of Raman spectroscopy[11] and the presence of vibrational sidebands in the ruby infrared spectrum show the presence of optical modes in the frequency range 140 cm^{-1} to 900 cm^{-1}. For the experimental range of temperatures, these modes should certainly contribute to the linewidth comparably with the acoustic modes with a Debye temperature, based on calculations from the elastic constants, of 600°K. Despite this complexity, a few remarks may be useful.

It seems unlikely that the width is due to acoustic modes alone. The fact that the observed width is much less than kT over the whole range of interest, or that $\Delta \ll \delta$, allows the use of Eqs. (29, 30) even though $\alpha \sim 1$. But these equations imply a T^7 dependence of Δ which is in marked disagreement with experiment.

It is proposed that the breadth is, in fact, dominated by optical rather than acoustical modes, since there appear to be modes available which would achieve appreciable thermal excitation at these temperatures. By a suitable choice of the coupling to the various modes and of the breadth of the branches it should be possible to fit almost any experimental curve. Hence attempts to fit the experimental curve in detail seem rather pointless. It would certainly be fruitful to study the width of narrow line electronic spectra in hosts with a simple phonon spectrum.

CONCLUSIONS

A greatly simplified Hamiltonian is proposed and studied in an attempt to understand the linewidth of certain narrow optical and γ-ray transitions in solids. The analysis illustrates how to obtain meaningful results for the observable linewidths in terms of the calculable moments of the line. Several models for the phonon spectrum are treated and shown to have markedly different qualitative behavior as regards their influence on the observed line width. The study shows that in principle the Mössbauer line has a finite breadth as a result of the coupling to the phonon field via the second-order Doppler shift, though, except in the case of localized modes, the breadth is probably not observable. In the case of the ruby narrow line spectrum, though the mechanism of line broadening proposed by Kiel[4] is probably qualitatively correct, the complexity of the phonon spectrum for Al_2O_3 prevents detailed comparison of theory with experiment.

ACKNOWLEDGMENTS

This analysis resulted from an attempt to clarify the broadening mechanism suggested by Dr. A. Kiel and I am indebted to him for the preprint of reference 4 which is the starting point for this paper. Dr. G. Chester has contributed greatly in discussion and criticism of the manuscript.

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PHYSICAL REVIEW VOLUME 128, NUMBER 4 NOVEMBER 15, 1962

Anomalous Quadrupole Coupling in Europium Ethylsulfate*

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Hyperfine structure, apparently of pure quadrupolar form, has been observed in the Eu^{3+} ion in a neodymium ethylsulfate lattice. It has twice the predicted magnitude and opposite sign to that calculated on the basis of a pure ground electronic configuration of the type $4f^n$. Arguments are presented for ascribing the anomaly to the admixing, through the crystal-field potential, of the state $5p^5 6p\ {}^1D_2$ into the closed-shell state $5p^6\ {}^1S_0$. For Eu^{152}, we find $P_{152} = -(6.7 \pm 0.5) \times 10^{-4}$ cm^{-1} and for Eu^{154}, $P_{154} = -(8.3 \pm 0.7) \times 10^{-4}$ cm^{-1}. The spin and parity assignments of 2− for the 1531-keV state in Sm^{152} and the 1400- and 1723-keV states in Gd^{154}, as well as the electric-dipole multipolarities of the radiations depopulating these states, are confirmed. The quadrupole moment of Eu^{154} is found to be 3.29 ± 0.37 b.

I. INTRODUCTION

ONE of the significant trends in chemical and atomic physics in the past few years has been the increasing awareness, both experimental and theoretical, of small hyperfine structure effects which cannot be explained by the very simplest models, involving only valence electrons in pure, noninteracting hydrogen-like orbitals. These effects are observed, for example, in some internal magnetic fields, in antishielding, and in the influence on hyperfine structure of higher-order crystal-field interactions and deviations from Russell-Saunders coupling.

We report herein a case in which such subtle effects are clearly present, namely, the existence of hyperfine structure in the ground state of Eu^{3+}. This ion has (in the usual approximation) the electronic configura-

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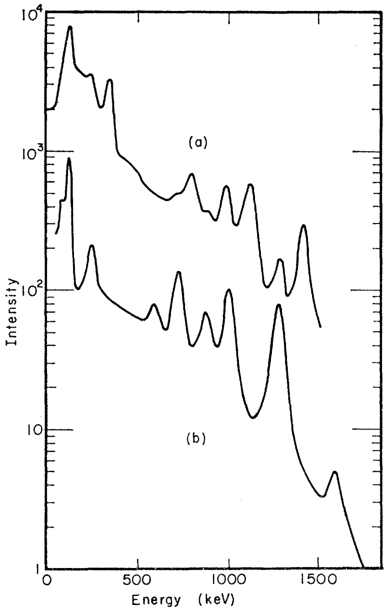

FIG. 1. Gamma-ray spectra of (a) $Eu^{152}+Eu^{154}$, (b) Eu^{154}. These spectra were taken with 3-in. × 3-in. NaI(Tl) detectors and samples consisting of the europium isotopes in single crystals of neodymium ethylsulfate. The γ-ray peaks may be identified in Figs. (2) and (3).

tion $4f^6$, from which it follows by Hund's rule that the ground state is the singlet $^7F_0$, with no hyperfine structure possible. The optical spectrum of Eu^{3+} in an ethylsulfate lattice has been analyzed; this state being confirmed, and others of the multiplet ^7F assigned.[1]

Elliott[2] has shown, using second-order perturbation theory, that a weak electric quadrupole coupling should arise in Eu^{3+} in an ethylsulfate lattice through the $V_2{}^0$ term in the crystal-field potential, which connects the ground state $^7F_0$ with the Stark level characterized as $|^7F_2, J_z=0\rangle$. He considered the influence of other small quadrupole-like interactions (by this we mean quadrupole and pseudoquadrupole interactions) within the usual crystal-field theoretical framework and found that the contributions of such interactions were orders of magnitude smaller than this second-order $V_2{}^0$ effect.

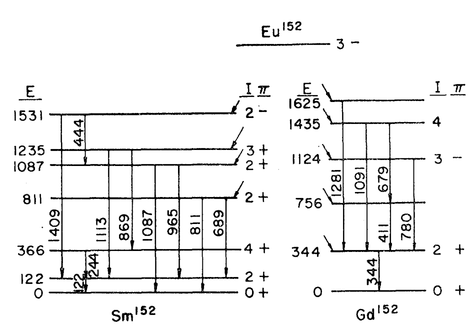

FIG. 2. Partial decay scheme of Eu^{152}, showing transitions of interest in this research. The 2− spin and parity assignment for the 1531-keV state of Sm^{152} was confirmed.

We have looked for this interaction experimentally in nuclear orientation experiments on radioactive europium isotopes in an ethylsulfate lattice. Hyperfine structure was observed, at least predominantly quadrupolar and of the expected order of magnitude, but of different magnitude and sign.

In the following, the experiments and interpretation are described in some detail. Several nuclear parameters, which are of particular importance in establishing the sign of the coupling constant, must first themselves be independently established. In this process some new nuclear information is gained. Finally, possible explanations of the hyperfine structure are discussed.

II. EXPERIMENTAL

Neodymium ethylsulfate was chosen as a lattice because of its usefulness in nuclear alignment experiments. The crystal-field parameters for europium are expected to be nearly the same in this lattice as in europium ethylsulfate, for which they are known.[1]

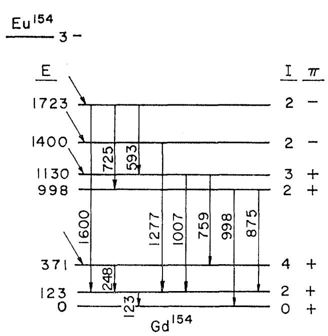

FIG. 3. Partial decay scheme of Eu^{154}. The spin assignments of the states at 1400 and 1723 keV in Gd^{154} were confirmed in this work.

The apparatus has been briefly described elsewhere.[3] Care was taken to minimize the heat leak into the sample and to insure that the entire single crystal of neodymium ethylsulfate was at an essentially uniform, constant temperature during the counting period. At the lowest temperatures the average temperature of the crystal changed by only about 1% during a 5-min counting period.

The gamma-ray spectra of Eu^{154} and a mixture of Eu^{152} and Eu^{154} are shown, for reference, in Fig. 1. Partial decay schemes showing portions relevant to our discussion are drawn in Figs. 2 and 3. In Figs. 4 and 5 are shown the temperature dependences of the angular distributions of the 1.277-MeV γ ray from Gd^{154} and the 1.409-MeV γ ray from Sm^{152}, following the decay of the oriented europium parents. Finally in Table I the anisotropies of the γ rays from both samples at 0.02°K are listed and compared with the level schemes in Figs. 2 and 3.

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

[3] C. E. Johnson, J. F. Schooley, and D. A. Shirley, Phys. Rev. **120**, 2108 (1960).

TABLE I. Angular distribution coefficients.

Isotope	E_γ (keV)	Spin sequence[a]	$B_2U_2F_2$ at 0.02°K	$B_2U_2F_2$ (calc) $P<0$	$B_2U_2F_2$ (calc) $P>0$
Sm^{152}	345	2(Q)0	-0.045 ± 0.010	-0.046[b]	$+0.023$[c]
Gd^{152}	965	2(Q)2	$+0.015\pm0.010$	$+0.010$	-0.005
Gd^{152}	1087, 1113	2(Q)0, 3(Q)2	-0.038 ± 0.010	-0.042	$+0.021$
Gd^{152}	1409	2(D)2	-0.060 ± 0.005	(-0.060)	(-0.060)
Gd^{154}	121	2(Q)0	-0.029 ± 0.005	-0.038[d]	$+0.019$
Gd^{154}	248	4(Q)2	-0.050 ± 0.016	-0.062	$+0.031$
Gd^{154}	593	2(D)3	small, >0	$+0.021$	-0.010
Gd^{154}	725, 759	2(D)2, 3(Q)4	-0.066 ± 0.017	-0.056	$+0.028$
Gd^{154}	875	2(Q)2	>0	$+0.023$	-0.012
Gd^{154}	998, 1007	2(Q)0, 3(Q)2	small, <0	-0.051	$+0.026$
Gd^{154}	1277	2(D)2	-0.074 ± 0.006	(-0.074)	(-0.074)[e]
Gd^{154}	1600	2(D)2	-0.057 ± 0.030	-0.074	$+0.037$

[a] Dipole and quadrupole are denoted by D and Q.
[b] Data for Sm^{152} and Gd^{152} are normalized to the 1409-keV γ ray.
[c] Normalized as in b, but using the sequence 3(0.85D, 0.15Q)2 required for $P>0$ (see text).
[d] Similar to b, but using the 1277-keV γ ray for Gd^{154}.
[e] As in c, but for the 1277-keV γ ray.

III. NUCLEAR INFORMATION

The angular (directional) distribution of γ radiation following the decay of oriented nuclei is given by an expression of the form[4]

$$W(\theta)=1+B_2U_2F_2P_2(\cos\theta)+\cdots. \qquad (1)$$

The dots represent higher order terms not present in this experiment. Thus, only the two terms in Eq. (1) are significant in interpreting these experiments. The first term gives the isotropic intensity, normalized to unity. The term in $P_2(\cos\theta)$, where θ is the angle from the crystalline c axis, describes the anisotropic component. The parameter B_2 is temperature dependent and is the same for all radiation from a given isotope, being a function only of properties of the parent nucleus. The reorientation parameter U_2 describes the effect of preceding (usually unobserved) transitions on the orientation. With each γ ray is associated a distinct F_2 which is a function only of the initial and final spins and of the multipolarity of the transition.

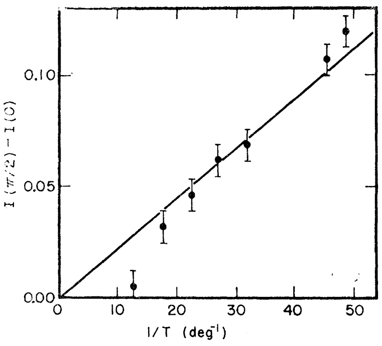

FIG. 4. Angular distribution function for the 1277-keV γ ray of Gd^{154} following the decay of Eu^{154} oriented in neodymium ethylsulfate, as a function of reciprocal temperature. The function plotted is the difference between the normalized intensities at 90° and 0° from the crystalline axis.

In treating the data to study the level schemes of the daughters, we first effectively eliminated B_2 and P_2 from the angular distributions by comparing, for different γ rays, data taken at the same temperature and at the same angle. Thus the anisotropic component of the angular distribution of each gamma ray is proportional to U_2F_2 for that gamma ray. Knowing one U_2F_2 reliably from other information on the decay scheme, one can then obtain the other U_2F_2's by direct comparison of the anisotropic components of angular distribution (i.e., the coefficients of P_2). The problem, then, is to establish one U_2F_2 reliably for the decay of each isotope, Eu^{152} and Eu^{154}.

In both spectra one γ ray stood out as the best from which to derive quantitative results: the 1277-keV γ ray of Gd^{154} and the 1409-KeV γ ray of Sm^{152} (Fig. 1). In each case the photopeak was clearly resolved and the background was quite low. Moreover, these γ rays exhibited the largest anisotropies. Unfortunately the published work was not unanimous in the multipolarity assignments for these two γ rays or in the spins of the states from which they are emitted. In each case the high-energy γ ray decays to the 2+ state of the ground-state rotational band, and angular correlation measurements have been made on both.[5–8] In Gd^{154}, polarization correlation measurements were also available.[9] The

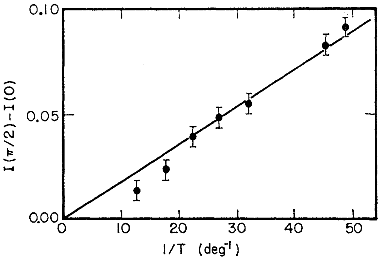

FIG. 5. Angular distribution function for the 1409-keV γ ray of Sm^{152} following the decay of oriented Eu^{152}, as in Fig. 4.

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

[5] S. Ofer, Nuclear Phys. 4, 477 (1957).

[6] G. D. Hickman and M. L. Wiedenbeck, Phys. Rev. **111**, 539 (1958).

[7] R. W. Lide and M. L. Wiedenbeck, Phys. Rev. **113**, 840 (1959).

[8] P. Debrunner and W. Kündig, Helv. Phys. Acta **33**, 395 (1960).

[9] C. V. K. Baba and S. K. Bhattercherjee, Phys. Rev. **123**, 865 (1961).

TABLE II. Conversion coefficients.

			$10^3\alpha_K$			
Isotope	E	Exp	$E1$	$M1$	$E2$	Reference
Sm^{152}	1409	0.499 ± 0.025	0.47	1.50	1.05	10
Gd^{154}	1277	$0.72\ \pm0.07$	0.63	2.1	1.48	11

angular correlation coefficients are identical within experimental error, and the other features of the transitions are very similar, each being populated by allowed beta decay from a parent $3-$ state and decaying to the $2+$ first-excited state; thus, we shall discuss them together.

The angular correlation data left only two possible combinations for the multipolarities of the high-energy γ rays and the spins of the states from which they proceed: (a) a spin of 2 and essentially pure dipole multipolarity, or (b) a spin of 3 and multipolarity of 85% dipole, 15% quadrupole, with relative phase $\delta<0$. A determination of the multipolarities of these γ rays from conversion coefficients would be expected to decide between these two combinations, and, indeed, the most precise measurements show pure $E1$ multipolarity in both cases,[10,11] clearly indicating alternative (a) above. On the other hand, an earlier measurement gave $\alpha_K\approx1.7\times10^{-3}$ for the 1277-keV γ ray,[12] consistent with alternative (b). Experimental and theoretical[13] conversion coefficients are given in Table II.

It is always desirable to overdetermine a set of physical quantities by obtaining one more equation than there are parameters, for only by so doing can one find errors which would otherwise go unnoticed. In this case a very definite choice can be made between (a) and (b) above from the *signs* of the F_2's of the 1277- and 1409-keV γ rays alone. The signs may easily be established by comparing the F_2's of these γ rays with the F_2's for other γ rays, of known multipolarity, in the daughter nuclei. In fact, it is easily shown (by direct calculation) that the U_2's are all positive, and it thus suffices to compare the signs of the U_2F_2 products. This is done in Table I, from which it is clear that the F_2's of the high-energy γ rays are negative, which is possible only for alternative (a) above. This then constitutes an independent confirmation of alternative (a).

Angular correlation data[8] but no conversion coefficients are available for the 1600-keV γ ray in Gd^{154}. Our data (Table I) establish $F_2<0$ for this γ ray, leading, in a manner similar to that discussed above, to a unique assignment of $2-$ for the 1723-keV state and $E1$ multipolarity for the 1600-keV γ ray.

As discussed before, the 1277- and 1409-keV γ rays have the most reliably interpreted anisotropies, lying as they do high in the level scheme and in the γ-ray spectrum. The preceding radiation in each case is an allowed beta transition of the type $3-(L=1)2-$ for which U_2 is $+0.828$. For the γ rays themselves, F_2 is -0.418. Thus, B_2 is readily evaluated using the data in Figs. 4 and 5, and is found to be

$$B_2(152)=+(3.45\pm0.28)\times10^{-3}T^{-1}, \tag{2a}$$

$$B_2(154)=+(4.28\pm0.34)\times10^{-3}T^{-1}. \tag{2b}$$

A T^{-1} temperature dependence of B_2 for low degrees of alignment characterizes hyperfine structure of the quadrupole form. In Figs. 4 and 5 we have fitted our data with curves of this form (straight lines as plotted). The fit, which is quite good, though not excellent, constitutes the chief evidence that the hyperfine structure Hamiltonian has, at least predominantly, a quadrupolar form

$$\mathcal{H}=P[M^2-\tfrac{1}{3}I(I+1)], \tag{3}$$

where M is the nuclear-spin magnetic quantum number. Combining this with the expression for B_2,[4,14]

$$B_2=\sum\frac{[3M^2-I(I+1)]W(M)}{[\frac{1}{5}I(I+1)(2I-1)(2I+3)]^{1/2}}, \tag{4}$$

we obtain B_2 in terms of P. On comparison with Eqs. (2) we find

$$P_{152}=-(6.7\pm0.5)\times10^{-4}\text{ cm}^{-1}, \tag{5a}$$

$$P_{154}=-(8.3\pm0.7)\times10^{-4}\text{ cm}^{-1}. \tag{5b}$$

We note that these values are slightly different from those reported earlier,[15] the major change being an increased magnitude for P_{154}. The present value was obtained using a sample of pure Eu^{154}, thus eliminating the background corrections which were necessary in the earlier experiment because of the presence of Eu^{152}. The change in P_{152} follows from improved thermometry.

If we assume that the quadrupole moment is proportional to P for each isotope, we can derive the ratio

$$Q_{154}/Q_{152}=1.24\pm0.10. \tag{6}$$

Alpert has given the ratios $|Q_{152}/Q_{151}|$ and $|Q_{152}/Q_{153}|$ as 2.75 ± 0.17 and 1.08 ± 0.07, respectively.[16] Krebs and Winkler have recently measured Q_{151} and Q_{153} as $+0.95\pm0.1$ and $+2.42\pm0.20$ b, respectively.[17] Combining all these data, we find

$$|Q_{154}|=3.24\pm0.37\text{ b}.$$

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[10] Paresh Mukherjee, Phys. Rev. **118**, 794 (1960).

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[12] J. O. Juliano and F. S. Stephens, Phys. Rev. **108**, 341 (1957).

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[14] There is an error of a factor of 3 in the expression on p. 565 of reference 4, from which this relationship was taken.

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

[16] Seymour S. Alpert (private communication); and University of California Radiation Laboratory Report UCRL-9850 (unpublished).

[17] K. Krebs and R. Winkler, Naturwissenschaften **47**, 490 (1960).

TABLE III. Quadrupole moments of europium.

Isotope	Q	Q_0	Reference
Eu^{151}	$+0.95(10)$[a]	$+2.66(28)$	17
Eu^{152}	$2.61(20)$	$6.26(50)$	16
Eu^{153}	$+2.42(20)$	$+6.78(56)$	17
Eu^{154}	$3.24(37)$	$7.78(0.88)$	this work

[a] Standard deviations are given in parentheses. We are responsible for assigning standard deviations to derived quantities.

It is, of course, the intrinsic, rather than the spectroscopic, quadrupole moments which are of interest in nuclear theory. Bohr and Mottelson have given the relationship between these two quantities.[18] Making appropriate substitutions and solving their expression explicitly for the intrinsic quadrupole moment Q_0, we obtain

$$Q_0=Q(I+1)(2I+3)/I(2I-1). \quad (7)$$

The quadrupole moments derived from the above discussion are listed in Table III, and intrinsic quadrupole moments derived therefrom are shown in Fig. 6. The error bars in Fig. 6 give the standard deviation for all sources of error. The *relative* magnitudes of the Q_0's are known with somewhat better accuracy. In fact the relative Q_0 magnitudes are on very firm grounds, inasmuch as they depend only on ratios of hyperfine structure constants. Thus, the relative magnitudes would not be subject to change if, for example, one of the sets of measurements (references 16, 17, or this work) should be found to be subject to an antishielding correction heretofore not considered.

Thus, we can interpret the trend in Fig. 6 with some confidence as indicating a rather sharp break in Q_0 between 88 and 90 neutrons, with a slower, monotonic rise in the three heaviest isotopes. This is in good accord with other data on collective nuclei in this region, and indicates both that the deformation increases with neutron number for these four isotopes and that there is no significant "odd-even" effect.

It should be borne in mind that there are two important assumptions leading to the derivation of Q_{154}, namely, (1) that the hyperfine-structure Hamiltonian is adequately represented by Eq. (3) and (2) that Q_{154} is proportional to P_{154}. We believe these assumptions to be true, as there is good evidence, experimental and theoretical, for them. It is always advisable, however, when using moment values, to bear in mind the assumptions which went into their derivations.

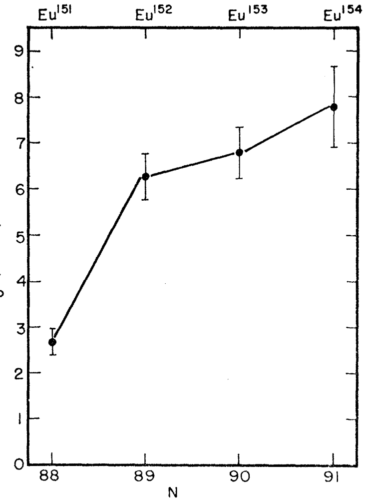

FIG. 6. Intrinsic quadrupole moments vs neutron number for the europium isotopes. Only in Eu^{151} and Eu^{153} are the signs of the Q_0's known; for the even isotopes the Q_0's are assumed to be positive. $(Q_0)_{152}$ and $(Q_0)_{154}$ are known to have the same sign. The *total* possible error is indicated in each case; the relative magnitudes are known more precisely.

IV. INTERACTIONS WITHIN THE GROUND MULTIPLET

In discussing the possible hyperfine structure in europium ethylsulfate, Elliott examined several types of interaction in various orders of perturbation theory, using as basis functions the states of the multiplet ^7F. The contribution to the Hamiltonian that he considered is

$$\mathcal{H}=V_C+V_Q+V_N+V_H. \quad (8)$$

In this expression, V_C stands for the energy of interaction of the electrons of Eu^{3+} with the electrostatic field of the ethylsulfate lattice, and possesses the leading term

$$A_2^0\sum_i(3z_i^2-r_i^2),$$

where the subscript i distinguishes the electrons. The next term stands for the interaction of the electrons of Eu^{3+} with the quadrupole moment of the nucleus, and is given by

$$V_Q=\frac{e^2Q}{2I(2I-1)}\sum_i\left[\frac{I(I+1)}{r_i^3}-\frac{3(\mathbf{r}_i\cdot\mathbf{I})^2}{r_i^5}\right].$$

The quantity V_N is the ordinary magnetic hyperfine interaction, namely,

$$(2\beta\beta_N\mu_N/I)\langle r^{-3}\rangle\sum_i\mathbf{N}_i\cdot\mathbf{I}.$$

The symbol $\langle r^n\rangle$ is a concise form for $(4f|r^n|4f)$, the mean value of r^n for a $4f$ electron. Lastly, V_H represents the interaction with an external magnetic field; this is zero for our experiment.

Since the level $^7F_0$ possesses zero total angular momentum,

$$(^7F_0|V_Q|^7F_0)=(^7F_0|V_N|^7F_0)=0.$$

According to Elliott, the largest contribution to the hyperfine structure should arise through the second-order mechanism

$$-2(^7F_0|V_Q|^7F_2)(^7F_2|V_C|^7F_0)/E(^7F_2), \quad (9)$$

where $E(\xi)$ is the energy of the level with designation ξ above the ground level. Taking a value of $A_2^0\langle r^2\rangle$ deduced from the crystal splitting of $^7F_1$, Elliott found a value of $+1.5Q\times10^{-4}$ cm^{-1} for the coupling constant

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

P of Eq. (3), measuring Q in barns. This figure should be corrected to $1.2Q\times10^{-4}$ to allow for the newer values of $\langle r^{-3}\rangle$ for $4f$ electrons,[19] which give 44.8 Å^{-3} for Eu^{3+} rather than the value of 57 Å^{-3} used by Elliott. He also showed that the direct interaction of the crystal field with the nuclear quadrupole moment gives a contribution to P of the order of 10^{-6} cm^{-1}, and that the mechanism

$$({}^7F_0|V_N|{}^7F_1)({}^7F_1|V_C|{}^7F_1)({}^7F_1|V_N|{}^7F_0)/E({}^7F_1)^2$$

produces a pseudoquadrupole coupling with P' of the order of 10^{-7} cm^{-1}. Clearly then, the second-order crystal-field term should dominate. In particular, P should have the same sign as Q, and for prolately deformed nuclei, with $Q>0$, P should be positive.

In fact, as discussed in Sec. III, P is clearly negative. Two main paths are possible in explaining this: Either (1) the quadrupole moments of Eu^{152} and Eu^{154} are actually negative, or (2) the crystal-field calculation presented above is inadequate. We cannot say that the quadrupole moments are positive from any direct experimental evidence, but there is a large systematic body of information available for nuclei in this region which strongly suggests that these nuclei are prolately deformed as are all neighboring nuclei. Thus, we reject alternative (1) above as highly unlikely, and the discussion below is based on alternative (2).

V. CONFIGURATION INTERACTION

The obvious way to improve the crystal-field calculation is to extend the range of states considered in the perturbation mechanism: At the same time, operators diagonal with respect to the states of ${}^7F$, and for that reason not explicitly contained in $\mathcal{H}$, must be included in the calculations.

As a first step, we consider all states of $4f^6$, not merely those belonging to ${}^7F$. Our Hamiltonian is augmented by the spin-orbit interaction, V_{SO}. However, it is not difficult to show that expressions in which V_{SO} plays a role, such as

$$-({}^7F_0|V_{\text{SO}}|{}^5D_0)({}^5D_0|V_C|{}^5D_2)({}^5D_2|V_{\text{SO}}|{}^7F_2)\\ \times({}^7F_2|V_Q|{}^7F_0)/E({}^5D_0)E({}^5D_2)E({}^7F_2),$$

are smaller than expression (9) by approximately 2 orders of magnitude. Such mechanisms, which reflect the partial breakdown of Russell-Saunders coupling, are thus too small to account for the negative sign of P.

There remains the effects of excited configurations to consider. By broadening the scope of our analysis to include configurations other than $4f^6$, all states of Eu^{+3} become eligible for study. Since the interelectronic Coulomb interaction, namely,

$$V_A=\sum_{i>j} e^2/r_{ij},$$

can couple states of different configurations, it too should now be included in the Hamiltonian. It is important to realize, however, that by using a form for V_C that has been deduced from experiment, a certain kind of configuration interaction has already been implicitly taken into account in the calculations. On the basis of a detailed crystal-field calculation, Wong and Richman give $A_2{}^0\langle r^2\rangle=903$ cm^{-1} for PrCl$_3$;[20] experimentally, it is observed to be only 47.26,[21] indicating a screening factor of 19. An effect of this kind is to be expected for all rare-earth ions, and is to be ascribed to the virtual cancellation of matrix elements such as

$$(4f^n\psi|V_C|4f^n\psi'),$$

by the sum of second-order terms of the type

$$-(4f^n\psi|V_C|T\psi'')(T\psi''|V_A|4f^n\psi')/E(T),$$

where T denotes an excited configuration. In searching for a possible explanation for the negative value of P, it would obviously be inadmissible to include mechanisms such as

$$(4f^65s^2\,{}^7F_0|V_A|4f^65s5d\,{}^7F_0)(4f^65s5d\,{}^7F_0|V_C|4f^65s^2\,{}^7F_2)\\ \times(4f^65s^2\,{}^7F_2|V_Q|4f^65s^2\,{}^7F_0)/E(4f^65s5d\,{}^7F_0)\\ \times E(4f^65s^2\,{}^7F_2),$$

since the first two matrix elements, when combined with the denominator $E(4f^65s5d\,{}^7F_0)$, represent a correction to

$$(4f^6\,{}^7F_0|V_C|4f^6\,{}^7F_2)$$

that has already been taken into account by using the experimental parameter $A_2{}^0\langle r^2\rangle$ in the evaluation of mechanism (9).

Another class of mechanisms in which V_A is employed can be considered as representing shielding or antishielding corrections that are equivalent to those studied by Sternheimer.[22] For example, the first two matrix elements of the product

$$(4f^65s^2\,{}^7F_0|V_A|4f^65s5d\,{}^7F_0)(4f^65s5d\,{}^7F_0|V_Q|4f^65s^2\,{}^7F_2)\\ \times(4f^65s^2\,{}^7F_2|V_C|4f^65s^2\,{}^7F_0)/E(4f^65s5d\,{}^7F_0)\\ \times E(4f^65s^2\,{}^7F_2),$$

when combined with the denominator $E(4f^65s5d\,{}^7F_0)$, can be considered as a shielding correction to

$$(4f^6\,{}^7F_0|V_Q|4f^6\,{}^7F_2).$$

Murakawa[23] has suggested that the quadrupole moments deduced from the interaction with $4f$ electrons should be subject to an antishielding factor of about 2.5; however, the quadrupole moment of Er^{167}, as found from resonance experiments on an ethylsulfate crystal,[24] and which seems to demand a factor of about

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

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[24] G. S. Bogle, H. J. Duffus, and H. E. D. Scovil, Proc. Phys. Soc. (London) **A65**, 760 (1952).

this size, has not been confirmed in experiments on the double nitrate.[25] Owing to the internal nature of the $4f$ electrons in rare-earth ions, we might expect corrections due to shielding or antishielding to be very small. But even if Murakawa's antishielding factor were accepted at its face value, we should be no nearer an explanation for the negative sign of P.

Of the possible mechanisms that are left, the most promising appear to be those of the type

$$-2(4f^6\,{}^7F_0|V_C|T\,{}^7L_2)(T\,{}^7L_2|V_Q|4f^6\,{}^7F_0)/E(T). \tag{10}$$

For, not only are they of only second-order in perturbation theory, but they should be important only in those exceptional cases, such as Eu^{+3}, where the first-order contribution to Q vanishes. The ratio of mechanisms (10) and (9) is given by

$$R=\frac{(4f^6\,{}^7F_0|V_C|T\,{}^7L_2)(T\,{}^7L_2|V_Q|4f^6\,{}^7F_0)E(4f^6\,{}^7F_2)}{(4f^6\,{}^7F_0|V_C|4f^6\,{}^7F_2)(4f^6\,{}^7F_2|V_Q|4f^6\,{}^7F_0)E(T)}. \tag{11}$$

To fit the experimental results, R should be about -3. The lowest excited configuration of the same parity as $4f^6$ is $4f^56p$, and lies roughly 150 000 cm^{-1} above the ground level[26]; on the other hand, $E(4f^6\,{}^7F_2)$ is approximately 1100 cm^{-1}.[1] To offset the smallness of $E(4f^6\,{}^7F_2)/E(T)$, the matrix elements in the numerator of the right-hand side of Eq. (11) have to be very much larger than those in the denominator. Since V_C and V_Q are single-particle operators, we can confine our attention to those configurations T that correspond to the excitation of a single electron from the ground configuration

$$1s^22s^22p^6\cdots4f^65s^25p^6.$$

If, for a given T, the electron (nl) is excited to the orbit characterized by $(n'l')$, then, after extracting the angular dependencies of the matrix elements, R can be thrown into the form

$$R=A\frac{(nl|r^2|n'l')(n'l'|r^{-3}|nl)E(4f^6\,{}^7F_2)}{(4f|r^2|4f)(4f|r^{-3}|4f)E(T)}. \tag{12}$$

The parameter A contains the angular factors, and vanishes if the triad $(l,l',2)$ does not satisfy the triangular condition. For cases of interest to us, A is about unity. Estimates of the radial integrals of Eq. (12) can be made by using the tabulated eigenfunctions for Pr^{3+} given by Ridley[27] and Rajnak.[28] We might hope that $4f^56p$, being the lowest relevant excited configuration, would provide a significant contribution to R; however, the large number of nodes in the $6p$ function gives rise to positive and negative contributions to both radial integrals in the numerator of the right-hand side of Eq. (12), and, in fact,

$$|(4f|r^n|6p)|<|(4f|r^n|4f)|$$

for both $n=2$ and $n=-3$. It seems unlikely that other configurations involving the excitation of a $4f$ electron, such as $4f^55f$ or $4f^56h$, could produce any appreciable contribution to R.

A more attractive class of configurations T are those that involve the excitation of an electron from a closed shell. For $E(T)$ not to be excessively large, and for $(nl|r^2|n'l')$ to compete advantageously with $(4f|r^2|4f)$, we need consider only the outer shells of the atom, namely $5s^2$ and $5p^6$. At first sight, we might expect the high density of an s electron near the nucleus to make the radial integrals $(5s|r^{-3}|n'd)$ outweigh $(4f|r^{-3}|4f)$. However, for $n'>4$, the first node of the $n'd$ function almost exactly coincides with the third node of the $5s$ function, and the contribution to the integral from the region near the nucleus, which we would hope to be very large, consists of positive and negative parts that cancel to a large extent.

We are left with excitations of a $5p$ electron to consider. For $(5p|r^{-3}|n'l')$ to be large, the function characterized by $(n'l')$ should follow the $5p$ function near the nucleus, and have as high a density there as possible. The $6p$ function fulfills these conditions. Using the tabulated eigenfunctions for Pr^{3+},[27,28] we find

$$(5p|r^2|6p)=-2.5\text{ a.u.},$$

and

$$(5p|r^{-3}|6p)=18\text{ a.u.}$$

These are to be compared to the integrals

$$(4f|r^2|4f)=1.45\text{ a.u.},$$

and

$$(4f|r^{-3}|4f)=4.35\text{ a.u.}$$

From the energies of the $5p$ and $6p$ electrons given by Ridley and Rajnak, we estimate $E(5p^56p)=200\,000$ cm^{-1} for Pr^{3+}. The only state of $5p^56p$ that contributes to R is ${}^1D_2$; for all others $A=0$. Summing over all L in Eq. (11), we find $A=\frac{3}{2}$. Since both $5p$ and $6p$ electrons are essentially outer electrons, we should remove the screening factor of 19 for V_C, mentioned earlier in this section. In all,

$$R=19\frac{3(-2.5)(18)(1100)}{2(1.45)(4.35)(200\,000)}=-1.1. \tag{13}$$

VI. DISCUSSION

Equation (13), we feel, gives a convincing explanation for the observed negative value of P. As for the magnitude of R, no doubt some allowance should be made for the use of eigenfunctions for Pr^{3+}, rather than for Eu^{3+}; however, such corrections might well be comparable to errors arising through our assumption that all effects of the crystal lattice can be represented by the term V_C in $\mathcal{H}$. The outer maximum of the $6p$ eigenfunction for a free ion Pr^{3+} occurs at $r=2.0$ Å—a distance that, for an ion in the ethylsulfate lattice, would extend from the nucleus of Pr^{3+} well into the interior of the oxygen atoms of the neighboring water molecules. Clearly, the central fields of these atoms would strongly perturb the $6p$ eigenfunction. According

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to Marshall and Stuart,[29] there is a general tendency for free-ion eigenfunctions to expand when the ion is embedded in a crystal lattice, and this effect would almost certainly increase $(5p|r^2|6p)$ by a greater factor than that by which $(5p|r^{-3}|6p)$ is decreased, thereby affording a possible mechanism for bringing the number -1.1 of Eq. (13) closer to the experimental value of -3.

It is interesting to draw a comparison with the work of Foley, Sternheimer, and Tycko on the quadrupole antishielding factor for Cs^+.[30] They find that the effective quadrupole moment for an external observer should be not Q, but $(1+\gamma)Q$, where $\gamma=86.8$. The greatest contribution to γ comes from the excitation of the $5p$ electrons to higher p orbits. If the effect is treated by perturbation theory, taking the np orbitals as the basis functions (a procedure that Foley *et al.* did not follow), it is not difficult to show that this contribution to γ can be written as

$$-\frac{4e^2}{25}\sum_{n>5}\frac{(5p|r^2|np)(np|r^{-3}|5p)}{E(5p^5np)}. \tag{14}$$

Strictly, the sum should also include states in the continuum. The constituents of the term in the sum for which $n=6$ all occur in Eq. (12), though the greater extension of the $5p$ orbital in the outer reaches of the ion Cs^+, compared to the corresponding orbital of Pr^{3+}, indicates that $(5p|r^2|6p)$ for Cs^+ is larger in magnitude, possibly by an appreciable factor, than the corresponding radial integral for Pr^{+3}. Even if we ignore this increase, the contribution of the term $(np)=(6p)$ to the sum (14) is as large as 12, taking $E(5p^56p)$ as 130 000 cm^{-1}.[31] We may therefore conclude that the special properties of the $5p$ and $6p$ eigenfunctions, properties that permit the radial integrals of r^{-3} and r^2 linking the eigenfunctions to be both large and also opposite in sign, are responsible for the negative value of P for Eu^{3+} and also for a substantial part of the large antishielding factor for Cs^+.

Note added in proof. We wish to acknowledge the receipt of a manuscript by E. G. Wikner and G. Burns. These authors, by considering the direct interaction of the external crystal field with the quadrupole moment induced in the outer shells of the europium ion, come to essentially the same conclusion as us for the kind of mechanism that gives rise to the negative value of P.

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Nuclear Spins, Hyperfine Structures, and Nuclear Moments of Scandium-46 and Yttrium-91

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The atomic-beam magnetic-resonance method has been used to study some atomic and nuclear properties of 84-day Sc^{46} and 58-day Y^{91}. The results are

		$^2D_{3/2}$	$^2D_{5/2}$
Sc^{46}	$I=4$	$g_J=-0.7990(8)$	$g_J=-1.1995(18)$
	$(\mu_I)_{\mathrm{uncorr}}=+3.03(2)$ nm	$a=+150.576(9)$ Mc/sec	$a=+60.906(4)$ Mc/sec
	$Q_{\mathrm{uncorr}}=+0.119(6)$ b	$b=+14.38(14)$ Mc/sec	$b=+20.41(10)$ Mc/sec
Y^{91}	$I=1/2$	$a=\pm68.34(2)$ Mc/sec	$a=\pm34.35(3)$ Mc/sec
	$(\mu_I)_{\mathrm{uncorr}}=\pm0.1634(8)$ nm	$\Delta\nu=\pm136.69(3)$ Mc/sec	$\Delta\nu=\pm103.05(4)$ Mc/sec

I. INTRODUCTION

THE atomic-beam magnetic-resonance method has been used to continue hfs investigations of the radioactive yttrium isotopes[1,2] as well as to initiate similar experiments on the radioactive scandium isotopes.[3] Both elements have a $^2D_{3/2}$ electronic ground state which is separated from the next higher state ($^2D_{5/2}$) by only a few hundred wave numbers.[4,5] As a result, transitions

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