

points adjacent to the points for which the value is given. By comparison of (4) and the experimental values of  $dE/dX$  given in Table I, experimental values of  $\xi_\epsilon$  can be found. These values turn out to be  $\xi_\epsilon=0.57$  for aluminum,  $\xi_\epsilon=0.50$  for copper, and  $\xi_\epsilon=0.82$  for gold which are in reasonable agreement with the theoretical estimate of  $\xi_\epsilon=1$ .

The ranges reported here can be compared with values reported for protons since the energy loss due to ionization per unit path length is the same for deuterons and protons of the same velocity. However, the deuteron has twice the energy of a proton of the same velocity. Thus, the range of a deuteron should be twice the range of a proton of one half the deuteron energy. This argument neglects the differences in energy loss due to displacements that might be expected between protons and deuterons. However, from (1) the energy loss due to displacements predominates only below  $E=1.26$  keV for deuterons which is a small fraction of the total deuteron energy employed here. The range of a 15-keV deuteron of  $73 \mu\text{g}/\text{cm}^2$  in aluminum as reported here can be compared with twice the range reported by Young<sup>9</sup> for 7.5-keV protons. The actual values of twice the range in

aluminum reported by Young are  $76 \mu\text{g}/\text{cm}^2$  for  $\text{H}_2^+$  ion bombardment with 7.5 keV per atom, and  $62 \mu\text{g}/\text{cm}^2$  for 7.5-keV  $\text{H}^+$  ion bombardment. This agreement between the two experiments is as close as can be expected considering the assumptions involved in the comparison.

### CONCLUSIONS

Ranges of ions in materials that can be evaporated into thin films on quartz can be found using the radiation damage in quartz to detect the ions. Using this method, 5- to 27-keV deuteron ranges in aluminum, copper, and gold are bound to agree with theoretical predictions of energy loss per unit path length and with known experimental ranges of protons in aluminum.

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## Electric Quadrupole Interactions in Rare-Earth Ions

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Electric quadrupole interactions in rare-earth ions arising from electric field gradients due to valence electrons ( $q_{4f}$ ) and/or crystal fields external to the ion ( $q_{\text{lat}}$ ) are discussed. The contribution of the Sternheimer antishielding factors to both  $q_{4f}$  and  $q_{\text{lat}}$  are calculated for the  $\text{Ce}^{3+}$  ion using the method (based on the unrestricted Hartree-Fock formalism) reported earlier. The ionic antishielding factor ( $\gamma_\infty$ ) is  $-73.5$ , and it is found that the total ionic contribution to the electric field gradient can be comparable in magnitude (and may be opposite in sign) with the valence electron contribution (augmented by the internal antishielding factor). The possible relation of these results to the temperature dependence of measured electric quadrupole interactions is noted.

### I. INTRODUCTION

MEASUREMENTS of hyperfine interactions in rare-earth ions, by specific heat, electron spin resonance, Mössbauer, and other methods, have revealed very large electric quadrupole contributions.<sup>1</sup>

In addition, unusual temperature-dependent electric field gradients, including a change in sign,<sup>2</sup> have been reported. These experiments have pointed out the need for a deeper theoretical understanding of the origin of electric quadrupole interactions in these materials, and more particularly, of the role played by the distur-

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<sup>1</sup> See B. Bleaney, *Suppl. J. Appl. Phys.* **34**, 1024 (1963); *J. Phys. Soc. Japan* **17**, *Suppl. B-I*, 435 (1962) for a recent review of these data. See R. Bauminger, S. G. Cohen, A. Marinov, and S. Ofer, *Phys. Rev. Letters* **6**, 467 (1961); and R. Cohen, V. Hauser, and R. L. Mössbauer, in *The Mössbauer Effect*, edited by D. M. J.

Compton and A. H. Schoen (John Wiley & Sons, Inc., New York, 1962), for some Mössbauer data on the temperature dependence of the electric quadrupole interaction.

<sup>2</sup> R. L. Cohen, Ph.D. thesis, California Institute of Technology, 1962 (unpublished); see in particular, Fig. 18.

tions of closed electron shells (Sternheimer antishielding<sup>3</sup>). We have recently<sup>4</sup> considered the role played by Sternheimer antishielding<sup>3</sup> in an ion's magnetic and electric hyperfine interactions utilizing a method based on the self-consistent field unrestricted Hartree-Fock (UHF) formalism. In the present paper we shall extend this study to the problem of electric quadrupole interactions in rare-earth ions.<sup>5</sup>

Two different sources of the electric field gradient must be considered for an ion in a crystalline environment:

(1) The electric field gradient produced at the nucleus by the open  $4f$  shell of a non- $S$ -state ion  $q_{4f}$ . This gradient will be modified by a Sternheimer antishielding correction, yielding a resulting field gradient

$$q = q_{4f}(1 - R_Q), \quad (1)$$

where  $R_Q$  is an antishielding factor associated with the closed shells of the ion which have been aspherically distorted by the  $4f$  shell.<sup>6,7</sup> One can introduce this antishielding into the standard equations for  $q$ , i.e., into

$$e^2qQ = [e^2Q/2I(I-1)]\langle r^{-3} \rangle_{4f} \times \sum_i [I(I+1) - 3(\mathbf{I} \cdot \mathbf{r}_i/r_i)^2], \quad (2)$$

by replacing the  $\langle r^{-3} \rangle_{4f}$  integral by the effective parameter

$$\langle r^{-3} \rangle_Q \equiv \langle r^{-3} \rangle_{4f}(1 - R_Q). \quad (3)$$

In Eq. (2),  $I$  is the nuclear spin, and the operators inside the sum involve angular and spin, but not radial, coordinates of the open shell. Assuming the conventional Hartree-Fock description of the ion [implicit in Eq. (2)], the radial dependence of the  $4f$  shell occurs in

$$\langle r^{-3} \rangle_{4f} = \int_0^\infty r^{-3} [U_{4f}(r)]^2 dr, \quad (4)$$

where  $U_{4f}(r)$  is the  $4f$  shell's radial orbital.

<sup>3</sup> 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); **80**, 102 (1950); **84**, 244 (1954); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956).

<sup>4</sup> A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. **6**, 166 (1961); R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 250 (1963), henceforth denoted as I; A. J. Freeman and R. E. Watson, Phys. Rev. **131**, 2566 (1963), henceforth denoted as II; and see R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955) for the pioneering investigation into the symmetry properties of Hartree-Fock orbitals which are appropriate to the aspherical UHF problem.

<sup>5</sup> A preliminary account of this work was presented at the International Conference on Paramagnetic Resonance, Jerusalem, Israel, 1962 [*Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963)].

<sup>6</sup> To within second-order perturbation theory one can conversely speak of the nuclear quadrupole moment distorting the closed shells and these in turn interacting with the  $4f$  shell. See the Appendix of Das and Bersohn (Ref. 7).

<sup>7</sup> T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

(2) If the ion's environment also makes a contribution ( $q_{\text{lat}}$ ) to the field gradient at the nucleus,  $q$  becomes

$$q = q_{4f}(1 - R_Q) + q_{\text{lat}}(1 - \gamma_\infty), \quad (5)$$

where  $\gamma_\infty$  is the external field Sternheimer antishielding factor associated with the distortions of the electronic shells of the ion by the external crystalline field.

A  $q_{4f}$ , which is nonzero, will, in general, be much larger than  $q_{\text{lat}}$ . Such observations hold for the open valence shells of any ion and this has led to the common practice of neglecting the second term of Eq. (5) if the first term is nonzero. While  $q_{\text{lat}}$  may be much smaller than  $q_{4f}$ ,  $\gamma_\infty$  may be sufficiently large for rare-earth ions so that the second term can become experimentally significant. We will be particularly interested in the relative roles of these two terms in this paper.<sup>8</sup> The methods described in I and II will be used to estimate  $R_Q$  (or rather  $\langle r^{-3} \rangle_Q$ ) and  $\gamma_\infty$ . Calculations are reported for the  $\text{Ce}^{3+}$  ion which, with its single  $4f$  electron, offers a particularly simple case to deal with; calculations for  $\gamma_\infty$  for other rare-earth ions are in progress and will be reported in the future.

## II. ANTISHIELDING CALCULATIONS

An  $\langle r^{-3} \rangle_Q$  or  $\gamma_\infty$  consists of a sum of closed shell "angular" and "radial" distortion terms. The radial distortions are associated with differing radial behavior of the one-electron orbitals within a shell, whereas the angular distortions arise from the admixture of angular components (of different symmetry) into the one-electron orbitals of the undistorted shell (See I for details). As in I and II, the calculations will be limited to estimates of the radial antishielding for which existing Hartree-Fock computational machinery can be used readily. These calculations yield a quite accurate value for  $\gamma_\infty$ , for which the angular distortions are unimportant. The resulting estimate of  $\langle r^{-3} \rangle_Q$ , which neglects these terms, will be less satisfactory. In what follows, we shall be particularly interested in  $\gamma_\infty$ .

Three  $m_l$  UHF calculations, i.e., calculations where orbitals of differing  $m_l$  (but *not*  $m_s$ ) within a shell are allowed differing radial behavior, will be reported for  $\text{Ce}^{3+}$ ,  $4f^1$  in its  ${}^3F(M_L=0; M_S=\frac{1}{2})$  state:

(A) A free ion calculation in which the closed shells are distorted by the aspherical terms introduced into the H-F Hamiltonian by the  $4f$  shell and, in turn, by the distortions of the other shells. This calculation yields an estimate of the radial antishielding contributions to  $\langle r^{-3} \rangle_Q$ .

(B) A calculation identical to (A) except that an external crystalline potential of  $F_0^2(\theta, \varphi)$  symmetry has been added to the H-F Hamiltonian. Such a calculation simultaneously and inextricably yields the contributions of a closed shell to both  $\langle r^{-3} \rangle_Q$  and  $\gamma_\infty$ .

<sup>8</sup> A comparison of these terms, calculated by the perturbation-variation (Ref. 7) method using Hartree wave functions has been given by E. G. Wikner and G. Burns, Phys. Letters **2**, 225 (1962).

(C) Thirdly, a calculation for the ion in the same external potential but with the aspherical Coulomb and exchange potential terms due to the  $4f$  electron omitted from the Hamiltonian. Such a calculation yields the  $\gamma_\infty$  terms alone and, since the perturbations so introduced are small, it is to be expected that the closed-shell contributions to  $q$  given by calculations (A) and (C) sum to yield those predicted by (B). We will see that this is, indeed, the case. In all three calculations the Hamiltonian associated with a particular orbital in a particular shell contains aspherical Coulomb and exchange terms arising from other distorted shells and other orbitals within its own shell, i.e., the set of radial distortions are treated self-consistently.

Results will be reported in terms of contributions to an  $\langle r^{-3} \rangle_q$ , appropriate for insertion into Eq. (2) with the  $4f$  electron having  $m_l=0$ . In other words,  $4f$  and external distortion effects will be merged [for calculation (B) then cannot be separated], making comparisons easier. Results of calculation (C) will also be expressed as contributions to a  $\gamma_\infty$ , i.e., normalized with respect to the external field gradient.

The applied crystalline potential is taken to be of the (crude) form due to an array of charges completely external to the ion, namely,

$$V_2^0 = Cr^2 Y_2^0(\theta, \varphi), \quad (6)$$

where  $C$  is a constant defining the sign and strength of the field. The coefficient  $C$  was chosen with a sign such that the  $4f$  orbital with  $m_l=0$  has lowest energy in the field (consistent with our choice of ionic state for the calculations). Its magnitude is equivalent to the field due to a pair of point charges, 2 a.u. in magnitude, located 5 a.u. along the  $z$  axis to either side of the Ce nucleus. While 5 a.u. is a characteristic nearest-neighbor distance for a rare-earth ion, it should be remembered when viewing the results that the resulting  $V_2^0$  field is somewhat stronger than what will be encountered in the rare-earth salts. Though unrealistic, potentials of this form are (by definition) commonly used in  $\gamma_\infty$  investigations and this represents a severe shortcoming. The tight-binding model of an ion being perturbed by an external Coulomb potential is at best a poor one (See I).

The calculations utilize the analytic nonrelativistic H-F methods<sup>9</sup> applied in I and II. For basis set wave functions, we have used a slightly reduced version of a set used in a previous Ce<sup>3+</sup> investigation<sup>10</sup>—a requirement introduced by computational considerations. As discussed in II, our choice of calculations (the ion in the  $M_L=0$  state and calculations which are  $m_l$  but not  $m_s$  unrestricted) do not yield estimates of closed-shell contributions to the magnetic hyperfine  $\langle r^{-3} \rangle$  param-

eters. The inclusion of these would have considerably increased the size of the computations; in view of the uncertainties associated with such results (see II) we do not consider the increase to be warranted.

Finally, these closed-shell distortions also contribute to the interaction between the crystal field and the  $4f$  shell. The radial distortion results of (C), which make an antishielding contribution to this interaction, will be discussed in a forthcoming paper on crystal field effects in rare-earth ions.

### III. RESULTS

The results of the three calculations are summarized in Table I. Included is the conventional H-F (RHF) value for  $\langle r^{-3} \rangle_{4f}$  of 4.71 a.u., obtained in a separate calculation with the same analytic basis set as was used here in the UHF runs. More accurate nonrelativistic calculations<sup>10,11</sup> yield a value of 4.72 to 4.73 a.u.

The most prominent feature of the results is the reversal in sign, relative to the result of calculation (A), of  $\langle r^{-3} \rangle_q$ , hence  $q$ , for calculations (B) and (C). The external field term  $q_{\text{lat}}(\gamma_\infty)$  is of opposite sign to the  $4f$  shell term and has overpowered it. This would not occur for a more realistic, weaker,  $V_2^0$  field but the  $q_{\text{lat}}(\gamma_\infty)$  term will, in general, remain an experimentally significant term.

The free ion results (calculation A) show a 40% antishielding contribution to  $\langle r^{-3} \rangle_q$  from the closed-shell radial distortions. (This is a substantially larger shift than was obtained for either Fe<sup>2+</sup> or Cl in II). The inclusion of angular antishielding would tend to reduce  $\langle r^{-3} \rangle_q$ , perhaps reducing the effect of radial antishielding by half. The inner  $2p$ ,  $3p$ , and  $3d$  shells have made positive contributions to  $\langle r^{-3} \rangle_q$ , while those shells which overlap the  $4f$  (i.e.,  $4p$ ,  $5p$ , and  $4d$ ) make smaller negative contributions. Such a sign reversal on going from interior shells to those which overlap the open valence shell (and the dominance of the interior terms as well) is a not unfamiliar phenomenon; it occurs for the spin polarization of an ion<sup>12</sup> and in spin-orbit exchange interactions.<sup>13</sup>

A  $\gamma_\infty$  of  $-73$  has been obtained in calculation (C). This is a large antishielding factor and it will be reduced slightly (i.e., by 1 or 2) by the inclusion of angular antishielding. These results contrast with the predictions of the analytic perturbation-variation method, using RHF wave functions, which yield<sup>14</sup> a  $5p$  shell term of  $\sim -100$  and substantially reduced antishielding (relative to Table I) for the other shells of Ce<sup>3+</sup>. Similar perturbation-variation results have been obtained by Wikner and Burns<sup>9</sup> using Ridley's<sup>15</sup> Hartree functions

<sup>11</sup> P. Bagus (unpublished).

<sup>12</sup> See R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

<sup>13</sup> M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A271**, 565 (1963).

<sup>14</sup> A. J. Freeman, A. Hansen, and R. E. Watson (unpublished).

<sup>15</sup> E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

<sup>9</sup> For example, see C. A. Coulson, Proc. Cambridge Phil. Soc. **34**, 204 (1938); C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955); Rev. Mod. Phys. **35**, 552 (1963).

<sup>10</sup> A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

TABLE I. Results of  $m_l$  UHF calculations for the  $Ce^{3+}$  ion in its  $^3F$  state. Calculations (A), (B), and (C) are defined in detail in the text. Atomic units are used throughout. (Conventional Hartree-Fock  $\langle r^{-3} \rangle = 4.71$ .)

Calculation	(A)	(B)	(C)	
	Free ion $\langle r^{-3} \rangle_Q$	Ion in $V_0^2$ field $\langle r^{-3} \rangle_Q$	Ion in $V_0^2$ field with spherical $4f$ potential $\langle r^{-3} \rangle_Q$	$\gamma_\infty$
$2p$	1.09	0.90	-0.18	-1.5
$3p$	2.25	1.74	-0.47	-4.0
$4p$	-0.23	-1.55	-1.32	-11.0
$5p$	-1.26	-7.82	-6.48	-54.0
$3d$	0.20	0.13	-0.07	-0.5
$4d$	-0.03	-0.34	-0.31	-2.5
$4f$	4.71	4.66	4.66	...
Total	6.72	-2.27	-4.17	-73.5

for  $Pr^{3+}$  and  $Tm^{3+}$ . The increase in inner-shell contributions to  $\gamma_\infty$  is primarily due to the self-consistent field treatment which is used here; for example, the inner shells are perturbed by the large  $5p$  shell distortion as well as by  $V_2^0$ . (Similar increases were seen in the inner shell results reported for  $Cl^-$  and  $Cu^+$  in I.) The large change in the  $5p$  shell antishielding from  $\sim -100$  (the perturbation-variation result) to  $-54$  (the present result) is apparently due to the fact<sup>16</sup> that intershell orthogonality is not maintained appropriately in the standard perturbation-variation method. This is the first time that the UHF method has yielded a decrease in an outer shell term relative to the perturbation-variation result; a substantial increase was obtained (in I) for the dominant  $3p$  shell contribution to the  $\gamma_\infty$  of  $Cl^-$ . These results indicate that one cannot easily estimate the magnitude and sign of the deviations of the perturbation-variation results from the UHF results.

#### IV. DISCUSSION

The calculations have indicated appreciable Sternheimer antishielding for both the free ion  $\langle r^{-3} \rangle_Q$  and the  $\gamma_\infty$  terms. These results, however, are subject to all the shortcomings of such calculations discussed in I and II. Among these is the question of relativistic effects which are expected to be important for the one-electron orbitals of an ion such as  $Ce^{3+}$ . We expect the  $4f$  shell, and its  $\langle r^{-3} \rangle_{4f}$ , to be but slightly affected by the inclusion of relativistic effects,<sup>17</sup> but the  $s$  and  $p$  shells

<sup>16</sup> R. Ingalls, Phys. Rev. **128**, 1155 (1962).

<sup>17</sup> This is based in part on the work of R. G. Boyd, A. C. Larson, and J. T. Waber [Phys. Rev. **129**, 1629 (1963)] which indicates few direct relativistic repercussions on the  $d$  and  $f$  shells of large ions. See also D. F. Mayers, Proc. Roy. Soc. (London) **A241**, 93 (1957).

to be severely affected. The repercussions that this will have on  $\gamma_\infty$  or  $\langle r^{-3} \rangle_Q$ , are not obvious because differences in one-electron orbitals are involved; a naive estimate would suggest an enhancement of these values.

As in I and II, the UHF scheme for estimating Sternheimer antishielding yields results which are qualitatively similar but quantitatively different from those obtained by Sternheimer's perturbation approach,<sup>3</sup> the analytic perturbation-variation method,<sup>7</sup> or modifications thereof.<sup>18</sup> The differences are due to the proper and natural handling of exchange, orthogonality, and self-consistency by the UHF method.

Assuming the computational results to be at least qualitatively correct, they suggest that the  $q_{lat}(\gamma_\infty)$  term of Eq. (5) can be experimentally significant and should not be ignored out of hand. In fact, this term may be necessary for understanding the temperature dependence of rare-earth quadrupole interactions. Strong temperature-dependent variations have been observed as well as a sign reversal for a salt with large crystal field parameters.<sup>2</sup> The temperature variation of  $q$  is commonly understood to be largely due to the temperature variation in the (Boltzmann) occupation of the crystal field levels with its attendant repercussions on  $q_{4f}$ . One would expect the  $q_{lat}$  term to be relatively temperature-independent, and so contribute only negligibly to the temperature variation of  $q$ . However, because of its relatively large magnitude (due to the large  $\gamma_\infty$ ) and the possibility of its sign being opposite to that of the  $q_{4f}$  term,  $q_{lat}$  can play an important role in understanding why and where sign reversals do or do not occur. An investigation into these matters requires detailed knowledge of the crystal field levels and of the wave functions associated with them; to our awareness such an investigation has yet to be done.

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<sup>18</sup> See for example, A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959); Advan. Phys. **11**, 281 (1962).