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Shielding and Distortion of Rare-Earth Crystal-Field Spectra

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The electronic spectra of rare-earth ions in crystalline fields are generally analyzed in terms of a static crystalline field, $V_c=\Sigma_{n,m}A_n{}^m r^n Y_n{}^m(\theta,\varphi)$, which acts on the open shell of $4f$ electrons. In this paper, the contributions of the closed atomic shells to this electrostatic interaction are examined and are found to be significant in several respects: First, the magnitude of the crystal-field splittings are reduced from the values obtained by considering just the $4f$ shell alone; this result supports the familiar assertion that the $4f$ electrons are *shielded* from the external crystalline field. Secondly, and quite striking, is the result that the ordering and relative spacing of the crystal-field levels are not necessarily those implied by the $4f$ crystal-field matrix elements alone. It is shown that in some cases the distortion of the ion's charge distribution produces severe deviations from the $4f$ crystal-field level scheme predicted by V_c directly. When such "nonlinear" deviations occur, they make questionable the standard crystal field parametrization schemes used for fitting observed rare-earth spectra. In addition, we also investigate the role played by the crystal field in producing by means of the distortion of the closed and $4f$ shells, and the interaction of these distortions with the open $4f$ shell, contributions to the magnetic (and electric) hyperfine interactions.

I. INTRODUCTION

BASIC to current methods for analyzing the electronic energy levels of rare-earth ions in crystalline fields is the assumption of a static crystalline field, V_c, which acts on the open shell of $4f$ electrons. Assuming that there is no overlap between the $4f$ electrons and the surrounding ionic charge distribution, V_c has the general form

$$V_c=\sum_{n,m} A_n{}^m r^n Y_n{}^m(\theta,\varphi)\,. \tag{1}$$

Most simply, the $A_n{}^m$ are taken to be lattice sums and represent the effects from static charges of the lattice of neighboring ions and the $Y_n{}^m(\theta,\varphi)$ are the usual spherical harmonics. Generally, in fitting observed spectra, matrix elements of V_c over the $4f$ electrons alone are considered; since integrations over the angular coordinates are easily done,[1] one is left with the quantities $V_n{}^m=A_n{}^m\langle r^n\rangle$ (where $\langle r^n\rangle$ is the integral of r^n over the $4f$ radial density) which are taken to be empirical parameters which somehow absorb all the various environmental effects not included in the simple description given by Eq. (1).

In this paper we investigate two postulates of crystal field interactions:

(1) The crystal field interacts only with the open $4f$ shell, i.e., contributions from closed electron shells (generally referred to as shielding effects) are negligible.

(2) The ordering of the $4f$ crystal-field energy levels is determined by the group transformation properties associated with a Hamiltonian which has the symmetry of V_c acting on the $4f$ shell, i.e., the ordering and relative spacing of the electronic energy levels is determined by the angular operators of V_c acting on the $4f$ electrons alone. The validity of this assumption, often cited as one strength of the crystal-field method, is used to justify the parametrization procedure.

In addition, we also investigate the role played by the crystal field in producing, by means of the distortion of the closed and $4f$ shells, contributions to the magnetic hyperfine interactions.

The validity of (1) has long been questioned. Indeed, until very recently, it has been fashionable to assert that the small crystal-field splittings observed for rare-earth ions, relative to (say) that for the $3d$ transition series, was caused by large shielding effects associated with the $5s$ and $5p$ electrons which lie outside the open $4f$ shell. However, in a recent publication, Burns has strongly challenged this view.[2] Using analytic perturbation techniques,[3] he estimated the shielding of the $V_4{}^0$ and $V_6{}^0$ components of the field in the trichlorides and ethyl sulfates to amount to less than 10%, and presented arguments (as well as calculations for lighter ions) to show that similar results should be expected for the $V_2{}^0$ component. Burns concluded that shielding in the rare-earth ions is unimportant and hence, that the difference between the iron series and rare-earth ion behavior is *not* due to the fact that the

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[1] Crystal-field theory dates back to H. Bethe, Ann. Physik **3**, 133 (1929). See the more recent work of K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952), R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952); *ibid.* **A218**, 553 (1953); *ibid.* **A219**, 387 (1953); and B. R. Judd, *ibid.* **A227**, 552 (1955).

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

[3] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

outer electrons shield the $4f$ electrons from the crystal fields. Instead, Burns attributes these differences to two predominant factors: (1) In iron series ions the crystal-field strengths are as much as ten times larger than for rare-earth lattices; (2) $\langle r^n \rangle$ for $3d$ ions are two times larger than their counterparts for the $4f$ ions. In a very recent publication, Lenander and Wong[4] (henceforth denoted as L & W), did perturbation-configuration interaction calculations and found substantial shielding of the $V_2{}^0$ and $V_4{}^0$ fields (59 and 17%, respectively). Using these results and comparing point charge calculations with experiment for the trichlorides they concluded that as much as 90% shielding could occur. Adding to these widely divergent views, is the conclusion of Bleaney[5] based on data[6] for Tm^{2+} in CaF_2, that the crystal-field interaction is far larger (i.e., *antishielding*) than that expected from estimates based on Eq. (1). Finally, Jørgensen, Pappalardo, and Schmidtke[7] have emphasized the role of covalent bonding in rare-earth crystal-field interactions. This effect is quite outside the conventional approach associated with Eq. (1) and despite its probable importance, we will not consider these effects here.

To our knowledge, the validity of (2) has not previously been questioned. Our results show that in addition to producing large shielding effects, the crystalline potential gives rise to distortions of the ion's charge distributions which, in turn, produce deviations from the predicted $4f$ crystal-field level scheme given by V_c directly. Such deviations will not always be of significant magnitude but when they are, the standard parametrization procedure yields parameters which contain crystal-field components of inappropriate symmetry. The application of this procedure to fit rare-earth spectra is most questionable in such a case. The present calculations supply crude information concerning these deviations, information which indicates that, on occasion, these deviations are of experimental importance.

The computations, to be reported, were carried out for Ce^{3+} which, with its single $4f$ electron, offers a particularly simple case to deal with; however, the implications of these results for other rare-earth ion spectra may be readily extended. We will simplify the computations by staying within a (L, M_L, S, M_S) coupling scheme rather than within the (J, M_J, L, S) intermediate coupling scheme which is more appropriate to the rare earths. We believe this to have but minor qualitative repercussions on our estimates for Ce^{3+} (although this could be more serious for other rare-earth ions). This approximation lets us deal entirely with single-determinant antisymmetric many-electron functions.

II. CLOSED-SHELL CRYSTAL-FIELD SHIELDING

Quite formally, consider a free rare-earth ion and represent its ground-state eigenfunction by Ψ_0, which is a solution of the Schrödinger equation for the free-ion Hamiltonian, H_0. For this ion in an external crystalline potential V_c, represented by an additional contribution to the Hamiltonian, we may take any of the new state functions to be given by

$$\Psi = \Psi_0 + \sum_K C_K \Psi_K \qquad (2)$$

in a manner similar to the method of configuration interaction (C.I.),[8] which is used to discuss the correlation problem in atoms and molecules.[9] In C.I. theory, the Ψ_K (including Ψ_0) form a complete set of many-electron functions; the combining coefficients C_K are determined as the solution of a secular equation formed by applying the variational principle to the total energy.

To understand the spectra of rare-earth ions, we must calculate the energy differences between crystal-field energy states for it is these and not abolute energies which are observed experimentally. For simplicity, first consider a set of $4f$ crystal-field energy levels which are obtained by the usual direct interaction of Eq. (1) with the $4f$ electrons. Now assume that one has obtained exact eigenfunctions [the Ψ's of Eq. (2)] and eigenvalues by solution of (say) the C. I. problem and compare these results with the approximate solutions. The differences take two forms. First, in going to the exact solutions all the energy levels have been lowered by a constant amount. Among the sources for this are any interactions solely involving the ion's closed shells which, by being distorted by the field, will have (to a first approximation) polarization energies which are constant for all the crystal-field states of the ion. These energy shifts are of no interest to us here. Secondly, the energy levels are displaced from one another relative to the predictions of Eq. (1) acting directly on the $4f$ electrons. We shall, in this paper, define any effect which causes such a displacement of the crystal-field levels, either in magnitude or in relative spacing, as a crystal-field shielding effect. However, we will not deal with the full crystal-field problem here; for example, we assume a potential of the form of Eq. (1) and thereby ignore the effects of covalency and ionic overlap. We will also concentrate on diagonal matrix elements of the interaction, i.e., we ignore mixing between the chosen states. These approximations (and others which will be introduced) are necessary because of the computational complexities of the problem; since they affect the quantitative nature of the results, detailed comparisons with experiment are not valid.

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

[5] B. Bleaney (to be published).

[6] Z. Kiss, Phys. Rev. **127**, 718 (1962).

[7] C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, J. Chem. Phys. **39**, 1422 (1963).

[8] See R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955) for a discussion of C.I. and H-F theory.

[9] J. C. Slater, Technical Report No. 3, Solid-State and Molecular Theory Group, MIT, 1963 (unpublished), and J. C. Slater, *Quantum Theory of Molecules and Solids, Electronic Structure of Molecules* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I.

To treat the problem let us choose a particular (approximate) representation within which we shall later carry out our computations. We shall take Ψ_0 to be the single determinant of one-electron orbitals which represents the conventional (or restricted) Hartree-Fock (RHF) ground state of the free ion. [We shall return later to consider the role of the unrestricted Hartree-Fock (UHF) representation in the computations.] For the Ψ_K, we shall consider only those determinantal states (made up of one-electron functions) which have nonvanishing matrix elements of V_c with respect to the ground state. The enumeration of the Ψ_K, follows simply and directly from the symmetry of V_c and the particular one-electron orbitals, φ_i^0, which make up Ψ_0. Since V_c is an one-electron operator, the matrix element $\langle\Psi_0|V_c|\Psi_K\rangle$ will be nonvanishing if (a) Ψ_K differs from Ψ_0 only in having one orbital φ_i^K different from the φ^0 of Ψ_0, and (b) $\langle\varphi_i^K|V_c|\varphi_i^0\rangle\neq 0$. Using the properties of the spherical harmonics in (b) leads to the following Ψ_K (listed in Table I) for the V_2^0 and V_4^0 components of V_c, where, for example, the notation $p\rightarrow f$ means that a p orbital in Ψ_0 is replaced by an f orbital in Ψ_K. Since the ground-state configuration of a rare-earth ion consists of the closed shells ($1s^22s^23p^6\cdots 5s^25p^6$) and an open shell ($4f^q$), where q= number of $4f$ electrons, it is readily seen what limitations are imposed by the selection rules of Table I on the excited configuration Ψ_K quite aside from any restrictions imposed by the exclusion principle.

TABLE I. Enumeration of the allowed interacting configurations for V_2^0 and V_4^0 fields; e.g., $p\rightarrow f$ denotes that Ψ_k obtained by replacing a p one-electron orbital by an f one-electron orbital.

V_2^0	V_4^0
$s\rightarrow d$	$s\rightarrow g$
$p\rightarrow p$	$p\rightarrow f$
$p\rightarrow f$	$p\rightarrow h$
$d\rightarrow s$	$d\rightarrow d$
$d\rightarrow d$	$d\rightarrow g$
$d\rightarrow g$	$d\rightarrow i$
$f\rightarrow p$	$f\rightarrow p$
$f\rightarrow f$	$f\rightarrow f$
$f\rightarrow h$	$f\rightarrow h$
	$f\rightarrow j$

Crystal-field shielding terms arise from the interaction between the distorted charge distribution and the $4f$ electrons. These energy contributions are straightforwardly evaluated, as they are expressed in terms of matrix elements of the two-electron Coulomb operator between, for example, Ψ_K and Ψ_0; i.e., $\langle\Psi_K|r_{12}^{-1}|\Psi_0\rangle$. Since Ψ_K and Ψ_0 differ by but a single orbital ($\varphi_i^0\rightarrow\varphi_i^K$), it follows simply that

$$\langle\Psi_K|r_{12}^{-1}|\Psi_0\rangle=\sum_{4f\text{ shell}}\int[\varphi_i^K(1)\varphi_{4f}^K(2)]^*\times\frac{1-P_{12}}{r_{12}}\varphi_i^0(1)\varphi_{4f}^0(2)dv_1dv_2 \quad (3)$$

represents the interaction with the $4f$ shell. Here, P_{12} is the permutation operator which exchanges coordinates 1 and 2 so that Eq. (3) contains both direct Coulomb and exchange contributions.[9a]

As in the C. I. case, the combining coefficients C_K should be determined by solution of the full secular equation obtained by minimizing the total energy of Ψ using the Hamiltonian $H=H_0+V_c$. This we shall not do. Instead, we shall rely on a perturbation theory approach which, although less accurate, offers a number of computational and conceptual advantages. In particular, it allows us to relate the crystal-field shielding problem to Sternheimer quadrupole antishielding,[10] to which it is formally quite similar, and to discuss the calculations in terms of the perturbation of the one-electron orbitals directly, rather than more cumbersomely in terms of determinants. It should be emphasized, however, that there are two important differences between the crystal-field and the Sternheimer antishielding cases. First, unlike the case of hyperfine interactions, the crystal-field shielding involves interelectronic interactions; hence, as shown in Eq. (3) the full two-electron Coulomb and exchange interactions between the $4f$ and the distorted closed shells must be accounted for. Secondly, the $4f$ shell is open and so we must account for any coupling between it and a closed shell which affects the closed shell's distortions. We will see that these couplings are important for crystal-field shielding but are not important in estimates of the quadrupole antishielding for an open shell rare-earth ion.

To analyze the results we shall find it convenient to use the concept of "linear shielding." As we shall see, the interaction terms may be classed as to whether or not they can be cast into the form of a shielding factor times the crystal field strength, i.e., as

$$\Delta E=\langle 4f|V_n^0(1-R_n)|4f\rangle, \quad (4)$$

where R_n accounts for the shielding. Terms which, for symmetry reasons, can be characterized by an R_n contribution, will be called "linear shielding" terms in what follows. However, a number of the shielding terms (including any second-order shielding) cannot be conveniently cast into the form of Eq. (4). For this reason we will compute the crystal-field shielding energy for each of the four $|M_L|(=|m_l|)$ states of the Ce^{3+} ion and will compare these with the levels appropriate to the unscreened potential. It is from such comparisons in these cases that we derive our conclusions concerning both linear and nonlinear shielding.

[9a] It should be noted that Eq. (3) equals the full matrix element of our free-ion multielectron Hamiltonian between Ψ_k and Ψ_0 *only* if the l values of φ_i^k and φ_i^0 differ (although m_l and m_s values are the same). Otherwise there are additional terms (see Ref. 8).

[10] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954); R. M. Sternheimer, *ibid.* **96**, 951 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956); R. M. Sternheimer, *ibid.* **80**, 102 (1950); **84**, 244 (1954); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957).

A. Radial Shielding

It is readily seen in Table I that the excited configurations Ψ_K fall into two categories depending on whether l, the orbital angular momentum quantum number of φ_i^K, is the same or is different from that in φ_i^0. Following Sternheimer, we shall call the $l\rightarrow l$ terms "radial" shielding and the $l\rightarrow l'$ terms (with $l'\neq l$) "angular" shielding.

As seen in Table I, closed-shell radial shielding occurs for p and d shells in a V_2^0 field and for d shells in a V_4^0 field. Since the occupied $3d$ and $4d$ shells of a rare-earth ion are well in its interior, they contribute but small shielding terms to V_4^0 and so we will not consider these here.

For calculating the V_2^0 radial shielding, we may simplify the calculations considerably by making use of a previous investigation[11] in which it was shown that the radial excitations (in a V_2^0 field) may be obtained from an UHF calculation. In this method, the electrons in a given nl shell having different m_l values are allowed to have different radial wave functions. Such a calculation for the Ce^{3+} ion in a V_2^0 field has been reported[12] and, as this supplies us with the radially distorted p and d shells, we now need only to investigate the interactions of these shells with the $4f$ electron. Of the set of calculations reported,[12] the results which are of particular use to us here come from the calculation in which (a) the single $4f$ electron was forced to make spherical (i.e., the conventional HF) contributions to the H-F potential and (b) the V_2^0 potential (plus intershell repercussions) was allowed to distort the closed shells.[13]

Given the distortions (in the form of UHF radial functions) and given the $4f$ orbital behavior, it then becomes a simple matter to evaluate the shielding. Noting that the radial behavior of individual orbitals within the distorted electron shells is independent of the sign of their m_s and m_l quantum numbers, the interaction energy of a distorted closed p shell with the $4f$ electron may be written as,

$$\begin{aligned}\Delta E_{p\rightarrow p}(4f,m_l')=\tfrac{4}{5}c^2(4f,m_l';4f,m_l')\\ \times[F^2(4f,m_l';p,0)-F^2(4f,m_l';p,\pm1)]\\ -[c^2(4f,m_l';p,0)]^2G^2(4f,m_l';p,0)\\ -\textstyle\sum_{\pm}[c^2(4f,m_l';p,\pm1)]^2G^2(4f,m_l';p,\pm1)\\ -[c^4(4f,m_l';p,0)]^2G^4(4f,m_l';p,0)\\ -\textstyle\sum_{\pm}[c^4(4f,m_l';p,\pm1)]^2G^4(4f,m_l';p,\pm1)\quad(5)\end{aligned}$$

and for a distorted d shell as,

$$\begin{aligned}\Delta E_{d\rightarrow d}(4f,m_l')=(4/7)c^2(4f,m_l';4f,m_l')\\ \times[F^2(4f,m_l';d,0)+F^2(4f,m_l';d,\pm1)\\ -2F^2(4f,m_l';d,\pm2)]+F^4,\ G^1,\ G^3,\\ \text{and}\quad G^5\ \text{terms}.\quad(6)\end{aligned}$$

Here the $c^k(l,m_l;l',m_l')$, the Condon and Shortley coefficients,[14] are integrals of the product of three spherical harmonics,

$$F^k(i,j)=R^k(ij;ij);\quad G^k(i,j)=R^k(ij;ji),$$

$$R^k(ab;cd)=\int_0^\infty\int_0^\infty U_a(r_1)U_b(r_2)(r_<^k/r_>^{k+1})\times U_c(r_1)U_d(r_2)dr_1dr_2,\quad(7)$$

and the U_i are one-electron radial functions. The F^2 terms of Eqs. (5) and (6) obviously produce linear shielding, since the unscreened matrix elements. $\langle 4f|V_2^0|4f\rangle$, of V_2^0 are proportional[15] to $c^2(4f,m_l;4f,m_l)$. Closer inspection of the remaining exchange terms (G^k) of $\Delta E_{p\rightarrow p}$ shows them also to produce linear shielding.[16] The G^1, G^3, and G^5 terms of $\Delta E_{d\rightarrow d}$ are linear shielding but are zero to the accuracy to which they can be computed. The F^4 term is zero valued from symmetry considerations. The inclusion of these terms would affect our results by no more than one unit in the last digit which we shall report; hence, we shall neglect them.

Given the distorted UHF wave functions for the p and d shells, the evaluation of their contribution to radial crystal-field shielding is, or rather would be, straightforward if it were not for the question of which $4f$ orbital (or orbitals) to insert into Eqs. (5) and (6). That there might be some question is indicated by Table II where we compare various $\langle 4f|r^n|4f\rangle$ integrals, i.e.,

$$\langle i|r^n|j\rangle=\int_0^\infty U_i(r)r^nU_j(r)dr\quad(8)$$

evaluated for the V_2^0 field UHF results[12] and for a RHF calculation done with the same basis set.[17] We see a several percent variation in $\langle 4f|r^2|4f\rangle$ and even larger variations for higher powers of r, which suggests that the $4f$ shell varies noticeably from one crystal-field level to another. In order to decouple the closed-shell shielding effects from such $4f$ orbital variation, we will

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[11] R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 250 (1963).

[12] A. J. Freeman and R. E. Watson, Phys. Rev. **132**, 706 (1963).

[13] In such a procedure, we take the second-order perturbation approach, common (Ref. 3) to Sternheimer antishielding investigations (cf. Appendix in Ref. 3), of letting one aspherical interaction (in this case the V_2^0 field) distort the ions closed shells and then studying the interaction of these with another aspherical source (the $4f$ electron). While this approach avoids certain serious complications, it has its limitations for treating the crystal shielding problem and will not always be followed in subsequent sections.

[14] See E. U. Condon and G. H. Shortley *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), Chap. VI. The c^k integrals are tabulated on pp. 178–179.

[15] The $c^2(4fm_l;4fm_l)$'s hence the $\langle 4f|V_2^0|4f\rangle$'s have values proportional to ±4, ±3, 0, ∓5 for the $m_l=0$, ±1, ±2, and ±3 levels, respectively.

[16] This follows from the symmetry of the c^k's irrespective of details of the radial distortions, as is shown in Appendix II.

[17] We are relying on analytic H-F calculations and computational considerations necessitated using a smaller basis set than was used in a previously reported RHF calculation for Ce^{3+} [A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962)].

TABLE II. Comparison of $\langle 4f|r^n|4f\rangle$ integrals as obtained from the Ce^{3+} UHF calculation (Ref. 10) used in the shielding estimates and from a RHF calculation using the same basis set (Ref. 17). All integrals are in a.u.

	UHF	RHF
$\langle 4f|r^{-3}|4f\rangle$	4.66	4.71
$\langle 4f|r^2|4f\rangle$	1.23	1.21
$\langle 4f|r^4|4f\rangle$	3.70	3.49
$\langle 4f|r^6|4f\rangle$	23.7	21.6

evaluate Eqs. (5) and (6) and their angular counterparts with a single $4f$ radial function. Rather arbitrarily we have selected this orbital from the V_2^0 field UHF calculation. We shall discuss the effects of $4f$ orbital variation in Sec. V.

B. Angular Shielding

The remaining and more numerous $l\rightarrow l'$ $(l'\neq l)$ terms of Table I make up the angular shielding contributions. Unfortunately, we cannot currently carry out a UHF treatment of the angular shielding[11] as this requires substantial modifications in existing H-F computational machinery. Instead, we shall use the C. I. scheme described above and determine estimates of the C_K from perturbation theory.

To first order, C_K is simply given by

$$C_K=\frac{\langle\Psi_K|V_c|\Psi_0\rangle}{E_0-E_K}=\frac{\langle\varphi_i^K|V_c|\varphi_i^0\rangle}{E_0-E_K}\tag{9}$$

and the energy contribution of Ψ_K to the same order is

$$\delta E=C_K\langle\Psi_K|V_c|\Psi_0\rangle=\frac{|\langle\varphi_i^K|V_c|\varphi_i^0\rangle|^2}{E_0-E_K}.\tag{10}$$

The leading shielding contributions, i.e., the additional electrostatic interactions (arising from the distorted closed shells) experienced by the $4f$ electrons, may now be written down quite simply as

$$\begin{aligned}\Delta E^{(1)}&=\langle\Psi|r_{12}^{-1}|\Psi\rangle_{4f}-\langle\Psi_0|r_{12}^{-1}|\Psi_0\rangle_{4f}\\&=2\sum_K C_K\langle\Psi_K|r_{12}^{-1}|\Psi_0\rangle_{4f}\\&=2\sum_K\frac{\langle\varphi_i^K|V_c|\varphi_i^0\rangle}{E_0-E_K}\langle\Psi_K|r_{12}^{-1}|\Psi_0\rangle_{4f},\end{aligned}\tag{11}$$

where the subscript $4f$ reminds us that we are interested here in just the $4f$ part of the interaction energy. In addition to the terms listed in Eq. (11), part of the second-order terms in C_K, arising from the normalization requirement for Ψ, make a second-order contribution to Eq. (11) which is

$$\begin{aligned}\Delta E^{(2)}&=\textstyle\sum_K C_K^2\{\langle\Psi_K|r_{12}^{-1}|\Psi_K\rangle-\langle\Psi_0|r_{12}^{-1}|\Psi_0\rangle\}\\&=\sum_K\left[\frac{\langle\varphi_i^K|V_c|\varphi_i^0\rangle}{E_0-E_K}\right]^2\\&\qquad\times\{\langle\Psi_K|r_{12}^{-1}|\Psi_K\rangle-\langle\Psi_0|r_{12}^{-1}|\Psi_0\rangle\}.\end{aligned}\tag{12}$$

These *incomplete* second-order terms are kept in what follows as a test of the validity of the first-order perturbation theory approach; we shall, in fact, later see a case, when dealing with hyperfine effects, where a small first-order term causes the second-order terms to dominate.

We shall concentrate our attention on the $5p\rightarrow 4f$ distortions, which one expects to be the most important contribution to the angular shielding because of the small denominator in its C_K for a correspondingly substantial numerator. This result is in fact, obtained by L & W who find a 30% shielding contribution to V_2^0 (out of a total of 59%) and almost the entire V_4^0 shielding (17%) from this term alone. [We shall rely on L & W for perturbation theory estimates of the other angular shielding terms (i.e., $5p\rightarrow 5f$ and $5s\rightarrow d$ for V_2^0).] Our approach will be to take the results of a H-F calculation for Ce^{3+}, and to estimate the effect of a V_2^0 or V_4^0 field in mixing $4f$-like excitations into the $5p$-shell orbitals. We will denote the unoccupied $4f$ orbitals involved in the mixing by $f^\star$, and will constrain them to have the same radial behavior as the single occupied $4f$ orbital obtained in the H-F calculations (for which the symbol $4f$ will be reserved).

In a V_n^0 field, the interaction of a p shell, distorted by a $p\rightarrow f^\star$ excitation, with the $4f$ electron (whose magnetic and spin quantum numbers are denoted by m_l' and m_s', respectively) is given by

$$\begin{aligned}\Delta E^{(1)}{}_{p\rightarrow f^\star}=\sum_{m_l,m_s}{}'\Bigg\{&\frac{2\langle p|V_n^0|f^\star\rangle}{E_p-E_{f^\star}}\\&\times\sum_{k=2,4}[c^k(4f,m_l';4f,m_l')c^k(p,m_l;f^\star,m_l)\\&\times\mathfrak{F}^k(f^\star,4f;p,4f)-\delta(m_s,m_s')c^k(p,m_l;4f,m_l')\\&\qquad\times c^k(f^\star,m_l;4f,m_l')\mathcal{G}^k(4f,f^\star;p,4f)]\Bigg\},\end{aligned}\tag{13}$$

with a second-order contribution from Eq. (12):

$$\begin{aligned}\Delta E^{(2)}{}_{p\rightarrow f^\star}=\sum_{m_l,m_s}{}'&\left[\frac{\langle p|V_n^0|f^\star\rangle}{E_p-E_{f^\star}}\right]^2\\&\times\{\sum_{k=0,2,4,6}c^k(4f,m_l';4f,m_l')c^k(f^\star,m_l;f^\star,m_l)F^k(4f,f^\star)\\&-\sum_{k=0,2}c^k(4f,m_l';4f,m_l')c^k(p,m_l;p,m_l)F^k(4f,p)\\&-\delta(m_s,m_s')\sum_{k=2,4,6}[c^k(4f,m_l';f^\star,m_l)]^2G^k(4f,f^\star)\\&+\delta(m_s,m_s')\sum_{k=2,4}[c^k(4f,m_l';p,m_l)]^2G^k(4f,p)\},\end{aligned}\tag{14}$$

TABLE III. Radial shielding contributions in au from the $4p$, $5p$, and $4d$ shells, obtained by evaluating Eqs. (5) and (6). The $5p$ shell F^2, G^2, and G^4 are given separately; for comparison, the unscreened $\langle 4f|V_2^0|4f\rangle$ matrix elements are also listed.

$4fm_l'$	5p shell terms F^2	 G^2	 G^4	 Total	4p shell total	4d shell total	All shells	$\langle 4f\|V_2^0\|4f\rangle$
0	−0.00183	0.00033	0.00009	−0.00142	−0.00002	−0.00012	−0.00155	−0.0105
±1	−0.00137	0.00025	0.00007	−0.00104	−0.00001	−0.00009	−0.00116	−0.0079
±2	...	...	...	...	...	...	...	...
±3	0.00228	−0.00041	−0.00011	0.00176	0.00002	0.00014	0.00193 ∼15% antishielding	0.0131

where we have used the notation

$$\mathcal{F}^k(f^\star 4f;p4f)\equiv R^k(f^\star 4f;p4f) \tag{15}$$

and

$$\mathcal{G}^k(4ff^\star;p4f)\equiv R^k(4ff^\star;p4f) \tag{16}$$

to emphasize direct and exchange terms, respectively. The $\sum'$ indicates that the m_l+m_s summation must exclude the m_l' and m_s' values of the $4f$ electron, as required by the exclusion principle. This means that $\sum'$ consists of five terms if $m_l'=0$ or ±1 for the $4f$ electron and six terms otherwise.

One other feature of the exclusion principle needs stating. Not only is a shielding term lost in this way, but there is in addition, a loss of energy, given by Eq. (10), which is associated with the distortion. Such a term provides an m_l'-dependent crystal-field energy, and so, as discussed earlier, contributes to the "shielding." We shall see that this contribution is not insignificant.

We will consider $\mathcal{F}^k$ and $\mathcal{G}^k$ terms separately in what follows but it should be noted that for Ce^{3+} the effect of the exclusion principle disappears if we consider a $(\mathcal{F}^k,\mathcal{G}^k)$ pair, of given k, together. That the excluded $\mathcal{F}^k$ term of Eq. (13) is exactly equal, but opposite in sign, to its partner $\mathcal{G}^k$ term becomes immediately apparent if we observe (1) that the $\mathcal{F}^k$ integral equals $\mathcal{G}^k$ (since the $4f$ and $f^\star$ orbitals have been constrained to have the same radial behavior) and (2) the obvious fact that $m_l'(4f)=m_l(f^\star)$ for the excluded terms. This is a nice, and often exploited, feature of the H-F treatment of interelectronic effects.

We will use the UHF Ce^{3+} orbitals when evaluating Eq. (13), i.e., the radially distorted $5p$ shell will be the starting point for the $5p\rightarrow 4f$ estimate. We will again require the individual $5p$ and $4f$ orbitals to maintain constant radial behavior for the various m_l' states.

A literal evaluation of Eq. (10), (11), (12), (13), or (14) is made tedious by the fact that the energy denominators are functions of the m_l and m_s values of both the $p\rightarrow f^\star$ and the $4f$ orbitals. In order to simplify matters we will use averaged $E_p-E_{f^\star}$ values of -0.72 and -0.68 a.u. for m_l (of $f^\star$)$=0$ and ±1, respectively, although individual $E_p-E_{f^\star}$ values actually differ by as much as 5% from these numbers. While a careful accounting of the individual terms which occur leads to an array of small contributions to the shielding, summing over sets of $\Psi_{p\rightarrow f^\star}$ orbitals reduces the effect of this for $\mathcal{F}^k$ shielding terms. The evaluation of Eq. (13) with these $E_p-E_{f^\star}$ values will lead to important nonlinear $\mathcal{G}^k$ shielding terms, terms which would be linear shielding only if we used a single-energy denominator in that equation. The treatment of the energy denominators is therefore critical to any detailed quantitative accounting of nonlinear shielding, a matter which we will not attempt in this paper.[18]

We will have occasion to inspect second-order as well as first-order crystal-field terms which involves abandoning a simple linear polarization approach to the shielding and requires that the calculation be done with a specific crystal-field potential. For the V_2^0 shielding calculations, we shall use the potential used previously,[12] namely, that due to a pair of point charges of 2 a.u. each, located 5 a.u. along the z axis to either side of the Ce nucleus, with sign such that the $m'_l=0$ state has lowest energy. This field is stronger than those normally encountered in rare-earth salts.

III. CLOSED-SHELL V_2^0 SHIELDING RESULTS

Radial shielding contributions arising from the $4p$, $5p$, and $4d$ shells were obtained by evaluating Eqs. (5) and (6) in the manner discussed in the preceding section. Results are listed in Table III, which also lists the individual $5p$, F^k, and G^k terms separately and, for comparison, the unscreened $\langle 4f|V_2^0|4f\rangle$ matrix elements. In Table III, and in subsequent tables, we follow a procedure of shifting the zero in a set of energy levels whenever convenient (e.g., this has been with the G^2 and G^4 columns of Table III so that zeros occur in the $|m_l'|=2$ row, thereby making their linear shielding apparent).

These radial terms have *enhanced* the crystal-field interaction by 15% due almost entirely to the $5p$ shell. It is seen that only a one percent antishielding arises from the inner $4p$ and $4d$ shells; it is perhaps surprising

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[18] One may have to abandon perturbation theory (and the associated questions of varying energy denominators and the exclusion principle) and utilize configuration interaction methods on any attempt at detailed results. Several $p\rightarrow f$ configuration interaction calculations will be reported in a subsequent paper in an effort to better resolve nonlinear shielding behavior.

TABLE IV. Summary of $5p \rightarrow f^\star$ shielding contributions to V_2^0. Individual $\mathcal{F}^k$ and $\mathcal{G}^k$ contributions are listed along with δE from Eq. (10) and the second order terms of Eq. (14). For comparison the shielding associated with just the $\mathcal{F}^2$ term ignoring the exclusion principle is also given (in au).

	First-order terms of Eq. (13)							
$4fm_l'$	$\mathcal{F}^2$	$\mathcal{F}^4$	$\mathcal{G}^2$	$\mathcal{G}^4$	δE of Eq. (10)	Total shielding energy	$\mathcal{F}^2$ terms only ignoring exclusion principle	Sum of second-order terms of Eq. (14)
0	0.00269	−0.00037	0.00026	−0.00026	0.00056	0.00288	0.00340	−0.00012
±1	0.00218	−0.00002	0.00003	−0.00044	0.00040	0.00215	0.00255	−0.00010
±2	...	...	...	...	...	...	...	...
±3	−0.00425	−0.00002	0.00064	0.00070	...	−0.00293 ∼25% Shielding	−0.00425 ∼32% Shielding	−0.00007

that these terms play even this large a role. The antishielding would be 25% larger if it were not for the exchange (G^k) terms which, as is common, are in opposition to the direct terms and are of significant magnitude. Lenander and Wong's 10% antishielding estimate was obtained for the $5p\,F^2$ term alone for which we obtain 18%. In addition to any differences introduced by the two computational methods, the difference is due primarily to their use of Hartree and approximate Hartree-Fock-Slater functions and the different ions considered (Pr^{2+} versus Ce^{3+}).

In Table IV, we summarize the angular $5p \rightarrow f^\star$ shielding contributions. Note that the four $\mathcal{F}^k$ and $\mathcal{G}^k$ terms of Eq. (13) which are listed do not make linear contributions to the shielding [i.e., to an R_n of Eq. (4)]: The $\mathcal{F}^4$, $\mathcal{G}^2$, and $\mathcal{G}^4$ terms do not, because of symmetry; the direct $\mathcal{F}^2$ term, which might otherwise, does not because the exclusion principle has knocked out terms in the sums for the $4f$ states having $m_l'=0$ and ± 1. (The radial integrals necessary for the evaluation of these terms are given in Appendix I.) Together, these terms add up to a 25% crystal-field shielding contribution. Table IV shows the four shielding energies of the m_l' states to conform roughly to the 4, 3, 0, −5 spacing characteristic[15] of the $\langle 4f|V_2^0|4f\rangle$ values. The agreement would be very good if the $m_l'=\pm 3$ term were somewhat larger in magnitude; the deviation of this level's position is largely due to the contribution from $\mathcal{G}^2$ and $\mathcal{G}^4$ exchange terms.

As an instructive comparison, we also list in Table IV the $\mathcal{F}^2$ term evaluated ignoring the exclusion principle (i.e., $\sum'$ is replaced by $\sum$ which goes over six terms for all $4fm_l'$ values) as this is the form of Lenander and Wong's estimate. Our result, which shows a 32% linear shielding value, is remarkably close to the 30% value obtained by L & W; both values are somewhat larger than the 25% shielding obtained above from the more exact treatment.

Also listed in the Table IV are the $p \rightarrow f$ perturbation energies, i.e., δE of Eq. (10), arising from the exclusion principle. Their effect is to compensate for the effect of the exclusion principle (via $\sum'$) on the dominant $\mathcal{F}^2$ term, as is seen from Table IV. Finally, the sum of second-order terms of Eq. (14) are listed in Table IV (but are not included in the shielding summations); as one would hope, these have proven to be unimportant.

The sum of radial and $5p \rightarrow f$ shielding is listed and compared with $\langle 4f|V_2^0|4f\rangle$ values in Table V. Here the depression of the $m_l'=\pm 3$ level is more apparent.

TABLE V. Comparison of radial plus $5p \rightarrow f^\star$ shielding energies (Tables III and IV) with the unscreened $\langle 4f|V_2^0|4f\rangle$ terms (in au).

$4fm_l'$	Radial plus $5p \rightarrow f^\star$ shielding energies	$\langle 4f\|V_2^0\|4f\rangle$	Shielding (col. I/col. II) in %
0	0.0013	−0.0105	−11
±1	0.0010	−0.0079	−13
±2	...	...	...
±3	−0.0010	0.0131	−7.6

To these terms we must add the $5s \rightarrow d$ and $5p \rightarrow$ (higher) f contributions. Lenander and Wong have estimated these from the $\mathcal{F}^2$ terms (with the exclusion principle omitted) to produce almost a 40% shielding. We believe this value to represent a small underestimate of the actual direct electrostatic $\mathcal{F}^2$ effect: The exchange terms are expected to be less important than in the $p \rightarrow f^\star$ case discussed above because the overlap charge densities appearing in these integrals are correspondingly less effective. Of course, these exchange terms (along with others which have been omitted) must be included for any detailed quantitative shielding estimate. Adding the L & W estimate of the $5s \rightarrow d$ and $5p \rightarrow$ (higher) f contributions to our radial and $5p \rightarrow f^\star$ values yields a total shielding of 50%, in rough agreement with their 59% estimate. Since these additional terms are linear shielding in nature, their presence reduces the relative importance of the $m_l'=\pm 3$ level displacement thus making the set of four shielding energies conform quite well to the V_2^0 level scheme.

We must emphasize that the above estimate for Ce^{3+} includes a 25% shielding contribution from the $5p \rightarrow f^\star$ distortion. In going to other rare-earth ions, where one fills the $4f$ shell, this distortion is given less freedom to act and will almost disappear as one ap-

TABLE VI. Closed shell V_4^0 $5p \rightarrow f^\star$ shielding results using Eq. (13). The individual $\mathcal{F}^k$ and $\mathcal{G}^k$ contributions are listed along with their sum (Σ), the unscreened $\langle 4f|V_4^0|4f\rangle$ values, the shielding expressed as in percent and the $\mathcal{F}^4$ term alone ignoring the exclusion principle.

$4fm_l'$	$\mathcal{F}^2$	$\mathcal{F}^4$	$\mathcal{G}^2$	$\mathcal{G}^4$	Σ	$\langle 4fm_l'\|V_4^0\|4fm_l'\rangle$ $[=c^4(4f,m_l';4f,m_l')]$	$\Sigma/\langle\|V_4^0\|\rangle$ (in %)	$\mathcal{F}^4$, ignoring exclusion principle
0	0.0238	−0.0235	−0.0057	0.0060	0.0006	0.1818	0.2	−0.0327
±1	−0.0070	−0.0048	−0.0130	0.0004	−0.0244	0.0303	−81	−0.0054
±2	···	0.0380	0.0324	0.0041	0.0745	−0.2121	−35	0.0380
±3	−0.0025	−0.0163	−0.0142	−0.0023	−0.0353	0.0909	−40	−0.0163
								18% shielding

proaches Yb^{3+} ($4f^{13}$). Inspection of this process, however, is complicated by the fact that a proper treatment requires dealing with multideterminantal functions (in the J, M_J, L, S representation) but qualitatively it does appear that there will be a trend as one goes from Ce^{3+} to Yb^{3+}, from ~50 to ~25% shielding. We shall return to this matter later.

IV. CLOSED-SHELL V_4^0 SHIELDING RESULTS

As seen from Table I, a V_4^0 field induces $p \rightarrow f$, $s \rightarrow g$, and $p \rightarrow h$ distortions in the $5s$ and $5p$ shells. The effectiveness of the latter two are penalized by the high energies of the excited orbitals; hence, as is usual, we will ignore them. We will again concentrate on the contributions of the terms of Eq. (13) to the $5p \rightarrow f^\star$ shielding. These terms proved to be most important in the V_2^0 case and by limiting ourselves to them we need not again assume a specific field strength for V_n^0 (except for the energy denominators). As in the V_2^0 case, these terms are not linear in their shielding [cf. Eq. (4)] although the shielding energy associated with any one of them is proportional to the field strength. Their nonlinear nature follows from the exclusion principle for $\mathcal{F}^4$ (i.e., from the prime terms on the summation) *and* from symmetry (in combination with the varying energy denominators) as well for the other terms. Since we cannot simply compute an R_n, we must again evaluate the shielding energy as a function of the $4fm_l'$ value and this reintroduces the necessity of some (not necessarily physical) crystal field energy scale. We have quite arbitrarily found it convenient[19] to use one such that, very simply,

$$\langle 4fm_l|V_4^0|4fm_l\rangle \equiv c^4(4f,m_l;4f,m_l). \tag{17}$$

Using this scale, the individual terms of Eq. (13) are listed in Table VI. (The radial integrals used in the evaluation of these terms are given in Appendix I and Table II; the RHF $\langle 4f|r^4|4f\rangle$ value was used.)

Also listed in Table VI is the linear shielding version of the $\mathcal{F}^4$ term, obtained by ignoring the exclusion principle. This yields an 18% shielding in close agreement with the L & W value but in sharp contrast with our more detailed results which differ markedly from the $\langle 4fm'|V_4^0|4fm'\rangle$ energy level scheme.

When dealing with atomic multiplet spectra, one usually encounters the fact that the lower the k value, the more important the F^k and G^k energy contributions tend to be. A parallel effect appears to be operative here since, as seen from Table VI, there are substantial energy contributions which arise from the $\mathcal{F}^2$ and especially from the $\mathcal{G}^2$ terms. The result is a set of shielding energies which are almost unrecognizable related to the parent V_4^0 field. For Ce^{3+}, this is not due to the exclusion principle, since, as we have noted (see Sec. II), these effects cancel out when $\mathcal{F}^k$-$\mathcal{G}^k$ pairs are taken together.

If we adopt this alternative point of view in analyzing the results for Ce^{3+}, i.e., we ignore the exclusion principle, we see that the $\mathcal{F}^4$ term is linear shielding and the $\mathcal{F}^2$ terms lead to very small energy contributions which conform to the V_2^0 level scheme (as they must). These $\mathcal{F}^2$ terms would be zero valued if it were not for the fact that differing energy denominators were used for $5p \rightarrow f^\star$ distortions corresponding to different $|m_l|$ values. In such a description, the deviations of the energy levels in Table VI from the V_4^0 level scheme are then almost entirely due to the $\mathcal{G}^2$ and $\mathcal{G}^4$ exchange terms, with the former dominating. These contributions would have been entirely linear shielding if we had used a common energy denominator (−0.70 a.u.) in Eq. (13). In such a case we would have linear contributions of 0, 18, −15, and −2% from the $\mathcal{F}^2$, $\mathcal{F}^4$, $\mathcal{G}^2$, and $\mathcal{G}^4$, respectively, for a total of 1% shielding. We again see the extreme importance of accounting for the $\mathcal{G}^2$ behavior.

If one were faced with analyzing such a set of nonlinearly displaced energy levels for an ion in an actual crystal, one might well try to fit them by assuming the ion to be in a crystal potential of $V_2^0+V_4^0+V_6^0$ symmetry. Let us do just this using the numerical results of Table VI. Using Eq. (1) in its integrated form leads to setting up an equation of the form

$$\Delta E_c = \sum\nolimits_n \langle 4f|V_n^0|4f\rangle + D, \tag{18}$$

where D incorporates all contributions which are

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[19] In this scheme, represented by Eq. (17), the shielding energy divided by $c^4(4f,m_l';4f,m_l')$ is simply the R_n appropriate to that $4fm_l'$ value. We cannot manipulate the resulting set of four R_n's (e.g., shiting the zero of energy, or doing a crystal-field fit of the levels) and have therefore resorted to the closely related set of energy levels defined so that Eq. (17) holds.

TABLE VII. The V_2^0, V_4^0, and V_6^0 energies of Eqs. (18) obtained by solving Eq. (19). (See text for discussion and compare with Table VI.)

$4fm_l'$	$\langle 4f\vert V_2^0\vert 4f\rangle$	$\langle 4f\vert V_4^0\vert 4f\rangle$	$\langle 4f\vert V_6^0\vert 4f\rangle$	Center of gravity (D term)	Total
0	0.0100	−0.0507	+0.0370	+0.0043	0.0006
±1	0.0075	−0.0084	−0.0278	+0.0043	−0.0244
±2	···	+0.0591	+0.0111	+0.0043	0.0745
±3	−0.0124	−0.0253	−0.0019	+0.0043	−0.0353

independent of m_l' and affects only the center of gravity of the set of levels. For our specific case, we must solve the following crystal-field energy expressions:

$$\begin{aligned} 0.0006&=4\langle\bar{V}_2^0\rangle+6\langle\bar{V}_4^0\rangle+20\langle\bar{V}_6^0\rangle+D\,,\\ -0.0244&=3\langle\bar{V}_2^0\rangle+\langle\bar{V}_4^0\rangle-15\langle\bar{V}_6^0\rangle+D\,,\\ 0.0745&=0\langle\bar{V}_2^0\rangle-7\langle\bar{V}_4^0\rangle+6\langle\bar{V}_6^0\rangle+D\,,\\ -0.0353&=-5\langle\bar{V}_2^0\rangle+3\langle\bar{V}_4^0\rangle-\langle\bar{V}_6^0\rangle+D\,. \end{aligned} \tag{19}$$

We have simplified the form of Eq. (19) by writing only the numerator of the $c^n(4f,m_l';4f,m_l')$ coefficients; the denominators have been incorporated in the radial part of the V_n^0 matrix elements, as denoted by the bar. The solutions of Eqs. (19), expressed as values of $\langle 4f|V_n^0|4f\rangle$, are given in Table VII. A set of V_4^0 terms equivalent to 28% shielding plus V_2^0 and V_6^0 energies of similar magnitude have been produced. The V_4^0 shielding result is to be compared with the 18% obtained by the simpler approach of L & W. However, it is the V_2^0 and V_6^0 terms which are of greatest interest to our discussion as these terms would contribute additively to the energies associated with any V_2^0 or V_6^0 crystalline potential actually present. If the results of Table VII are typical, these additive contributions would most seriously affect the apparent V_6^0 energies for these tend to run smaller, whereas V_2^0 terms usually run larger than the V_4^0 energies themselves. This phenomenon has serious implications for observed crystal-field spectra and will be returned to later.

There are additional V_4^0 shielding terms such as $5p\rightarrow h$ and $4d\rightarrow d$; we expect that the net effect of these to be a small (i.e., one or a few percent) and approximately linear shielding contribution. The $5p\rightarrow h$ distortion also occurs for V_6^0 fields (likewise the $4d\rightarrow d$ appears for V_2^0) with shielding contributions coming from $\mathcal{F}^4$, $\mathcal{F}^6$, $\mathcal{G}^4$, and $\mathcal{G}^6$ integrals. These terms create a similar situation to that seen for the $5p\rightarrow f$ term and raise the possibility of yet further shielding which also deviate away from the parent V_n^0 field. These terms are already small; hence, any such deviations would be of but minor interest.

V. THE ROLE OF 4f ORBITAL VARIATION

In the above investigations, we require that the $4f$ and $f^\star$ orbitals have identical radial functions and that this dependence be common to all the crystal-field levels. If we had dealt with an ion with more than a single $4f$ electron in its ground configuration we would have followed the standard procedure of requiring, in addition, a common radial orbital for all $4f$ electrons. The experience of the preceding sections and the integral values quoted in Table II, suggest that the relaxation of one or several of these constraints could have experimentally observable repercussions on the predicted crystal-field levels of a rare-earth ion. We expect these effects to be smaller, however, than those already reviewed and we will, therefore, not attempt quantitative estimates.

Ce^{3+} with its single $4f$ electron avoids the question of angular and radial distortions causing varying $4f$ orbital behavior within an open $4f$ shell and their effects on its crystal-field interaction. Here we need only consider the distortions associated with a single $4f$ electron and their variation for different crystal-field levels. Such variations (or any angular distortion for that matter) will tend to distort the crystal-field levels away from the splitting scheme appropriate to the unscreened crystal field. This is best seen by a simple example.

Consider the $4f$ electron in a V_2^0 field of the form given by Eq. (1). Its energy levels are displayed in Fig. 1 showing the familiar −4, −3, 0, +5 level scheme (assuming the $m_l'=0$ state is lowest). Allowing the $4f$ orbital to have different radial functions in the different levels results in an expanded radial function for the $m_l'=0$ and ±1 states, an unmodified distribution for $m_l'=\pm2$, and a contracted function for $m_l'=\pm3$. To a first approximation this will cause the second-order energy shifts, in units of the parameter δ, shown in Fig. 1. Also shown are the effects of the allowed $4f\rightarrow h$ and $4f\rightarrow p$ angular distortions, in units of the parameters δ' and δ''; the various splittings are proportional to the appropriate $[c^2(4f,m_l';nl,m_l')]^2$ values. Since the V_2^0 field preserves the m_l quantum number, only the $m_l=0$ and ±1 levels are affected by the $4f\rightarrow p$ distortions. Unrealistically large δ, δ', and δ'' values (relative to Δ) were used in the figure. Only by accident will these distortions make a linear shielding contribution to the crystal-field levels; their main effect will be to cause deviations from that level scheme and only the small magnitude of these terms saves us from having to consider these complications. Table II indicates that the radial distortions cause but a two percent lowering

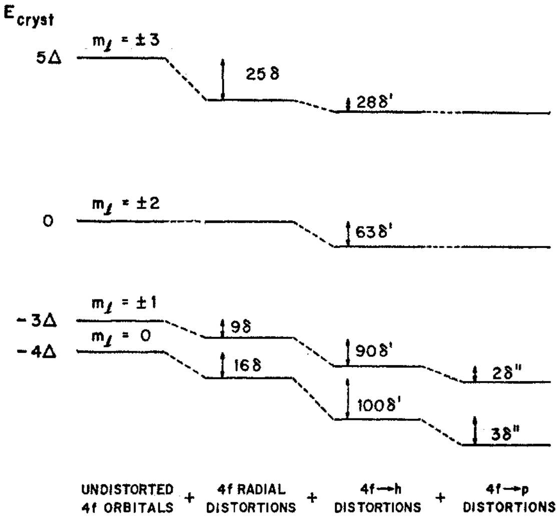

FIG. 1. Energy levels of a $4f$ electron in a V_2^0 field showing the effects of various distortions in arbitrary units of the parameters Δ, δ, δ', and δ'' (not to scale).

of the $m_l=0$ level when obtained from a UHF calculation in a strong field. We expect that the combined influence of radial and angular distortions will, for more normal V_2^0 field strengths, lead to level shifts of under one percent.

The situation is further complicated if we consider the ion under the combined influence of several V_n^0 fields and the complications increase as we go to ions with more $4f$ electrons and/or go over to the more appropriate (JM_JLS) coupling scheme. Whatever the case, there will be a tendency for the crystal fields to cause an expansion of the $4f$ radial wave function for the negative m_l energy levels and a contraction for the positive energy states. Again we expect the repercussions to be negligibly small except perhaps for the V_6^0 energies. Table II shows the $\langle 4f|r^6|4f\rangle$ integral to be approximately five times as sensitive to orbital variation as is $\langle 4f|r^2|4f\rangle$. This sensitivity is of course not surprising and leads to the distinct possibility that V_2^0 and V_4^0 fields in concert with a V_6^0 field could produce $4f$ shell distortions which have repercussions of observable magnitude on the direct V_6^0 energies alone. Such effects, if they did occur, would probably be hidden by the crystal-field level distortions discussed in the preceding section.

VI. CRYSTAL-FIELD CONTRIBUTIONS TO HYPERFINE INTERACTIONS

In this section, we examine the role of the crystalline field in producing, by means of the distortions of the electronic shells of the system, both electric quadrupole and magnetic dipole contributions to the hyperfine interaction. As mentioned in Sec. II, the crystal-field shielding problem is formally similar to the calculation of the Sternheimer external field quadrupole antishielding factor (γ_∞). We shall, therefore, consider this contribution first and then go on to discuss the magnetic hyperfine interactions.

We have previously computed[12] (γ_∞) for the Ce^{3+} ion, in a study which was limited to the dominant radial antishielding terms. There exist, however, small angular terms as well as it is instructive to inspect the behavior of $\gamma_{5p\to f^\star}$ here. The $5p\to f^\star$ quadrupole field contributions are easily obtained by using Eqs. (11) and (12) only with the operator r_{12}^{-1} replaced everywhere by the operator

$$H_q=(16\pi/5)^{1/2}Y_2^0(\theta,\varphi)r^{-3}=(3\cos^2\theta-1)r^{-3}. \quad (20)$$

In the sum over K states, we must again take all the appropriate $5p$ and $f^\star$ values, and divide the result by the unshielded external field gradient to obtain[10] the resulting $\gamma_{5p\to f^\star}$ contribution to γ_∞. Values of γ_∞ are listed in Table VIII as a function of the m_l' value of the $4f$ electron; the variation in values is due to the exclusion principle which is *not* compensated for by an exchange term (since we are here dealing with a one-electron operator). Including the (incomplete) second order terms of Eq. (12), however, appreciably perturbs the results, and is due to the small magnitude of the linear term of Eq. (11) which is in turn caused by the very small $\langle 5p|r^{-3}|f^\star\rangle$ value of 0.07 au as compared with $\langle 5p|r^{-3}|5p\rangle$ and $\langle f^\star|r^{-3}|f^\star\rangle$ values of ~40 and 4.6 au, respectively. The $5p$ radial orbital has a number of nodes near the nucleus while the $4f$ does not; hence, the overlap charge density varies in sign in this region and produces a small $\langle f^\star|r^{-3}|5p\rangle$ matrix element. (Since these nodes are concentrated in the interior of the ion, they do not cause a reduction in the $\langle f^\star|r^n|5p\rangle$ integrals, for $n>0$, which are vital to all $5p\to f^\star$ effects.) The $\gamma_{5p\to f^\star}$ results of Table VIII are to be compared with a radial antishielding[12] of -73.5 and are seen to be insignificant.

TABLE VIII. The $5p\to f^\star$ contributions to γ_∞ as a function of crystal field level (i.e., $4fm_l'$ value) for Ce^{3+}.

$4fm_l'$	$\gamma_{5p\to f^\star}$ from Eq. (11)	$\gamma_{5p\to f^\star}$ including terms from Eq. (12)
0	0.19	0.52
±1	0.21	0.02
±2	0.24	0.22
±3	0.24	0.22

Let us now consider the repercussions a crystal field may have on the direct $4f$ magnetic hyperfine interactions. These too will be seen to be small but not insignificant.

The hyperfine effects of interest to us can be introduced[20] by using $\langle r^{-3}\rangle_i$ *parameters* in place of the

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[20] For example, see A. J. Freeman and R. E. Watson, Phys. Rev. **131**, 2566 (1963); A. J. Freeman and R. E. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published) for a discussion of this.

$\langle 4f|r^{-3}|4f\rangle = \langle r^{-3}\rangle$ *integrals* appearing in the standard expressions

$$H_{\mathrm{L \cdot I}} = (\mu/I)\langle r^{-3}\rangle \sum_{i}^{4f\text{ shell}} \mathbf{l}\cdot\mathbf{I}, \tag{21}$$

$$H_{\mathrm{SD}} = (\mu/I)\langle r^{-3}\rangle \sum_{i}^{4f\text{ shell}} \{3(\mathbf{s}_i\cdot\mathbf{r}_i/r_i)(\mathbf{I}\cdot\mathbf{r}_i/r_i) - \mathbf{s}_i\cdot\mathbf{I}\}, \tag{22}$$

where $H_{\mathrm{L \cdot I}}$ and H_{SD} are the orbital and spin dipolar $4f$ hyperfine expressions, respectively, I and μ are the nuclear spin and magnetic moment, and the operators inside the sums involve spin and angular, but not radial, $4f$ orbital coordinates. The crystal field can contribute to an $\langle r^{-3}\rangle_{\mathrm{L \cdot I}}$ or $\langle r^{-3}\rangle_{\mathrm{SD}}$ in three ways. The exact contributions will be functions of the ion's crystal-field state as well as of the field itself. They are:

(i) As discussed in the preceding section, the crystal field will have direct repercussions on the orbital behavior of the $4f$ shell. The results of Table II indicate a one percent decrease in $\langle 4f|r^{-3}|4f\rangle$ for $m_l'=0$, for the V_2^0 radial distortion. Angular effects would, of course, also contribute.

(ii) Noting that the energy denominators of Eq. (9) are functions of both $4f$ shell occupancy and the m_l and m_s values of the perturbed orbital, suggests that the radial and angular distortions of closed shells which might otherwise be expected to be magnetically inert, are not. The variation in denominators will "open" the shells, which then make very small contributions to $\langle r^{-3}\rangle_{\mathrm{L \cdot I}}$ and $\langle r^{-3}\rangle_{\mathrm{SD}}$; the resulting array of small terms could conceivably combine to make of the order of a tenth of a percent contribution to an $\langle r^{-3}\rangle_i$. A full detailed treatment of this matter is liable to be involved with the symmetry controversy discussed previously[20,21] for the UHF method as applied to free ions.

(iii) Quite aside from any question of the energy denominators, there is yet another contribution which must be considered. For m_l' of the $4f$ electron equal to ± 2 or ± 3, the set of six $5p \rightarrow f^\star$ distorted orbitals make a zero valued contribution to the magnetic hyperfine interaction. However, if the $4fm_l'$ value is 0 or ± 1, the exclusion principle introduces a hole into this set of six terms. This hole does have a magnetic hyperfine interaction with the nucleus and is just the negative of the interaction evaluated for the excluded $p \rightarrow f^\star$ orbital. The resulting hyperfine field contributions, written so that they can be simply added to the $\langle 4f|r^{-3}|4f\rangle$ value of Table I, are listed in Table IX. These rely on the same V_2^0 field and the same matrix elements used in earlier sections. The orbital hyperfine interaction is zero valued for the $m_l'=0$ level; hence, the distortion contributes only to its $\langle r^{-3}\rangle_{\mathrm{SD}}$ interaction and is *enhanced* by 0.009 au (a 0.2% effect). For the $m_l'=\pm 1$ state, both $\langle r^{-3}\rangle_{\mathrm{SD}}$ and $\langle r^{-3}\rangle_{\mathrm{L \cdot I}}$ are *reduced* by 0.006 au. If we had limited our estimates to the first-order terms of Eq. (11), the $\langle r^{-3}\rangle_i$'s of both states would have been reduced by ~0.001 au. The relative importance of the (incompletely described) second-order term [Eq. (12)] is again due to the small magnitude of $\langle f^\star|r^{-3}|5p\rangle$.

TABLE IX. The $5p \rightarrow f^\star$ exclusion principle contributions parameters of Ce^{3+} in a V_2^0 field for the $4fm_l$ values of 0 and ± 1 (in au).

$4fm_l'$	Contributions to	1st-order terms of Eq. (11) only	Eq. (11)+Eq. (12)
0	$\langle r^{-3}\rangle_{\mathrm{SD}}$	-0.0016	$+0.009$
± 1	$\langle r^{-3}\rangle_{\mathrm{SD}}$ and $\langle r^{-3}\rangle_{\mathrm{L \cdot I}}$	-0.0011	-0.006

All three contributions occur for V_2^0 and V_4^0 fields while (i) and (ii) occur for V_6^0 as well. While the estimates quoted above were based on a strong V_2^0 field, we expect the effect of all three terms on an observed $\langle r^{-3}\rangle$ parameter to be of the order of one percent or less. This is not insignificant for as Bleaney has recently observed,[5] rare-earth hyperfine interactions appear to vary by one or two percent under the influence of crystalline environments. Bleaney ascribes this to orbital reduction,[22] i.e., covalency effects; we believe these to dominate over the contributions discussed above. Unfortunately, the presence of these latter terms may severely complicate the analyses of experiment.

VII. DISCUSSION

The Ce^{3+} calculations have shown that substantial linear shielding *and* severe level deviations (or nonlinear shielding) from the simple $4f$ crystal-field level scheme may occur. Exchange effects were not only significant but were also the most important single source of the deviations. Similar effects should occur for the more complicated larger rare-earth ions.

It should be emphasized that the assumption of a potential in the form of Eq. (1) affects the quantitative but not the qualitative nature of the results. In fact, any treatment involving a potential or an *effective* potential, written as a sum of spherical harmonics times radial functions, is liable to yield shielding results of a similar nature. In other words, nonlinear effects will very likely remain with us when we go to a more "realistic" treatment of the problem. In our treatment of Ce^{3+}, we found these effects to be sizable for the V_4^0 field and small for the V_2^0 field, suggesting that the standard rare-earth crystal-field parametrization need

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[21] Reference 20 gives a fairly complete referencing to the UHF method. Regarding the symmetry controversy, see, in particular, N. Bessis, H. L. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **124**, 1124 (1961).

[22] For example, see K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

not always be destroyed by the presence of nonlinear shielding. This does not mean that an apparently successful crystal-field fit automatically implies the nonexistence of such terms. We believe nonlinear shielding to be more important in making misleading contributions to a set of crystal-field parameters than in causing obvious breakdowns of such fitting schemes.

The appearance of strong nonlinear shielding for the rare earths raises the question of whether similar effects occur for transition metal ions. We do not believe that the dominant closed-shell effects discussed above are important for such ions since their closed shells lie inside the open d shells. Also, with the possible exception of a $3s \rightarrow 3d$ distortion (which we expect to be benign), the various allowed distortions are penalized by large energy denominators [e.g., see Eq. (9)]. On the other hand, the open valence shell effects, which were small for the rare earths, will be relatively more important here. The radial and angular effects will be inextricably bound up with covalency and a detailed treatment of all of these might very well lead to the partial breakdown of such familiar parameters as 10 Dq. Such a nonlinear effect, however, would have an almost unrecognizably different source than its rare-earth counterpart.

The level deviations are perhaps the most interesting feature of the results, but their importance depends strongly on how the levels are observed experimentally. If, for example, we had "observed" the splitting between the $m_l=0$ and ± 1 ($5p \rightarrow f^\star$ shielding plus unscreened field) energy levels of Table VI, we would have concluded that there was a 15% enhancement of the V_4^0 field rather than the shielding indicated in Table VII. Such complications are, of course, a byproduct of these deviations.

As already discussed, the repercussions from the exclusion principle on $5p \rightarrow f^\star$ shielding could be ignored for Ce^{3+} by including self-energy Coulomb *and* exchange terms. This is not the case as soon as there is a second electron in the $4f$ shell and our experience with Ce^{3+} indicates (e.g., see Tables IV and VI) that adherance to the exclusion principle will cause shielding and level deviations of significant magnitude. As we gradually fill the $4f$ shell, the $5p \rightarrow f^\star$ distortion will be given less freedom to act and aside from any resulting level deviations there will be a tendency for its shielding to disappear. For example, as seen earlier, the V_2^0 shielding will (in a treatment omitting LS coupling) be reduced from 50% to 25%. The V_4^0 effects are far more complicated and even with the complete disappearance of the $5p \rightarrow f^\star$ distortions, some small shielding and some small level deviations are expected. It should be noted that Powell and Orbach, in their investigation[23] of rare-earth ethyl sulfate data, observed a trend in the V_2^0 crystal-field term consistent with a substantial decrease in crystal-field shielding on going to larger ions. This is the same direction as the $5p \rightarrow f^\star$ effect. We believe the latter to be, at most, only partially responsible for what Powell and Orbach saw. Their observations, which were based on only a few of the ions, showed no similar strong trend associated with the V_4^0 or V_6^0 terms.

As for the existence or nonexistence of (linear) shielding, previous investigations have presented widely divergent conclusions. As stated in Sec. I, Lenander and Wong,[4] considering earlier work on the trichlorides,[24] concluded that huge V_2^0, strong V_4^0, and weak V_6^0 shielding occurred. Burns[2] also considered trichlorides as well as the ethyl sulfates and concluded that there was essentially *no* shielding. These differing conclusions were based on investigations which involved the same experimental data *but* different computed estimates of the crystal field. In addition, in the analytic variation-perturbation method used by Burns, one limitation arises because the variation functions are constrained to have the same radial nodes as the unperturbed orbitals. This makes it impossible for the mixing of $4f$ (in $5p \rightarrow f$) or $5d$ (in $5s \rightarrow d$) character to be properly accounted for. The smaller V_4^0 shielding obtained by Burns arises from the insufficient variational freedom allowed by the method. In this regard, the effect of these shortcomings would have been even more severe if an estimate of the V_2^0 shielding had been attempted. We believe that the shortcomings of the perturbation-variation method to be the primary source of the differences between Burn's and the L & W conclusions.[24a]

As mentioned earlier, Bleaney's conclusion[5] of an *antishielding* of RHF predictions for Tm^{2+} in CaF$_2$ appears to be at variance with the other results. However, Tm^{2+} is in an octahedral environment in this crystal and Bleaney's observations may be associated with an empirical suggestion[25] of Jørgensen's to the effect that rare-earth crystal-field energies will prove to be substantially larger for cubic environments.

Again, discussion of any conclusions are complicated by questions of details of the crystal-field estimates and, if we accept the existence of the level deviations, their varying repercussions on the analyses of experimental data. We do agree with Lenander and Wong that the V_2^0 shielding can be large and that for V_4^0 significant. Conclusions beyond this would at best be tentative.

In the investigations reported here, we have been besieged by an array of small effects contributing to both hyperfine and crystal-field interactions. The crudity of the present calculations allow only qualitative conclusions. Details of the perturbation calcula-

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[23] M. J. D. Powell and R. Orbach, Proc. Phys. Soc. (London) **78**, 753 (1961); also see Fig. 3 in Ref. 17 and the accompanying discussion.

[24] C. A. Hutchison and E. Wong, J. Chem. Phys. **29**, 754 (1958) and J. S. Margolis, *ibid.* **35**, 1367 (1961).

[24a] *Footnote added in proof.* D. K. Ray [Proc. Phys. Soc. (London) **82**, 47 (1963)] has also investigated rare-earth crystal field and γ_∞ linear shielding.

[25] C. K. Jørgenson (private discussions, 1962).

tions (e.g., the averaged energy denominators) and the use of perturbation theory[18] contribute to this. Quite aside from such matters, the situation is more complicated than Burns and Lenander and Wong have suggested. This is in part associated with such matters as exchange terms, 4f shell distortions and nonlinear shielding, and in part with questions associated with the crystal "field" itself. Crystalline fields of the form of Eq. (1) have geen used, with one exception,[7] in the various investigations to date and this probably represents the most severe shortcoming of the calculations. Various inadequacies of such a field are well known[26] for the case of iron series ions and these and other effects occur here as well. While Eq. (1) is not completely adequate for discussing the interaction of the 4f electrons with the crystalline environment, it is undoubtedly a poorer description as regards the 5s and 5p shells. Finally, covalent bonding arising directly from the open 4f shell (as discussed by Jørgensen *et al.*[7]) *and* from the distorted outer closed shells must be inspected before quantitative conclusions are made concerning the nature of crystal-field effects on rare-earth spectral levels.

In closing, it should be restated that appreciable nonlinear shielding was found for one of the two calculations reported in the paper. We believe that characteristically, nonlinear shielding will at times have severe and at other times benign effects on rare-earth crystal field spectra (e.g., Yb^{3+} which has no linear $5p\rightarrow f$ shielding will have insignificant nonlinear terms).

ACKNOWLEDGMENTS

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APPENDIX I

In this appendix we list the integrals which we have used in evaluating the terms of Eq. (13) which appear in Tables IV and VI. They are:

	$5p\rightarrow f^\star(m_l=0)$	$5p\rightarrow f^\star(m_l=\pm1)$
$\mathcal{F}^2=\mathcal{G}^2=$	0.121	0.119
$\mathcal{F}^4=\mathcal{G}^4=$	0.100	0.100
$E_p-E_{f^\star}=$	-0.72	-0.68
$\langle 5p\|r^2\|f^\star\rangle$	1.604	1.604
$\langle 5p\|r^4\|f^\star\rangle$	7.332	7.332

All quantities are given in atomic units. The $c^k(l,m_l;l',m_l')$ integrals can be obtained from Condon and Shortley[13] or by evaluating

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

where

$$\begin{pmatrix} l & k & l' \\ 0 & 0 & 0\end{pmatrix} \text{ and } \begin{pmatrix} l & k & l' \\ -m & m-m' & m'\end{pmatrix}$$

are the familiar $3j$ coefficients. Note that we have chosen field strengths such that

$$(i|V_2^0|j)\equiv -0.032c^2(i,m_l;\,j,m_l')\langle i|r^2|j\rangle$$

and

$$(4f|V_4^0|4f)\equiv c^4(4f,m_l';4f,m_l'),$$

hence,

$$(5p|V_4^0|f^\star)=c^4(5p,m_l;f^\star,m_l)\frac{\langle 5p|r^4|f^\star\rangle}{\langle 4f|r^4|f^\star\rangle}.$$

APPENDIX II

In Sec. II we assert that the radially distorted p-shell exchange terms (occurring for a V_2^0 field) are linear shielding. Let us inspect this matter here. The G^2 contribution to $\Delta E_{p\rightarrow p}$ [Eq. (5)] is

$$-[c^2(4f,m_l';p,0)]^2G^2(4f,m_l';p,0) -[c^2(4f,m_l';p,\pm1)]G^2(4f,m_l;p,\pm1), \quad \text{(A1)}$$

and evaluating the c^2 coefficients we have the shielding contribution

$$\begin{aligned}
\Delta&=-(1/175)[27G^2(p,0)+18G^2(p,\pm1)]; & m_l'&=0,\\
\Delta&=-(1/175)[24G^2(p,0)+21G^2(p,\pm1)] & &\pm1,\\
\Delta&=-(1/175)[15G^2(p,0)+30G^2(p,\pm1)] & &\pm2,\\
\Delta&=-(1/175)[0G^2(p,0)+45G^2(p,\pm1)] & &\pm3,
\end{aligned} \quad \text{(A2)}$$

as a function of $4fm_l'$ value. (We have, and will henceforth, use an abbreviated notation for the G^k integrals.) Let us define

$$\delta_k=G^k(p,\pm1)-G^k(p,0), \quad \text{(A3)}$$

then

$$\begin{aligned}
\Delta&=\text{const}+(12/175)\delta_2; & m_l'&=0,\\
\Delta&=\text{const}+(9/175)\delta_2; & m_l'&=\pm1,\\
\Delta&=\text{const}+0\delta_2; & m_l'&=\pm2,\\
\Delta&=\text{const}-(15/175)\delta_2; & m_l'&=\pm3,
\end{aligned} \quad \text{(A4)}$$

where

$$\text{const}=(45/175)G^2(p,0)+(30/175)\delta_2. \quad \text{(A5)}$$

Now we are not interested in any constant contribution to the crystal-field energies and therefore are interested *only* in the δ_2 terms which display the ∓4, ∓3, 0, ±5 spacing familiar[15] to linear V_2^0 shielding. This behavior is common to *any* radial distortion of a closed p shell providing (1) that the distortion is held constant for the various states of the open 4f shell and (2) that p orbitals with $m_l=\pm1$ have the same radial behavior.

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[26] For example, see S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

The radial distortions induced by a pure electrostatic field always meet this second requirement.

The $G^4(4f,m_l';p,m_l)$ terms act in much the same way, i.e.,

$$\Delta' = -\frac{1}{189}[16G^4(p,0)+20G^4(p,\pm1)] = \text{const}+\frac{4}{189}\delta_4;\quad m_l'=0,$$

$$\Delta' = -\frac{1}{189}[15G^4(p,0)+21G^4(p,\pm1)] = \text{const}+\frac{3}{189}\delta_4;\quad m_l'=\pm1,$$

$$\Delta' = -\frac{1}{189}[12G^4(p,0)+24G^4(p,\pm1)] = \text{const}+0\delta_4;\quad m_l'=\pm2,$$

$$\Delta' = -\frac{1}{189}[7G^4(p,0)+29G^4(p,\pm1)] = \text{const}-\frac{5}{189}\delta_4;\quad m_l'=\pm3, \tag{A6}$$

where here

$$\text{const}=\frac{36}{189}G^4(p,0)+\frac{24}{189}\delta_4, \tag{A7}$$

so again we have linear shielding. Such behavior does not occur for the d-shell exchange terms.

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Reversal in Optical Rotatory Power—"Gyroelectric" Crystals and "Hypergyroelectric" Crystals

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A crystal is provisionally referred to as being "gyroelectric," when its optical rotatory power or gyration is nonzero at no biasing electric field and can be reversed in sign by means of a suitable biasing electric field. The gyroelectric crystals must be ferroelectric. It is found that, of the 19 kinds of regular ferroelectrics, only 9 kinds are gyroelectric. It is further shown that the other 10 kinds are divided into 5 "hypergyroelectric" and 5 optically inactive kinds. The rate of change of the gyration with the biasing electric field at zero value of the biasing electric field is provisionally referred to as the "electrogyration." The hypergyroelectric crystals are, somewhat roughly speaking, those crystals whose electrogyration is nonzero and can be reversed in sign by means of a suitable biasing electric field. Also, as a first step in the investigation of the properties of the gyroelectric and hypergyroelectric crystals, a theoretical inference is made into the change with temperature T of the gyration G_s at no biasing field and electrogyration η of the gyroelectric and hypergyroelectric crystals in the neighborhood of their Curie temperature T_0. On some assumptions, the following are presumed. In the gyroelectrics, G_s changes like $(T_0-T)^{1/2}$ with T below T_0 and vanishes above T_0. In the hypergyroelectrics, G_s changes linearly with T both below and above T_0, but breaks at T_0. In the gyroelectrics, η changes like $(T_0-T)^{-1}$ below T_0 and changes like $2(T-T_0)^{-1}$ above T_0. In the hypergyroelectrics, η changes like $(T_0-T)^{-1/2}$ below T_0 and vanishes above T_0.

1. INTRODUCTION

We provisionally refer to the crystals as being "gyroelectric" whose optical rotatory power or gyration[1] is nonzero at no biasing electric field and can be reversed in sign by means of a suitable biasing electric field. (A crystal which has a nonzero gyration is also called optically active. The reason why the term "biasing electric field" is used in place of the simpler term "electric field" lies in the distinction of it from the "electric field" of the light.) From this definition it may be obvious that the gyroelectric crystals must be ferroelectric. (A most reasonable and exact definition of ferroelectricity has been given in the preceding papers.[2,3]) In general, the ferroelectric crystals are divisible into the *regular* ferroelectric crystals and the *irregular* ones.[2,3] We refer to those gyroelectric crystals which are regularly ferroelectric as the regular gyroelectric crystals.

In this paper the gyroelectric crystals considered are limited to the regular ones. In Sec. 2, a determination is made as to which of the regular ferroelectric crystals should be gyroelectric. On this occasion it will be shown that the regular ferroelectric crystals consist of the gyroelectric, the "hypergyroelectric," and the optically inactive crystals. The rate of change of the gyration with the biasing electric field at zero value of the biasing electric field is provisionally referred to as the "electro-

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[1] See, for example, J. F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, England, 1957).

[2] K. Aizu, Rev. Mod. Phys. 34, 550 (1962).

[3] K. Aizu, Phys. Rev. 133, A1350 (1964).