Korringa relation holds when both T_1 and K are contributed to only from the electrons near the Fermi surface, we would expect to observe a departure from the Korringa relation in the present case. Measurement of the Knight shift would enable one to differentiate between this mechanism and the other mechanisms discussed previously, since they do not lead to a departure of T_1K^2 from constancy.

III. CONCLUSIONS

It is not possible at this time to establish the exact mechanism which is responsible for the temperature-dependent product of T_1T. The observation may well be a reflection of the rather complicated band structure of Ga. When the results of the Knight shift are available, it is hoped that some additional insight will be gained into the problem although it will not be possible to differentiate between the influence of the density of states and the amplitude of the electronic wave function.

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Systematic Variation of Quadrupole Crystal-Field Shielding in Rare-Earth Ethyl Sulfates*

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Quadrupole-coupling constants were obtained from measurements on La^{140}, Eu^{154}, Gd^{159}, and Lu^{177} nuclei oriented in neodymium ethyl sulfate at temperatures down to 0.01°K. These results are combined with the other available quadrupole-coupling data on La, Dy, Tm, and Lu in ethyl sulfate lattices to determine the quadrupole-antishielded term transforming as Y_2^0 in the crystal-field potential, i.e., $(1-\gamma_\infty)\,A_2^0$. This term increases fairly slowly throughout the rare earths, with an average value of approximately $(3\times10^4\,\mathrm{cm}^{-1})a_0^{-2}$. These values were compared with theoretical estimates of -80 for γ_∞ to yield the quantities A_2^0. Comparison of the A_2^0's with the corresponding V_2^0's taken from optical spectroscopy, using Hartree-Fock radial moments $\langle r^2\rangle$ for the $4f$ electrons, together with some extrapolation, gives a complete set of shielding factors $(1-\sigma_2)$ for the crystal-field component V_2^0. These factors vary from 0.6 in Lu^{3+} to 0.4 in Eu^{3+} and drop to -0.2 in La^{3+}. Thus not only is there substantial shielding of V_2^0, but this shielding seems to vary considerably in the $4f$ series. The σ_2's are typically larger by about 50% than theoretical estimates.

I. INTRODUCTION

THE splitting of ionic terms and levels in crystals[1] comprised the first extensive application of group-theoretical methods to quantum-mechanical problems. Applied first to the iron ($3d$) group, these methods were also used in the early 1930's for the rare earths.[2] Elliott and Stevens introduced a systematic formulation of crystal-field theory for the rare earths,[3–6] using the method of operator equivalents. The remarkable success of this formulation in explaining optical spectra of rare-earth ethyl sulfates, where many energy levels can be fitted with only four adjustable parameters, is among the best experimental evidence for the validity of crystal-field theory.

Even in the relatively straightforward rare earths there are several levels of sophistication at which crystal-field theory may be applied. The simplest assumptions are that only the lowest term(s) of the appropriate $4f^n$ configuration need be considered, and that the crystalline field is adequately represented by point charges of appropriate magnitude at neighboring lattice sites. A rigorous treatment would consider all configurations of the ion in question, including those arising from promotion of electrons from closed shells, and would account for such subtleties as covalent bonding.[7] That these refinements are necessary for a realistic description of the problem is clearly demonstrated by the lack of agreement between the crystal-field parameters V_L^M deduced by fitting optical data and those calculated from lattice sums,[8] as well as by the effects

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[1] H. Bethe, Ann. Physik 3, 133 (1929).

[2] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

[3] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[4] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952).

[5] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

[6] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1963).

[7] C. K. Jorgensen, R. Pappalando, and H. H. Schmidthe, J. Chem. Phys. **39**, 1422 (1963).

[8] E. Y. Wong and I. Richman, J. Chem. Phys. **36**, 1889 (1962).

discussed below. At present attention is being focussed on the response of the rare-earth ion to the crystal field without questioning the origin of the field, beyond the usual lattice-sum calculations. The simple assumptions regarding the ion are being repaired by introducing "shielding factors" to account for the effects on the crystal-field parameters of shielding by closed shells. The purpose of this paper is to evaluate the shielding factors that modify the leading crystal-field term V_2^0 in rare-earth ethyl sulfates. Both experiment and theory indicate that shielding should be largest for this term. The key data that are used are the "antishielding" components of quadrupole coupling constants.

Quadrupole antishielding by excitation of nominally closed shells (the Sternheimer effect) has been predicted[9]; it is particularly dramatic because it involves the *enhancement* of the field gradient at the nucleus by closed-shell electrons, sometimes by one or two orders of magnitude. A very large antishielding factor in the rare earths was first found[10] in $\mathrm{Eu}^{3+}(4f^6)$ and was recognized as an antishielding factor by Judd, *et. al.*[11] Edmonds[12] found large antishielding factors in $\mathrm{La}^{3+}(4f^0)$ showing their presence in several lattices, and, together with subsequent work by the present authors[13] on Gd^{3+} and Lu^{3+}, demonstrating their presence throughout the $4f$ series. A correlation was established between the antishielded field gradients and V_2^0 into which later measurements on Tm^{3+},[14] and Dy^{3+},[15] have fitted fairly well. Antishielded field gradients are derived in Sec. II.

Only the ratio of the antishielding factor $(1-\gamma_\infty)$ to the shielding factor $(1-\sigma_2)$ can be directly assessed from experimental data, and in the interpretations of the early work[11–13] it was not possible to resolve and discuss these two factors separately. Several detailed theoretical estimates of $(1-\gamma_\infty)$ are now available.[16–20] Their agreement is encouraging, and we shall use these estimates, as discussed in Sec. III, to deduce shielding factors for trivalent rare earths in the ethyl sulfate lattice. In Sec. IV these factors are compared with the available theoretical estimates.

II. THE ANTISHIELDED FIELD GRADIENTS

A. Formalism

The notation in the literature relevant to this work is far from uniform. We therefore define the terms with which we shall work before deriving antishielded field gradients for the various ions below. We believe that this notation is least ambiguous of the choices available.

In the crystal-field model the Coulombic interaction of the $4f$ electron level with the crystal field may be written[3–6,14,21,22]

$$\mathcal{H}=\sum_k \sum_{L,M} \{A_L^M[r_k^L+S_L(r_k)]+T_L^M(r_k)\}\Phi_L^M(\theta_k,\phi_k). \qquad (1)$$

Here r_k, θ_k, and ϕ_k are the coordinates of the kth $4f$ electron, Φ_L^M is a linear combination of spherical harmonics Y_L^M and Y_L^{-M}, A_L^M is a multiplicative factor giving the strength of the crystal field, and S_L is the *linear* shielding term arising from deformation of closed electronic shells. Nonlinear shielding is described by T_L^M, which depends on several A_L^M. This latter effect has been discussed by Freeman and Watson,[22] who find that it may often be appreciable. Experimentally, optical data are fitted with crystal-field parameters $V_L^M=A_L^M(1-\sigma_L)\langle r^L\rangle_{4f}$. This may be regarded as the defining equation for σ_L. It is important to note that both linear and nonlinear shielding terms are contained in σ_L in a completely empirical way. This is the same σ_L used in Ref. 14 if one regards it as an empirical parameter, rather than as a linear shielding factor. Thus σ_2 is not independent of A_2^0. The symbol α_L (or α_n if C_n^m was used for A_L^M) has been used for σ_2. In Edmonds' notation[12] $(1-\sigma_2)$ is designated γ_E, and $(1-\gamma_\infty)$ is called $-\gamma_N$.

Interaction of the rare-earth ion with the crystal field sets up field gradients at the nucleus through a variety of mechanisms. Experimentally one finds that the nuclear-spin Hamiltonian has a term of the form

$$\mathcal{H}=P[I_z^2-\tfrac{1}{3}I(I+1)]. \qquad (2)$$

We have omitted an anisotropy term because the crystals that we have studied have trigonal symmetry axes. We refer to the directly measurable quantity P as the *quadrupole coupling constant.* P may be a linear combination of several terms,

$$P=\sum P_i=P_{4f}^{(1)}+P_{pq}+P_{\mathrm{Lat}}+P_{4f}^{(2)}+\cdots. \qquad (3)$$

Here $P_{4f}^{(j)}$ arises from the $4f$ configuration in jth-order perturbation theory. While $P_{4f}^{(1)}$ is most common, $P_{4f}^{(2)}$ is very important in Eu^{3+} in the ${}^7F_0$ ground state.[11,23] The pseudoquadrupole term P_{pq} is, in fact, a magnetic effect unrelated to the nuclear quadrupole

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[9] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).

[10] D. A. Shirley and C. A. Lovejoy, Bull. Am. Phys. Soc. **6**, 512 (1961).

[11] B. R. Judd, C. A. Lovejoy, and D. A. Shirley, Phys. Rev. **128**, 1733 (1962).

[12] D. T. Edmonds, Phys. Rev. Letters **10**, 129 (1963).

[13] Johan Blok and D. A. Shirley, J. Chem. Phys. **39**, 1128 (1963).

[14] R. G. Barnes, R. L. Mössbauer, E. Kankeleit, and J. M. Poindexter, Phys. Rev. **136**, A175 (1964).

[15] H. Hollis Wickman, Bell Telephone Laboratories, Murray Hill, New Jersey (private communication).

[16] E. G. Wikner and G. Burns, Phys. Letters **2**, 225 (1962).

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

[18] R. M. Sternheimer, Phys. Rev. **132**, 1637 (1963).

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

[20] R. E. Watson and A. J. Freeman, Phys. Rev. **135**, A1209 (1964).

[21] A. J. Freeman and R. E. Watson, Phys. Rev. **139**, A1606 (1965).

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

[23] R. J. Elliott, Proc. Phys. Soc. (London) **B70**, 119 (1957).

TABLE I. Crystal-field data for the rare-earth ethyl sulfates.

n in $4f^n$	Ion	Isotope	Method[a]	$P_{\rm Lat}$ ($\times10^{-5}$ cm^{-1})[b]	Q(b)	$(1-\gamma_\infty)A_2^0$ (10^4 cm^{-1} a_0^{-2})	A_2^0 (cm^{-1} a_0^{-2})[m]	$A_2^0\langle r^2\rangle$ (cm^{-1})[n]	$A_2^0\langle r^2\rangle$ (cm^{-1})[o]	$(1-\sigma_2)A_2^0$ (cm^{-1})[q]	σ_2[aa]	$\sigma_{\rm theory}$	References
0	La^{3+}	139	NMR	1.98[c]	+0.27(1)[h]	1.43(6)	177			(−40)	1.23		12, 31
		140	NA	−1.42(12)[d]	+0.13(2)[i]								this work
1	Ce^{3+}									−13(8)[r]	(1.1)		
2	Pr^{3+}								616[p]	14.1[s]	(1.0)	0.68[cc] 0.52[dd] 0.59[ee]	
3	Nd^{3+}									58.4[t]	(0.9)		
4	Pm^{3+}									(73)	(0.8)		
5	Sm^{3+}									87[u]	(0.75)		
6	Eu^{3+}	154	NA	−78(4)[d,e] $P=-41.7(28)$	+3.75(37)[i]	+2.9(3)	362	317		96[v]	0.73		this work
7	Gd^{3+}	159	NA	−144(5)[d]	(+1.56)[j]	+2.54(26)	314	246		(121)	0.61		this work
8	Tb^{3+}									146[w]	(0.65)		
9	Dy^{3+}	161	M	−120(6)[e,f]	+2.6[k]	+4.29(22)	530	385		171[x]	0.68		15
10	Ho^{3+}									180[w]	(0.6)		
11	Er^{3+}								313,[p]406	188[y]	(0.6)		
12	Tm^{3+}	169	M	[g]	+1.5[l]	+5.10	630	403		204[z]	0.68[bb]	0.50[cc]	14
13	Yb^{3+}									(220)	(0.6)		
14	Lu^{3+}	175	NMR	108.64(20)[c]	+3.6[j]	+5.9	730			(236)	0.68		31
		177	NA	−67(2)[d]	+3.6[j]	+3.65(12)	450				0.48		this work

[a] NA = nuclear alignment; NMR = nuclear magnetic resonance; M = Mössbauer effect.
[b] Signs are given where known.
[c] La^{139} in lanthanum ethyl sulfate at 77°K; Lu^{175} in lutetium ethyl sulfate at 20°K.
[d] In neodymium ethyl sulfate at 10^{-2} °K.
[e] Quoted error does not include uncertainty in a possible atomic Sternheimer factor for $4f$ electrons.
[f] In dysprosium ethyl sulfate at 4.2°K.
[g] See Ref. 14.
[h] Y. Ting, Phys. Rev. **108**, 295 (1957).
[i] See Ref. 27.
[j] Obtained from nuclear systematics. See text.
[k] B. Elbek, K. O. Nielson, and M. C. Oleson, Phys. Rev. **108**, 406 (1957).
[l] M. C. Oleson and B. Elbek, Nucl. Phys. **15**, 134 (1960).
[m] Assuming $\gamma_\infty=-80$. The uncertainties associated with these quantities are not included, but are surely large.
[n] Using the $\langle r^2\rangle_{4f}$ values given in Ref. 22.
[o] Here we have combined Burns' calculated values for PrES and ErES (Ref. 46) with appropriate $\langle r^2\rangle_{4f}$ values from Ref. 22.
[p] Calculated using nearest oxygens only. See Ref. 43.
[q] These entries were obtained from analysis of optical spectroscopy and paramagnetic resonance data, and by extrapolation or interpolation (values in parentheses).
[r] Reference 6.
[s] J. B. Gruber, J. Chem. Phys. **38**, 946 (1963).
[t] J. B. Gruber and R. A. Satten, J. Chem. Phys. **39**, 1455 (1963).
[u] H. Lammerman, Z. Physik **150**, 551 (1958).
[v] Reference 33.
[w] S. Hüfner, Z. Physik **169**, 417 (1962).
[x] M. J. D. Powell and R. Orbach, Proc. Phys. Soc. (London) **78**, 753 (1961).
[y] E. H. Erath, J. Chem. Phys. **34**, 1985 (1961).
[z] Reference 14.
[aa] Obtained from columns 8 and 11. Values obtained from extrapolated values of A_2^0 are given in parentheses.
[bb] Here we omitted the R_Q correction for consistency.
[cc] R. M. Sternheimer, Bull. Am. Phys. Soc. **10**, 597 (1965).
[dd] Reference 17.
[ee] Reference 45.

moment. It is the dominant term for Pm^{3+} in the double nitrate lattice,[24,25] but is expected to be negligible for all the cases treated here. The antishielded lattice contribution is given by[9,12,14,26]

$$P_{\rm Lat}=-[3Q/I(2I-1)](1-\gamma_\infty)A_2^0, \qquad (4)$$

and the first-order $4f$ term by[5,14,19,22]

$$P_{4f}^{(1)}=-[3e^2Q/4I(2I-I)](1-R_Q)\times[3J_z^2-J(J+1)]\langle r^{-3}\rangle_{4f}\langle J\|\alpha\|J\rangle. \qquad (5)$$

Here γ_∞ is the Sternheimer factor for the lattice and R_Q is the "atomic Sternheimer factor."[14,19,22] The quantity $\langle J\|\alpha\|J\rangle$ arises in application of the Wigner-Eckart theorem to evaluation of the crystal-field interaction by the "operator equivalent" technique,[3,5] and $\langle r^{-3}\rangle_{4f}$ is the *actual* expectation value of r^{-3} for $4f$ electrons in the ion. The effective $\langle r^{-3}\rangle_Q$ for quadrupole interactions is given by[19]

$$\langle r^{-3}\rangle_Q=(1-R_Q)\langle r^{-3}\rangle_{4f}. \qquad (6)$$

With sufficient knowledge of the behavior of a given ion in a crystal along with the values of P, P_{4f}, where necessary, Q, and I for a specific isotope, it is possible to obtain the quantity $(1-\gamma_\infty)A_2^0$. In the cases reported below that were studied by nuclear orientation, we have omitted discussion of the details of the alignment experiments and that part of the data reduction that involves nuclear decay properties or the absolute temperature scales of the cooling salts explicitly. This part of the work will be reported elsewhere.[27,28] For this paper we shall simply note that the problem of obtaining a value of P from nuclear alignment parameters is straightforward,[29] and will use the values of P so obtained as our point of departure. The objective in this section is

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[24] C. J. S. Chapman, M. A. Grace, J. M. Gregory, and C. V. Sowter, Proc. Roy. Soc. (London) **A259**, 377 (1960).

[25] R. W. Grant and D. A. Shirley, Phys. Rev. **130**, 1100 (1963).

[26] An alternative notation was introduced by Edmonds (Ref. 12) and used by Blok and Shirley (Ref. 13). The symbol γ_N was used for $(\gamma_\infty-1)$. Other workers have uniformly used the latter notation, and we shall adopt it for uniformity and because it is better suited to theoretical calculations.

[27] J. Blok and D. A. Shirley, Phys. Rev. (to be published).

[28] J. Blok, D. A. Shirley, and N. J. Stone, this issue, Phys. Rev. **143**, 78 (1966).

[29] See the review article by R. J. Blin-Stoyle and M. A. Grace, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 42, p. 555.

to obtain $(1-\gamma_\infty)A_2$ from P. During the interval since we reported preliminary values for some of the coupling constants discussed below the absolute temperature scales of the two cooling salts, neodymium ethyl sulfate (NES) and cerium magnesium nitrate (CMN), have been redetermined in this Laboratory[28,30] and the values of P are substantially modified.

B. Lanthanum

Edmonds has determined the magnitudes of P_{139} for La^{3+} in lanthanum ethyl sulfate (LES), lanthanum magnesium nitrate (LMN), and lanthanum trichloride,[12,31] using NMR. The results for the first, together with derived values of $(1-\gamma_\infty)A_2^0$, are given in Table I. Abragam and Chapellier[32] have determined the sign of P_{139} for La^{3+} in (99% La, 1% Nd) magnesium nitrate as positive. The quadrupole moment Q_{139} is positive: it follows that $(1-\gamma_\infty)A_2^0$ is negative for lanthanum in the double nitrate lattice. From nuclear orientation experiments on La^{140} in CMN and NES we find P_{140}(CMN $=+1.10(16)\times 10^{-5}$ cm^{-1}, and $P_{140}(\text{NES})=-1.42(12)\times 10^{-5}$ cm^{-1}. The ratio of these two constants is probably known to about 10%. Its magnitude (1.29) is in fair agreement with Edmonds' ratio of $[P_{139}(\text{LES})/P_{139}(\text{LMN})]=1.06$. The sign of P_{140}(NES) is especially important, because the positive sign of $(1-\gamma_\infty)A_2^0$ for La^{3+} in NES is derived from it, and on this derived quantity rests the interpolation (below) from which we shall infer values of A_2^0 and $(1-\sigma_2)$ for Ce^{3+} through Sm^{3+} in the ethylsulfate lattice. Our value for P_{140}(NES) is based on a γ-ray anisotropy of $(\frac{3}{2})B_2U_2F_2=-0.0045(4)$ at 0.01°K.

C. Europium

The most accurate nuclear orientation data[27] give the values of P_{154} and Q_{154} quoted in Table I. The evaluation of $(1-\gamma_\infty)A_2^0$ from P is complicated by a second-order term $P_{4f}^{(2)}$ arising from matrix elements of the form $\langle J=2, J_z=0|\,V_2^0\,|J=0, J_z=0\rangle$ that connect the ground level $^7F_0$ with the $^7F_2$ level.[11,23] Thus Eq. (3) simplifies to

$$P=P_{\text{Lat}}+P_{4f}^{(2)}. \tag{7}$$

We may write

$$P_{4f}=\frac{6e^2QA_2^0\langle r^2\rangle_{4f}(1-\sigma_2)\langle r^{-3}\rangle_{4f}(1-R_Q)\,|\langle 20\|\alpha\|00\rangle|^2}{I(2I-1)(E_{20}-E_{00})}. \tag{8}$$

This is essentially Elliott's original expression, with appropriate shielding factors inserted to make the notation consistent with current usage. Using[23,33–35]

$$V_2^0=A_2^0(1-\sigma_2)\langle r^2\rangle_{4f}=80\text{ cm}^{-1},\quad \langle r^{-3}\rangle_{4f}=7.28a_0^{-3},$$
$$\langle 20\|\alpha\|00\rangle=\tfrac{2}{5}\sqrt{3},\quad I=3,$$

and

$$E_{20}-E_{00}=1015\text{ cm}^{-1},$$

we find $P_{4f}^{(2)}=0.97\times 10^{-4}Q(1-R_Q)$ cm^{-1}, with Q in barns. Estimates of the atomic Sternheimer factor R_Q exist in part: the angular portion has been estimated as +0.29 for Eu^{3+},[14,36] and the radial portion for Ce^{3+} as −0.43.[14,19] Experimental values in the range 0–0.2 have been given for Tm^{3+}.[14] We shall take $(1-R_Q)$ as unity in correcting for $P_{4f}^{(2)}$. We feel that this is a reasonable estimate in light of the above data, but note that this factor could be in error by as much as 30%. The final value of $A_2^0(1-\gamma_\infty)$ for Eu^{3+} in NES is $+2.9(3)\times 10^4$ cm^{-1} a_0^{-2}. For Eu^{3+} in CMN a similar calculation, with $V_2^0=-18.5$ cm^{-1},[37] yields $A_2^0(1-\gamma_\infty)=-0.35(8)\times 10^4$ cm^{-1}.

D. Gadolinium

There are two subtleties in the analysis of the Gd^{159} data that should be noted. First, the spin Hamiltonian Gd^{3+} in an NES lattice in zero field may be written

$$\mathcal{H}=B_2^0P_2^0+B_4^0P_4^0+B_6^0P_6^0+B_6^6P_6^6+A(\mathbf{S}\cdot\mathbf{I})+P_{\text{Lat}}[I_z^2-\tfrac{1}{3}I(I+1)]+CT_zS_z. \tag{9}$$

Here the first four (crystal-field) terms are well-known and have been measured[38] for a lanthanum ethyl sulfate lattice. The last term accounts for dipole-dipole interactions between the two nearest-neighbor Gd^{3+} ions and the host Nd^{3+} ions.[39] The magnetic and quadrupole hfs terms are of the form expected for the $4f^7(^8S_{7/2})Gd^{3+}$ ion. When this Hamiltonian is diagonalized the crystal-field terms tend to establish lowest energy basis states (i.e., basis states that are appreciably populated at 0.01°K) in which the A term produces anisotropic magnetic hfs that opposes the "axial" nuclear orientation arising from the P term. Thus a correction is necessary before P can be calculated. We have used an A value of 0.0005 cm^{-1} for Gd^{159} in making the 24% correction: this is based on published values of A for Gd^{155} and Gd^{157} together with the available information on the nuclear structure of Gd^{159}.[27,40] The value of P so obtained is -1.44×10^{-3} cm^{-1}.

In order to obtain $(1-\gamma_\infty)A_2^0$ from P we have employed the collective nuclear model, which is very well-

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[30] R. B. Frankel, D. A. Shirley, and N. J. Stone, Phys. Rev. **140**, A1020 (1965).

[31] D. T. Edmonds, Clarendon Laboratory, Oxford University, Oxford, England (private communication).

[32] A. Abragam and M. Chapellier, Phys. Letters **11**, 207 (1964).

[33] B. Judd, Mol. Phys. **2**, 407 (1959).

[34] B. Bleaney (private communication).

[35] E. V. Sayre and S. Freed, J. Chem. Phys. **24**, 1216 (1956).

[36] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **95**, 736 (1954).

[37] Obtained by extrapolation; see Ref. 13.

[38] B. Bleaney, H. E. D. Scovil, and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

[39] G. A. Westenbarger and D. A. Shirley, Phys. Rev. **123**, 1812 (1961).

[40] W. Low, Phys. Rev. **103**, 1309 (1956).

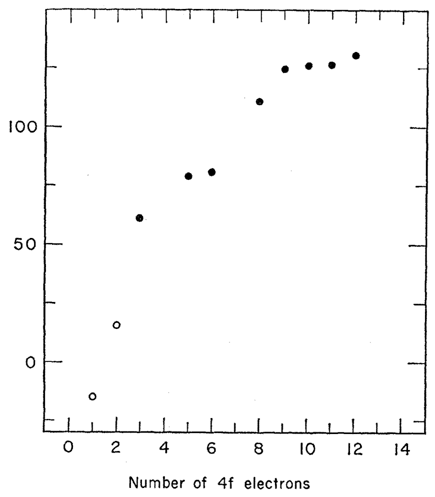

FIG. 1. Experimental values of $V_2^0=A_2^0(1-\sigma_2)\langle r^2\rangle_{4f}$, for trivalent rare-earth ions in the ethyl sulfate lattice, obtained from optical and paramagnetic resonance data. References are given in Table I. V_2^0 seems to change sign in the very light rare earths.

established in this region of the periodic table, to estimate[41] an intrinsic quadrupole moment of $Q_0=+7.8$ b, which yields[42] a spectroscopic quadrupole moment of $+1.56$ b. Combining this with $I_{159}=\frac{3}{2}$, we find $(1-\gamma_\infty)A_2^0=2.54(26)\times10^4$ cm^{-1} a_0^{-2}.

E. Lutetium

Nuclear orientation experiments on Lu^{177} in NES yielded in a very straightforward manner $P_{\text{Lat}}=-6.7(2)\times10^{-4}$ cm^{-1}. No experimental determination of the quadrupole moment, corrected for antishielding, is available, so we have resorted again to nuclear systematics[41,42] to estimate $Q=+3.6$ b, from which we find $(1-\gamma_\infty)A_2^0=+3.65(11)\times10^4$ cm^{-1} a_0^{-2}.[11] This may be compared with Edmonds' value (Table I) for the lutetium ethyl sulfate lattice.

III. DERIVATION OF A_2^0 AND 1-σ_2

We now have values for $(1-\gamma_\infty)A_2^0$ obtained from orientation experiments for four of the fifteen rare earths (including the first and last) in the NES lattice. Additional estimates for $(1-\gamma_\infty)A_2^0$ of La^{3+},[12,31] Dy^{3+},[15] Tm^{3+},[14] and Lu^{3+},[12,31] may be obtained from NMR and Mössbauer resonance on concentrated salts. Agreement among the different estimates is only moderately good. Probably this is in part due to the use of different lattices for the various experiments. There is a general upward trend in $(1-\gamma_\infty)A_2^0$, and the values of $(1-\sigma_2)$ derived below show sufficient regularity to permit interpolations of some credibility. Of course $(1-\sigma_2)$ need not vary smoothly; some of the mechanisms that contribute to σ_2 are expected not to vary smoothly with atomic number. There are several theoretical estimates of γ_∞ available for various trivalent rare earths.[16–20] With one exception they lie near -80, and are reasonably constant throughout the series. Following the advice of Watson and Freeman[20] we shall therefore adopt the value of -80 for γ_∞ for all the rare earths. We feel that the most serious objection to this procedure is the fact that the theoretical values are based on nonrelativistic p wave functions. Thus the magnitude of γ_∞ is very probably too low,[20] especially in the higher Z ions. The entries for A_2^0 in column 8 of Table I were obtained by taking $(1-\gamma_\infty)=+81$, and these are converted to $A_2^0\langle r^2\rangle_{4f}$ in column 9. The avaliable theoretical estimates are given for comparison in column 10.[43] Column 11 contains values of $(1-\sigma_2)A_2^0$ obtained from optical data. Comparison with column 8 yields derived values of σ_2, given in column 12. Theoretical values of this parameter are listed in column 13, for comparison.[17,44,45]

Figures 1, 2, and 3 show the variation of V_2^0, $(1-\gamma_\infty)A_2^0$, and $(1-\sigma_2)$ through the rare-earth ethyl sulfates.

IV. DISCUSSION

A great deal has been said in the literature about the applicability of crystal-field theory to real lattices, especially apropos of shielding. Particular reference is made to recent papers by Burns[46] and by Freeman and Watson,[47] in which shielding in rare-earth ions is dis-

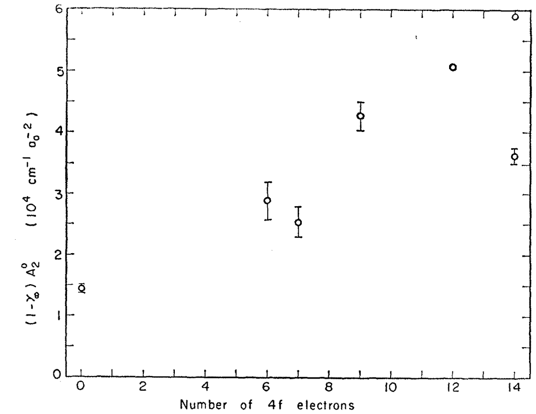

FIG. 2. Antishielded crystal-field gradient, $(1-\gamma_\infty)A_2^0$, derived from quadrupole coupling constants, for several trivalent rare-earth ions in the ethyl sulfate lattice. A definite upward trend is evident. This may arise from γ_∞ or from A_2^0. While we used the best available theoretical estimate of γ_∞ (a constant value of -80) in the subsequent analysis, we feel that the upward trend in $(1-\gamma_\infty)A_2^0$ probably arises from both factors. The discrepancy between the two Lu^{3+} points may arise in part from the fact that different host lattices were used.

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[41] C. H. Townes, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38/1, p. 377.

[42] A. Bohr and B. R. Mottelson, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **27**, No. 16 (1953).

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

[44] R. M. Sternhemier, Bull. Am. Phys. Soc. **10**, 597 (1965).

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

[46] G. Burns, J. Chem. Phys. **42**, 377 (1965).

[47] A. J. Freeman and R. E. Watson, Phys. Rev. **139**, A1606 (1965).

cussed carefully. The systematics derived in this paper should be studied with these discussions in mind. There are several rather obvious points of contact between the references and these results that we shall not discuss, both for reasons of brevity and because this field is still quite active and the conclusions are of necessity somewhat tentative. A definitive summary of shielding in the rare earths clearly awaits more theoretical and experimental work. In what follows we shall therefore concentrate on the questions raised by this work that are particularly in need of clarification if we are to understand shielding in greater detail.

The similarity of the values of $A_2^0\langle r^2\rangle_{4f}$ in columns 9 and 10 of Table I is encouraging: it suggests that theoretical lattice-sum estimates of A_2^0 are of approximately the right magnitude. Any undue optimism about the quantitative accuracy of these estimates is premature in light of Burns' discussion[43] of the assumptions entailed in a lattice-sum calculation. Still we may draw the conclusion that it is primarily to the shielding term, and not to A_2^0, that we must look for an explanation of the rapid variation of the crystal-field parameter V_2^0 in rare-earth ethyl sulfates.

The sign change of $(1-\sigma_2)$ in the light rare earths is intriguing. In accepting this result we must be cautious, because the usual assumptions have been made that the properties of a rare-earth ion are essentially independent of *which* rare-earth lattice it is in, and that some of these properties vary smoothly with Z, allowing a certain amount of extrapolation. There would be little point in studying the $4f$ series in a lattice in which isomorphous substitution is possible if these assumptions were not applied in the early stages (and shielding studies are in a very primitive stage), but they should be tested experimentally. Even if some of these assumptions are not valid, though, it still seems inescapable that σ_2 is near unity in the light rare earths in an ethylsulfate lattice. Of course the crossing through zero of $(1-\sigma_2)$ has in itself no theoretical significance. The large magnitude of σ_2, and particularly its Z dependence, are of importance. Of the few theoretical estimates available, Sternheimer's values for σ_2 are about $\frac{2}{3}$ of the experimental values and show the indicated Z dependence. Freeman and Watson have recently emphasized the importance of nonlinear contributions to shielding. Their calculations also show a Z dependence for σ_2.[47]

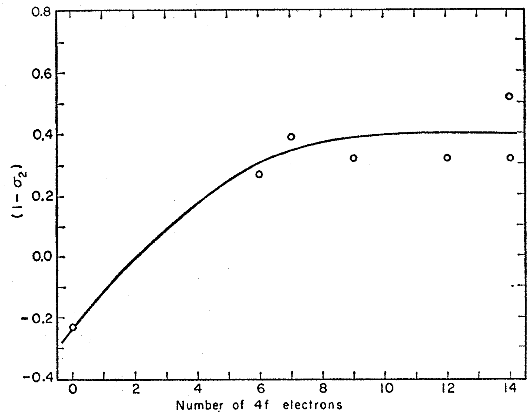

FIG. 3. Derived values of $(1-\sigma_2)$ for trivalent rare-earth ions in the ethyl sulfate lattice, obtained by combining points shown in Figs. 1 and 2, using $\gamma_\infty=-80$, and neglecting any possible variation of ions' properties with host. The curve has no theoretical significance but is drawn only to aid interpolation.

The prospects for understanding shielding in the rare-earth ethyl sulfates seem quite good: semiquantitative agreement is already available. Theoretical techniques for calculating σ_2 are still evolving.[44,46,47] It is to be hoped that more reliable estimates of γ_∞, and especially of its Z dependence will be made, using relativistic p wave functions, so that one may be certain that the experiments are studying shielding, rather than antishielding. On the experimental side accurate magnetic-resonance values of P_{Lat} in other lattices would be very useful. Several of the assumptions mentioned above should also be investigated.[48]

ACKNOWLEDGMENTS

We are grateful to Dr. Donald T. Edmonds, Dr. Arthur J. Freeman, and Dr. H. Hollis Wickman for communicating their results prior to publication.

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[48] *Note added in proof.* The value of $(1-\gamma_\infty)A_2^0$ for Lu^{3+} derived in Table I from Edmonds' NMR data is based on our estimate of the quadrupole moment of Lu^{175} from nuclear systematics. An alternative, lower value of 3.75×10^4 may be obtained by using the spectroscopic value of Q_{175}, which is, however, uncorrected for an atomic Sternheimer factor. S. Hüfner has recently determined $(1-\gamma_\infty)/(1-\sigma_2)=208$ for Ho^{3+} in the ethyl sulfate lattice. With our choice of -80 for γ_∞ this yields $\sigma_2=0.61$. We are indebted to Dr. Hüfner for communicating this result prior to publication.