rangle_{UV}$ behavior. In the case of the $3p$ shells, all parameters conspire to make the shielding unimportant. The small antishielding $4p$ R^4 behavior is due to relatively small $\mathcal{F}^4$ and $\mathcal{G}^2$ terms which strongly cancel one another.

V. NONLINEAR SHIELDING: Ce^{3+} AND Tb^{3+}

The diagonalization of $H_o + V_L{}^0(Z)$ has been done for a range of field strengths (Z's) for the four levels of Ce^{3+} and the four Tb^{3+} levels with $M_S = S$. In these cases there is no nonlinear shielding from other multiplet states of the ground $(5p)^6(4f)^n$ configuration. Given a set of four crystal energy levels, due to H_o plus a particular $V_L{}^0(Z)$, we have followed the procedure, initiated in I, of fitting these levels to obtain a set of three *effective* crystal-field parameters, $\mathcal{U}^0{}_{L',\text{eff}}(Z)$, where $L' = 2$, 4, and 6 [free-ion $\langle r^{L'} \rangle_{4f,4f}$ values have been used; cf. Eq. (2)]. We will plot the ratios of these to the

TABLE IV. Contributions from various p shells of Ce^{3+} and Tb^{3+} to R^L from $p \rightarrow 4f$ mixing.

	R^2			R^4		
	Direct	Exchange	Total	Direct	Exchange	Total
Ce^{3+}						
$3p$	+0.0003		+0.0003	+0.00001	−0.0001	−0.0001
$4p$	+0.039	−0.011	+0.028	+0.003	−0.004	−0.001
$5p$	+0.206	−0.051	+0.154	+0.071	−0.103	−0.031
Tb^{3+}						
$3p$	+0.0005	−0.0001	+0.0004	+0.0002	−0.0001	−0.0001
$4p$	+0.045	−0.012	+0.033	+0.005	−0.006	−0.001
$5p$	+0.102	−0.022	+0.080	+0.028	−0.059	−0.031

$\mathcal{U}_{L'}{}^0(Z)$ of Eq. (20) defined for the L' and Z in question. These ratios will then provide a measure of how the nonlinear shielding affects the apparent $V_L{}^0(Z)$ linear shielding and contributes to the $\mathcal{U}_{L'}$ behavior (where $L' \neq L$) which one might obtain by fitting experimental crystal field spectra.[19]

The ratios for $V_2{}^0(Z)$ perturbing fields appear in Fig. 1. As $Z \rightarrow 0$, the $L = 2$ curves should converge on the $5p \rightarrow 4f$ S^2 linear shielding values (indicated by the arrows), and the other curves to zero. The $L = 2$ curves do approach their limit reasonably well, but after arriving in the vicinity of zero, two of the $L \neq 2$ curves start to deviate away from zero for the smallest Z

TABLE III. The $5p \rightarrow 4f$ contributions to the linear shielding of a $V_4{}^0$ field.

		R^4			
Ion	$\mathcal{F}^4$ term	$\mathcal{G}^4$ term	$\mathcal{G}^2$ term	Total	S^4
$Ce^{3+}4f^1$	+0.071	−0.008	−0.095	−0.031	−0.049
$Tb^{3+}4f^8$	+0.028	−0.003	−0.056	−0.031	−0.067
$Dy^{3+}4f^9$	+0.059	−0.006	−0.125	−0.072	−0.103
$Ho^{3+}4f^{10}$	+0.024	−0.003	−0.054	−0.033	0
$Er^{3+}4f^{11}$	+0.020	−0.002	−0.050	−0.032	−0.041
$Tm^{3+}4f^{12}$	+0.019	−0.002	−0.049	−0.032	0
$Yb^{3+}4f^{13}$	+0.014	−0.001	−0.046	−0.033	0

[18] In the case of Ho^{3+} there is an excited $(5p)^5(4f)^{11}$ state of appropriate symmetry (see Table I) but it has a zero-valued H_o matrix element with the ground state due to the symmetry of the combined Coulomb *and* exchange potential coming from the $(4f)^{10}$ ground-state shell.

[19] As has already been indicated, the strength of a $V_L{}^0(Z)$ obtained for a given Z is inflated for low L values with respect to those of high L if one's criteria of relative strengths are the crystal field parameters actually encountered in real solids. Therefore, given a particular Z value, use of Eq. (20) in the denominator of the $\mathcal{U}^0{}_{L,\text{eff}}(Z)/\mathcal{U}_L{}^0(Z)$ ratios causes an inflation of the relative role of the nonlinear shielding for high L values (relative to that for $L = 2$) as compared with what one might obtain using experimentally based denominators appropriate to a particular crystal.

values plotted. This appears to be due to round-off errors in the H_o matrix elements.[20]

We see that the apparent linear shielding (the $L=L'=2$ curves) increases slowly with field strength. The $L'=4$ curves also vary roughly linearly with Z and are *shielding*. The $L'=6$ curves are neither linear nor do they display similar Z dependence for the two ions. This may, in part, be associated with the fact that the choice of Eq. (20) inflates the apparent $L'=6$ shielding repercussions.[19]

In viewing the $V_4{}^0(Z)$ shielding ratios, which appear in Fig. 2, we should immediately note that they are an order of magnitude smaller than those appearing in Fig. 1. We see some curves oscillating for smaller Z's.
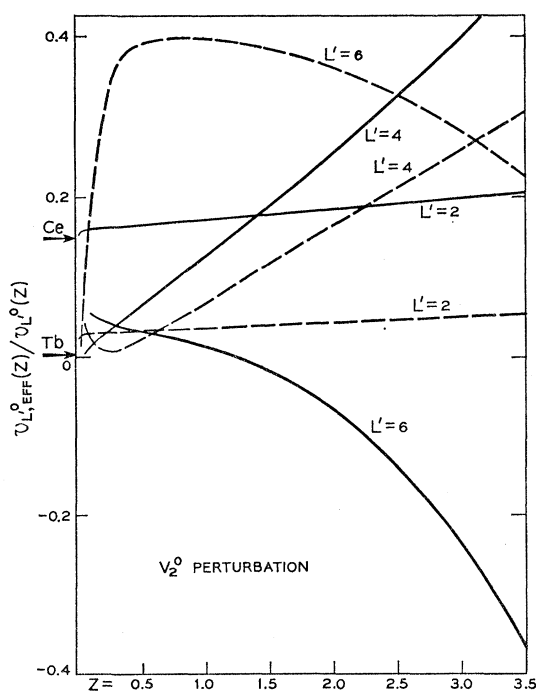

FIG. 1. Nonlinear shielding effects due to a perturbing $V_2{}^0(Z)$ field for Ce^{3+} (solid lines) and the $M_S=S$ levels of Tb^{3+} (dashed lines). Plotted are the $\mho^0{}_{L',\mathrm{eff}}(Z)/\mho_L{}^0(Z)$ ratios [see text] as a function of perturbing field-strength parameter Z [see text and Eqs. (19) and (20)].

These oscillations, as well as the deviations of the $L'\neq L$ curves from zero, are difficulties which one encounters with weak field calculations and the associated crystal field fits. Smooth curves lying within the shaded regions are a more appropriate measure of the intrinsic shielding effects.

Both $L=L'=4$ curves are antishielding as would be expected from Table III. The curve for Tb^{3+} is roughly constant over the range plotted while that for Ce^{3+}

[20] The process of plotting ratios rather than $\mho^0{}_{L,\mathrm{eff}}$ behavior, in conjunction with round off or other errors will cause such veering away from zero. This will eventually occur for any calculation involving a finite number of digits. We believe round off to be the error source here.
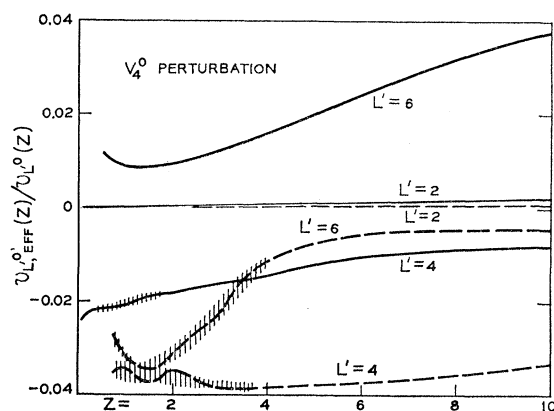

FIG. 2. Nonlinear shielding effects due to a perturbing $V_4{}^0(Z)$ field for Ce^{3+} (solid lines) and the $M_S=S$ levels of Tb^{3+} (dashed lines). Plotted are the $\mho^0{}_{L',\mathrm{eff}}(Z)/\mho_L{}^0(Z)$ ratios [see text] as a function of perturbing field-strength parameter Z [see text and Eqs. (19) and (20)].

shows a linear variation similar to the $L=L'$ terms of Fig. 1 though for slightly larger Z values (off the figure) it starts veering more sharply upward becoming shielding at $Z\sim12$. Both the Ce^{3+} and the Tb^{3+} S^4 linear shielding limits lie off the figure, approximately 0.03 below their respective curves. The curves of Fig. 1 showed a similar, though smaller, tendency to lie above the S^L limits. They also curved sharply towards their S^L values at the last minute. The Ce^{3+} curves shows the same behavior while the oscillations hide any such effect to Tb^{3+}.

Of the $L\neq L'$ curves, the ones for $L'=6$ again are different in character for the two ions; the Tb^{3+} curve shows a hump which is similar in character, but opposite in sign to that appearing in Fig. 1. Though insignificant in appearance, the $L'=2$ curves involve energies which are of the order of the $L'=6$ terms.[19]

Calculations were also done with $V_2{}^0(Z)$ and $V_4{}^0(Z)$ fields simultaneously present. Crudely speaking, the shielding effects proved additive (as might be expected) and hence these results will not be reported here.

The Ce^{3+} and Tb^{3+} results plotted in Figs. 1 and 2 suggest that the nonlinear shielding effects due to a $V_2{}^0$ field are liable to be more significant than those of a $V_4{}^0$ field. The exact effects depend, of course, on the relative magnitudes *and* signs of different field components.

VI. NONLINEAR SHIELDING: Tm^{3+} AND Er^{3+}

Unlike the case of Ce^{3+} and the states considered for Tb^{3+}, we encounter nonlinear shielding due to the excited multiplet states of the ground $4f^n5p^6$ configuration in the ions Tm^{3+} and Er^{3+}. We wish to separate this type of shielding, which is often properly accounted for in fits of experimental data, from the $5p\rightarrow4f$ effects. We also encounter more than four crystal field levels and rather than extending the fictitious crystal field fitting scheme of I and the preceding section, we will report simply the shielding energies associated with

particular levels. This choice gives a different view of the nature of the nonlinear shielding effects.

The total crystal field energy for our two-configuration $4f^n5p^6-4f^{n+1}5p^5$ function Φ is

$$\langle\Phi|H_o+V_L^0(Z)|\Phi\rangle-\langle\Phi'|H_o|\Phi'\rangle$$
$$\equiv\langle\Psi_o|V_L^0(Z)[1-S^L]|\Psi_o\rangle+5p\rightarrow4f\ \&\ 4f^n\rightarrow4f^n$$
$$\text{nonlinear terms,} \quad (21)$$

where Φ and Φ' are the results of diagonalizing $H_o+V_L^0$ and H_o, respectively. Staying within the $4f^n5p^6$ configuration we also have

$$\langle\Psi'|H_o+V_L^0(Z)|\Psi'\rangle-\langle\Psi_o|H_o|\Psi_o\rangle$$
$$\equiv\langle\Psi_o|V_L^0(Z)|\Psi_o\rangle+4f^n\rightarrow4f^n$$
$$\text{nonlinear terms,} \quad (22)$$

where, similarly, Ψ' results from diagonalizing $H_o+V_L^0$ within the ground configuration. Knowing $\langle\Psi_o|V_L^0(Z)|\Psi_o\rangle$, Eq. (22) yields the $4f^n\rightarrow4f^n$ nonlinear shielding energies and, knowing S^L as well, the difference between Eqs. (21) and (22) yields the nonlinear $5p\rightarrow4f$ contributions. The results listed in Tables V and VI have been obtained by this process.

The effect of a V_2^0 perturbation is seen in Table V. The zero of energy has not been shifted in any of the columns and all the zeroes appearing in the table follow from symmetry, i.e., from a lack of states having M_L and M_S appropriate for mixing. The zeros in the $5p\rightarrow4f$ column of Tm^{3+} immediately imply no linear shielding, in agreement with the observations of Sec. IV and Table I. Additional zeros appear in the V_4^0 results of Table VI; those not in common (for a given column and M_L value) with Table V are due to small nonlinear effects.

The $5p\rightarrow4f$ nonlinear contributions appear to be of the order of the $4f^n\rightarrow4f^n$ effects for a V_2^0 field and

are greater than the latter for a V_4^0 perturbation. This suggests that a reasonable criterion for anticipating the presence and magnitude of $5p\rightarrow4f$ effects may very well be the mixing between $4f^n$ multiplet states as deduced from experimental crystal field fits.

Beyond stating that the $5p\rightarrow4f$ terms are of experimental significance when compared with the bare $\langle\Psi_o|V_L^0|\Psi_o\rangle$ energies, it is difficult to make quantitative observations concerning the role of nonlinear shielding merely by inspection of Tables V and VI. There is the strong suggestion that the effects are more severe for the V_4^0 field. The reverse trend was suggested by Figs. 1 and 2, the disagreement being due largely to the different way of monitoring nonlinear effects in this and the preceding section. The exact significance of nonlinear effects depends, of course, on which diagonal (and off diagonal) crystal field matrix elements contribute to particular experimental data, and in what way.

Before leaving Tables V and VI, one comment must be made concerning computational accuracy. The last digits of the energies reported in these tables are typically the sixth digit which had to be carried in the matrix diagonalizations.[21] This loss of digits—digits which are significant to the crystal field energies— caused the weak field veerings seen in Figs. 1 and 2, and raises questions computational accuracy here. Diagonalizations of H_o to obtain the $\langle\Phi'|H_o|\Phi'\rangle$ values of Eq. (21) frequently produced errors (in the digits reported in Tables V and VI) when the diagonalizations were done for low M_L values.[22] We have assumed that similar errors occur in $\langle\Phi|H_o+V_L^0|\Phi\rangle$ causing a cancellation on the left-hand side of Eq. (21). It would be overly optimistic to assume that this cancellation is exact and the $5p\rightarrow4f$ terms most liable to error are in brackets in Tables V and VI. On the other hand,

TABLE V. V_2^0 shielding energies for Tm^{3+} and Er^{3+} where $M_S=S$. All energies in 10^{-5} atomic units.

	M_L	$\langle\Psi_o|V_2^0(Z)[1-S^2]|\Psi_o\rangle$	$f^n\rightarrow f^n$	$5p\rightarrow4f$
			Nonlinear terms	
$Tm^{3+}(^3H), Z=1$	0	-230	-14	(-12)
	1	-207	-13	-6
	2	-138	-10	-6
	3	-23	-4	$(+6)$
	4	$+138$	0	-3
	5	$+344$	0	0
$Tm^{3+}(^3H), Z=2$	0	-460	-54	(-32)
	1	-414	-49	-20
	2	-278	-34	-22
	3	-46	-19	$(+7)$
	4	$+278$	0	-12
	5	$+689$	0	0
$Er^{3+}(^4I), Z=1$	0	$+88$	-7.5	(-2)
	1	$+82$	7	(-0.6)
	2	$+63$	-6	-1
	3	$+32$	-5	-8
	4	-13	-1.5	-1
	5	-69	0	-4
	6	-138	0	-3

TABLE VI. $V_4^0(Z=2)$ shielding energies for Tm^{3+} and Er^{3+}, where $S=M_S$. All energies in 10^{-6} atomic units.

	M_L	$\langle\Psi_o|V_4^0(1-S^4)|\Psi_o\rangle$	$f^n\rightarrow f^n$	$5p\rightarrow4f$
			Nonlinear terms	
$Tm^{3+}(^3H)$	0	$+166$	-2	$(+13)$
	1	$+111$	-1	0
	2	-28	0	-13
	3	$+166$	-2	$(+11)$
	4	-166	0	0
	5	$+166$	0	0
$Er^{3+}(^4I)$	0	-115	-2	(-1)
	1	-88	-1	$(+2)$
	2	-15	-2	$+7$
	3	$+74$	0	-1
	4	$+132$	0	-6
	5	$+91$	0	-2
	6	-136	0	-1

[21] This situation arises because of the differences in diagonal H_o energies occurring between the $4f^n5p^6$ and $4f^{n+1}5p^5$ determinantal states.

[22] These errors were associated with the mixing of the excited $4f^{n+1}5p^5$ determinants because no such difficulties were encountered (to the digits of interest to us here) when the diagonalizations were limited to the ground $4f^n5p^6$ configuration.

insignificant errors crept into the terms of Eq. (22) and hence the $f^n \rightarrow f^n$ results are much more dependable. The numerical difficulties here and in the figures stem from the fact that even strong crystal fields are very weak when compared with the electrostatic (and correlation) energies involved in a rare-earth ion.

VII. CONCLUSION

While the present investigation represents, we believe, a distinct improvement over previous theoretical endeavors to inspect linear and nonlinear rare-earth crystal-field shielding, there remain many naive features. In particular, as was discussed in I, the use of an external electrostatic potential is a poor approximation when dealing with outer shell shielding because significant overlap and covalent effects are expected to occur. However, once the potential is given, we believe the calculated S^L to be very accurate estimates of the linear $5p \rightarrow 4f$ shielding for the ions reported. Problems of numerical accuracy, on the other hand, make it necessary to view the nonlinear estimates with care.

Perhaps the most significant feature of the $5p \rightarrow 4f$ linear shielding results is the zero-valued behavior for Ho^{3+}, Tm^{3+}, and Yb^{3+} which follows from symmetry. There are, of course, other substantial contributions to the shielding of a $V_0{}^2$ field. These total to approximately 50% and, to first crude approximation, are the same for all the rare earths.[23] Barnes et al.[24] have concluded from experiment that there is a 50 to 75% shielding of the $V_2{}^0$ field for Tm in the ethyl sulphate, oxide, and trifluoride. More recently, Wickman and Nowik[24a] have collected the existing data and conclude that S^2 varies from approximately 80 to 55% as one goes from the light to the heavy trivalent rare-earths. In other words, considering linear shielding, based on an external electrostatic field alone, theory almost, but perhaps not quite, accounts for the magnitude *and* trend seen experimentally, the $5p \rightarrow 4f$ mixing being largely responsible for the dependence on Z. We should note, by the way, that the experimental parametrization[24] yielding the (assumed linear) shielding observations, also assumed an external electrostatic field (and a knowledge of the Sternheimer nuclear quadrupole antishielding factor).[25] This assumption may have but limited validity in the experimental analysis, as it does with shielding calculations proper.

[23] R. M. Sternheimer, Bull. Am. Phys. Soc. 10, 597 (1965) and to be published. Dr. Sternheimer's results indicate that earlier estimates (see Ref. 4) of the $p \rightarrow nf$ (where $n \neq 4$) terms were too low.
[24] R. G. Barnes, R. L. Mössbauer, E. Kankeleit, and J. M. Poindexter, Phys. Rev. Letters 11, 253 (1963) and Phys. Rev. 136, A175 (1964); recently, Q. H. F. Vrehen and J. Volger [Physica, 1965 (to be published)] found a shielding of about 50% for Eu^{2+} in $PbCl_2$.
[24a] H. H. Wickman and I. Nowik (to be published).
[25] Barnes et al. (Ref. 24), Vrehen and Volger (Ref. 24), and Wickman and Nowik (Ref. 24a) assumed a crystal potential of the form of Eq. (1) and then experimentally obtained the ratio of the Sternheimer nuclear quadrupole (γ_∞) antishielding and the $V_2{}^0$ shielding factors.

In contrast with the $V_2{}^0$ case, the $V_4{}^0$ linear shielding is largely associated with the $5p \rightarrow 4f$ mixing, the other terms probably making a shielding contribution of but one, or a few, percent. Inspection of Table III suggests that a mild antishielding will then result for some of the ions, due to the dominance of the exchange contributions. These terms were seen to be important, but not dominant, in the crude calculations reported in I. The S^4 results of Table III provide the most striking indication that exchange most not be overlooked when dealing with crystal field shielding.

The nonlinear shielding results are much more difficult to catalog, largely because the effect of nonlinear shielding is strongly a function of how the crystal field levels are viewed. One can make the obvious observation that a weak crystal field term is liable to be seriously affected by nonlinear shielding from a stronger term but beyond this, conclusions must be drawn with care. For example, the results in Fig. 1 indicate a significant shielding of the $V_4{}^0$ term by nonlinear $V_2{}^0$ effects. One might be tempted to make something of this result since it has been frequently argued that, experimentally, there is substantial shielding of a $V_4{}^0$ field for a rare-earth ion when in an environment of lower than cubic symmetry and relatively little shielding when the environment is cubic. If the $V_2{}^0$ and $V_4{}^0$ [see Eq. (1)] were always of common sign (as was assumed in obtaining Fig. 1) one might be able to conclude something from this, but since in some systems the signs are reversed, this may only be done with caution. We do believe that the nonlinear shielding energies, appearing in Secs. V and VI, are of experimental significance.

The linear and nonlinear $p \rightarrow 4f$ shielding distortions, and to a lesser extent other terms, have a direct bearing on observables other than just the crystal field matrix elements. As was discussed in I, they make small environment-dependent contributions to the electric and magnetic hyperfine fields in a rare-earth ion. They also produce a spin density in the outer reaches of the ion which can be significant because of the highly local character of the $4f$ shell. [This spin density is, in addition to the free ion spin polarization, investigated previously[26] in Gd.] The $p \rightarrow 4f$ shielding produces an anisotropic density in the outer reaches of the ion which is parallel to the spin of the $4f$ shell. Since it involves the outer reaches of the ion, this density's role in ion-ion exchange coupling and in transferred hyperfine effects is enhanced, and, on occasion, may predominate over direct $4f$ terms. The crystal field matrix elements make these $p \rightarrow 4f$ terms environment-dependent.

ACKNOWLEDGMENTS

[26] R. E. Watson and A. J. Freeman, Phys. Rev. Letters 6, 277 and 529E (1961).