

in the partial disagreement of experimental results and the model predictions. Inspection of Fig. 5 reveals that the circuit Q , and therefore the equivalent resistance, are independent of the magnitude of the decaying output over the upper portion of the decay range. Exact determination of the field intensity was not possible. It is obvious, however, that because the Q exceeded 10^6 , the bulk critical field was not exceeded. As the output level continues to decrease a sudden break, or change in the time constant, is observed. This is taken as corresponding to the "effective local critical field" predicated in the model, and provides it with further substantiation. The abruptness of the change to lower loss indicates that most of the trapping centers are very much alike, a welcome feature but not expected on the basis of the model. The nature of the loss mechanism below the local critical field is as yet undetermined.

IX. CONCLUSION

The existence of rf flux trapping is confirmed through verification of the predicted model dependences. More study is required before the nature of the flux-trapping center is understood and the magnitude of residual

resistance can be predicted. The direction of the investigation seems clear from these efforts. A promising mechanism for flux trapping is associated with background magnetic fields trapped in the superconductor during the cooling process. This will shortly be reported on by J. M. Victor and the authors. The existence of an effective local critical field, as demonstrated by experiment, the abruptness of the Q change as the circuit energy decays, coupled with the annealing and impurity experiments, indicate that the trapping is dominated by sites with a common nature.

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Energy Levels of Trivalent Gadolinium and Ionic Contributions to the Ground-State Splitting*

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This paper represents an attempt to estimate the ionic contributions to the ground-state splitting of the trivalent gadolinium ion in a lanthanum ethyl sulfate lattice. The energy levels of the $4f^7$ configuration are calculated and compared with those observed experimentally. The calculated ground-state g factor is found to deviate significantly from its measured value. An attempt has been made to estimate the contributions to the ground-state splitting for eight different mechanisms: (1) a fourth-order mechanism that is *linear* in the crystal-field strength and *cubic* in the spin-orbit interaction; (2) fourth-order mechanisms that are *quadratic* in both the crystal-field strength and the spin-orbit interaction; (3) a third-order spin-spin mechanism acting within the $4f^7$ configuration; (4) Pryce's second-order spin-spin configuration mixing mechanism; (5) a second-order relativistic mechanism; (6) mechanisms involving configuration mixing by the crystal field; (7) mechanisms involving nonlinear electrostatically correlated crystal-field interactions; (8) fifth-order configuration interaction mechanisms. The total contribution due to these mechanisms is found to be *twice* the magnitude of the observed splitting and of *opposite* sign. It is suggested that no purely ionic model can account for the observed splitting and that the correct explanation must involve the detailed interaction of the gadolinium ion with its ligands. A semiquantitative explanation of some of the intensity features of the crystal and solution spectra of trivalent gadolinium is attempted.

I. INTRODUCTION

THE lack of an adequate interpretation of the ground-state splittings of ions having a half-filled shell of electrons has constituted a serious problem in crystal field theory. While considerable progress¹⁻¹⁰

has been made in the interpretation of the splittings for the transition ions, comparatively little progress

² M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).

³ H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).

⁴ M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Letters **5**, 145 (1960).

⁵ J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, Proc. Roy. Soc. (London) **264**, 503 (1961).

⁶ S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961).

⁷ A. S. Chakravarty, J. Chem. Phys. **39**, 1004 (1963).

⁸ W. Low and G. Rosengarten, J. Mol. Spectry. **12**, 319 (1964).

⁹ R. M. MacFarlane, J. Chem. Phys. **42**, 442 (1965).

¹⁰ M. D. Sturge, J. Chem. Phys. **43**, 1826 (1965).

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¹ J. H. Van Vleck and W. G. Penney, Phyl. Mag. **19**, 961 (1934).

has been made in obtaining an adequate explanation¹¹⁻¹⁷ for the splittings of the $f^7(^8S_{7/2})$ ground-states of Eu^{2+} , Gd^{3+} , Tb^{4+} , and Cm^{3+} . Experimentalists have studied the ground-state splittings of divalent europium¹⁸⁻²⁷ and trivalent gadolinium²⁸⁻⁴⁰ in many crystalline environments using the technique of paramagnetic resonance. These studies have shown conclusively that the ground-state splitting cannot be explained in terms of any single mechanism but rather must arise as the result of several different mechanisms. Thus, to study the ground-state splittings for rare earths having a half-filled shell we must examine each mechanism in turn and then attempt to assess the combined effect of all the mechanisms.

In the present paper we shall concentrate our attention on the explanation of the ground-state splitting of Gd^{3+} in lanthanum ethyl sulfate, $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, as studied experimentally by Bleaney *et al.*^{26,29} We shall first review some of the unique properties of half-filled shells and then consider the calculation of the energy levels of the $4f^7$ configuration to obtain a suitable wave-function for the ground-state. This wave-function will be used to compute the ground-state magnetic g -factor and the, as the starting point in our discussion of the ground-state splitting mechanisms.

We propose to restrict our discussion to those mechanisms that could be characteristically termed ionic as opposed to covalent. Specifically, we shall consider the following splitting mechanisms in detail: (1) A fourth-order mechanism that is *linear* in the crystal field strength and *cubic* in the spin-orbit interactions; (2) fourth-order mechanisms that are *quadratic* in the crystal field strength and the spin-orbit interaction; (3) a third-order spin-spin mechanism acting within the $4f^7$ configuration; (4) Pryce's second-order spin-spin mechanism acting *between* configurations; (5) a second-order mechanism that arises from the relativistic nature of the wave function; (6) mechanisms involving configuration mixing by the crystal field; (7) mechanisms involving nonlinear electrostatically correlated crystal field interaction with excited configurations; (8) fifth-order configuration interaction mechanisms. We have attempted to obtain numerical estimates of the contributions of each of these mechanisms. These calculations represent the first detailed attempt to compute many of these contributions. The total contribution to the ground-state splitting due to these mechanisms is found to be approximately *twice* the size of the observed splitting and, more importantly, of *opposite* sign. Thus we conclude that these mechanisms are inadequate to account for the observed result. We believe that the development of a successful theory of the ground-state splitting of trivalent gadolinium will have to take into account the more intimate details of the interaction of the gadolinium ion with its neighboring ligands.

II. PROPERTIES OF HALF-FILLED SHELLS

The $4f^7$ configuration represents an example of a half-filled shell of equivalent electrons. The possession of a half-filled shell results in the trivalent gadolinium ion having several distinctive features that are not associated with any of the other trivalent lanthanides.

The states of a half-filled shell may be conveniently divided into two classes, namely those whose zero-order eigenfunctions change sign under the operation of charge conjugation and those whose eigenfunctions do not change sign.⁴¹ For the f^7 configuration, states with seniority $v=7$ and 3 belong to the former class (I), whereas those with seniority $v=5$ and 1 belong to the latter class (II). A tabulation of the states of f^7 in terms of Racah's quantum numbers⁴² $vWUSL$ has been given elsewhere.^{43,44} The matrix elements of tensor operators of the type $\mathbf{T}^{(k_1k_2)} = \sum_i t_i^{(k_1k_2)}$ connecting two terms of the *same* class vanish if k_1+k_2 is *even* while matrix elements connecting two terms of *different* class vanish if k_1+k_2 is *odd*.⁴⁵ The matrix elements are further restricted by the seniority selection rule $\Delta v=0$,

¹¹ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc., (London) **A219**, 387 (1953).

¹² B. R. Judd, thesis, University of Oxford, 1955 (unpublished).

¹³ C. A. Hutchison, B. R. Judd, and D. F. D. Pope, Proc. Phys. Soc. (London) **B70**, 514 (1957).

¹⁴ R. Lacroix, Helv. Phys. Acta., **30**, 374 (1957).

¹⁵ R. Lacroix, Arch. Sci. (Geneva) **11**, 141 (1958); **14**, 149 (1961).

¹⁶ R. Lacroix, Proc. Phys. Soc. (London) **77**, 550 (1961).

¹⁷ A. M. Leushin, Fiz. Tverd. Tela **5**, 851, 2352, 3373 (1963) [Soviet Phys.—Solid State **5**, 623, 1711, 2477 (1964)].

¹⁸ C. Ryter, Helv. Phys. Acta. **30**, 395 (1957).

¹⁹ J. M. Baker, B. Bleaney, and W. Hayes, Proc. Phys. Soc. (London) **A247**, 141 (1958).

²⁰ M. Dvir and W. Low, Proc. Phys. Soc., (London) **A750**, 136 (1959).

²¹ P. B. Dorain, Phys. Rev. **120**, 1190 (1960).

²² A. J. Shuskus, Phys. Rev. **127**, 2022 (1962).

²³ R. S. Title, Phys. Rev. **133**, A198 (1964).

²⁴ A. J. Shuskus, J. Chem. Phys. **41**, 1885 (1964).

²⁵ W. Low and J. T. Suss, Phys. Letters **11**, 115 (1964).

²⁶ R. S. Title, Phys. Rev. **138**, A631 (1964).

²⁷ Q. H. F. Urethen and J. Volger, Physica **31**, 845 (1965).

²⁸ B. Bleaney, R. J. Elliott, H. E. D. Scovil, and R. S. Trenam, Phil. Mag. (London) **42**, 1062 (1951).

²⁹ B. Bleaney, H. E. D. Scovil, and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

³⁰ M. Weger and W. Low, Phys. Rev. **111**, 1526 (1958).

³¹ W. Low and D. Shaltiel, J. Phys. Chem. Solids **6**, 315 (1958).

³² D. A. Jones, J. M. Baker, and D. F. D. Pope, Proc. Phys. Soc. (London) **74**, 249 (1959).

³³ J. M. Baker and R. S. Rubins, Proc. Phys. Soc. (London) **78**, 1340 (1961).

³⁴ G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. (London) **79**, 775 (1962).

³⁵ J. E. Drumheller, J. Chem. Phys. **38**, 970 (1963).

³⁶ W. Low and A. Zusman, Phys. Rev. **130**, 144 (1963).

³⁷ W. Low and R. S. Rubins, Phys. Rev. **131**, 2527 (1963).

³⁸ J. Sierro, Helv. Phys. Acta **36**, 5 (1963).

³⁹ I. V. Vinokurov, Z. N. Zonn, and V. A. Ioffe, Fiz. Tverd. Tela **7**, 1012 (1965) [Soviet Phys.—Solid State **7**, 814 (1965)].

⁴⁰ M. M. Abraham, E. J. Lee, and R. A. Weeks, J. Phys. Chem. Solids **26**, 1249 (1965).

⁴¹ G. Racah, Phys. Rev. **63**, 367 (1943).

⁴² G. Racah, Phys. Rev. **76**, 1352 (1949).

⁴³ B. G. Wybourne, J. Chem. Phys. **35**, 334 (1961).

⁴⁴ B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (J. Wiley & Sons, Inc., New York, 1965).

⁴⁵ G. Racah, Phys. Rev. **62**, 438 (1942).

± 1 . Thus the matrix elements of the spin-orbit and crystal field interactions will vanish among states of the same class. Matrix elements of scalar products of the type $\sum_{i>j}(\mathbf{t}_i^{(k)} \cdot \mathbf{t}_j^{(k)})$ will be nonzero only *within* a class and according to the seniority selection rule $\Delta v=0, \pm 2$, or ± 4 . Thus the matrix elements of Coulombic, orbit-orbit and spin-spin interaction will be non-vanishing only for states of the same class. These types of interaction leave the class designation as a good quantum number even when $\tau v W U$ cease to be good quantum numbers.

As a result of these special properties of half-filled shells the energy levels of a multiplet will not be split in the Russell-Saunders approximation of neglecting second-order spin-orbit interactions (small splittings due to first-order spin-spin interactions could occur). Nevertheless, quite large splittings are observed⁴⁶⁻⁴⁸ and are clearly the result of spin-orbit coupling between states of different class. The order in which the levels of a multiplet occur will be determined by the intermediate coupling and will be particularly sensitive to the magnitude of the Coulombic and spin-orbit parameters and to the order of approximation to which the energy level calculations are pursued.

It also follows from our preceding discussion that the first-order crystal field matrix elements within the f^7 configuration all vanish and hence any explanation of the splittings of the ground state, or of the excited states, must involve second and higher orders, of crystal field interactions. Furthermore, since the diagonal crystal field matrix elements vanish for the 8S state it is necessary to consider mechanisms that mix into the ground state some of the character of certain excited states to obtain any splitting of the ground state. In a sense, we might regard the ground state splitting as a reflection of the splittings of some of the excited states.

III. ENERGY-LEVEL CALCULATIONS

Nielson and Koster^{49,50} have computed the complete Coulomb and spin-orbit interaction matrices for the f^7 configuration. Thus it is now possible to calculate the energy levels of the $4f^7$ configuration of trivalent gadolinium by diagonalization of the combined Coulombic and spin-orbit interaction matrices. The Coulomb interaction matrix elements are expressed in terms of the radial parameters (E^1 , E^2 , and E^3) of Racah⁴² while the spin-orbit interaction matrix elements are expressed in terms of a single spin-orbit coupling constant ζ_{4f} . To a first approximation, the energies of

the multiplets will depend linearly on the Coulomb parameters while the multiplet splittings will be a quadratic function of ζ_{4f} .

The observed spectra of trivalent gadolinium salts⁴⁶⁻⁴⁸ has revealed only 15 of the 327 SLJ states of the f^7 configuration. These 15 states are associated with just four multiplets, $^8S^6(PDI)$, and hence it would be unrealistic to fix the parameters by the usual least-squares method. Instead, the parameters have been interpolated from the other trivalent lanthanides. The values of the parameters finally adopted were

$$E^1 = 5480, \quad E^2 = 27.8, \quad E^3 = 565, \quad \text{and} \quad \zeta_{4f} = 1480 \text{ cm}^{-1}$$

The spin-orbit coupling constant is somewhat smaller than previous studies had suggested.^{15,51,52} Reducing ζ_{4f} appears to give a better representation of the multiplet splittings. A ζ_{4f} of 1600 cm^{-1} leads to multiplet splittings that are too large.

The calculated and experimental energy levels are compared in Table I. The levels of the $^6(PDI)$ multiplets are calculated to be in the same order as found by Hellwege *et al.*⁴⁸ The magnitudes of the multiplet splittings are in good accord with the experimentally observed splittings indicating that the choice of the spin-orbit coupling constant is indeed reasonable. The positions of the centers of gravity of the multiplets are only in fair agreement with experiment suggesting that the Coulomb parameters need some adjustment. The deviation ($\sim 1500 \text{ cm}^{-1}$) is particularly bad in the case of the 6I multiplet.

Clearly, to reduce this deviation a change in the electrostatic energies of the multiplets is required. Hence either the choice of the electrostatic parameters is inappropriate, or there is appreciable interaction with other odd-parity configurations. The E^k para-

TABLE I. Energies of the 8S and $^6(PDI)$ levels of Gd^{3+} .

SLJ	Calculated energy in cm^{-1}	Experimental energy ^a in cm^{-1}	LS coupling g	Intermediate coupling g
$^8S_{7/2}$	0	0	2.0023	1.9945
$^6P_{7/2}$	32269	32105	1.7159	1.6731
$^6P_{5/2}$	32839	32700	1.8878	1.8304
$^6P_{3/2}$	33470	33272	2.4032	2.3323
$^6I_{7/2}$	34356	35832	0.4432	0.4606
$^6I_{9/2}$	34705	36176	0.8279	0.8357
$^6I_{17/2}$	34910	36242	1.2948	1.2900
$^6I_{11/2}$	34996	36458	1.0350	1.0376
$^6I_{13/2}$	35176	36571	1.1593	1.1588
$^6I_{15/2}$	35183	36631	1.2398	1.2369
$^6D_{9/2}$	38795	39562	1.5568	1.5424
$^6D_{11/2}$	39642	40468	3.3387	3.3060
$^6D_{7/2}$	39953	40574	1.5887	1.5913
$^6D_{3/2}$	40005	40754	1.8687	1.9032
$^6D_{5/2}$	40234	40901	1.6587	1.6794

^a Reference 48.

⁵¹ W. A. Runciman, J. Chem. Phys. **30**, 1632 (1959).

⁵² W. A. Runciman, J. Chem. Phys. **36**, 1481 (1962).

⁴⁶ G. H. Dieke and L. Leopold, J. Opt. Soc. Am. **47**, 844 (1957).

⁴⁷ S. P. Cook and G. H. Dieke, J. Chem. Phys. **27**, 1213 (1957).

⁴⁸ K. H. Hellwege, S. Hüfner, and H. Schmidt, Z. Physik **172**, 460 (1963).

⁴⁹ C. W. Nielson and G. F. Foster, *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (M.I.T. Press, Cambridge, 1963).

⁵⁰ C. W. Nielson and G. F. Koster, "Energy Matrices for All Configurations of Equivalent f Electrons" (unpublished). (Available from M.I.T. Computing Laboratory as a magnetic tape.)

meters are simply linear combinations of the Slater F_k radial integrals which should satisfy the inequality⁵³

$$0.203 > F_4/F_2 > F_6/F_2 < 0.0306.$$

Bearing in mind this inequality, and recognizing that in general the ratio F_4/F_2 and F_6/F_2 are larger than those of a hydrogenic eigenfunction it does not seem possible to adjust the parameters so as to significantly reduce the deviations of the calculated multiplet energies from their experimental energies.

The electrostatic energy matrix elements of the 8S (6PDFGHI) multiplets of f^7 are, apart from a constant term, simply the negatives of those of the corresponding $^1(SDGI)$ (3PFH) multiplets of f^2 . In Pr IV ($4f^2$) the simple Slater-Condon treatment yields the 1I_6 state below the 3P_1 state whereas experimentally it occurs

above 3P_1 . Thus there is a resemblance between the deviations in f^7 and those of f^2 . Runciman and Wybourne⁵⁴ have shown that the addition of a term $\alpha L(L+1)$ to the energy matrices of the f^2 configuration ameliorates the agreement for Pr IV ($4f^2$) placing the 1I_6 level in its correct position with respect to the 3P multiplet. Sugar⁵⁵ has found $\alpha = 19 \pm 4 \text{ cm}^{-1}$ for the free-ion levels of Pr IV ($4f^2$). Thus the inclusion of a $\alpha L(L+1)$ term in the energy matrices of the $4f^7$ configuration would undoubtedly help to place the 6I multiplet in its correct position with respect to the 6P multiplet.

Rajnak and Wybourne⁵⁶ have shown that for a f^N configuration the second-order effects due to configuration interaction can be represented by the matrix elements of an effective operator \mathbf{Y} such that

$$(f^N \psi | \mathbf{Y} | f^N \psi') = \delta(\psi, \psi') [\alpha L(L+1) + 12\beta G(G_2) + 5\gamma G(R_7)] + \sum_{k, k', k'' \text{ even}} \Theta(k, k', l') (2k''+1) \begin{Bmatrix} k & k' & k'' \\ f & f & l' \end{Bmatrix} \times (f^N \psi | \sum_{i \neq j \neq h} \{ \mathbf{u}_i^{(k)} \mathbf{u}_j^{(k')} \} (k') \mathbf{u}_h^{(k'')} | f^N \psi'). \quad (1)$$

The *diagonal* matrix elements of the effective three-body interactions cancel in pairs for the particular case of the half-filled shell and hence we may write

$$(f^7 \psi | \mathbf{Y} | f^7 \psi) = \alpha L(L+1) + 12\beta G(G_2) + 5\gamma G(R_7), \quad (2)$$

where $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the groups G_2 and R_7 used to classify the states of f^N configurations,^{42,44,57} and α , β , and γ are interaction parameters.

Trees⁵⁸ and Rajnak⁵⁹ have studied the role of the parameters β and γ in the Pr III ($4f^3$) configuration and found them to be of negative sign. The effect of β and γ will be to bring the 6D and 6I multiplets closer to the 6P multiplet by the same amount while the α correction will tend to force them apart. The study of the parameters α , β , and γ has not, as yet, progressed sufficiently to permit a reliable estimate of their magnitude but it does seem clear that the $4f^7$ configuration is perturbed by other configurations. The energy levels of Pr IV ($4f^2$) are known to be perturbed by the $5d^2$ configuration^{60,61} and, therefore, it is most likely that the $4f^7$ configuration is perturbed by the $4f^5 5d^2$ configuration.

The principal components of the eigenvectors obtained for the levels of the 8S (6PDI) multiplets are listed in Table II. The $^6(PDI)$ multiplets show moderate departures from pure LS coupling as would be expected. There is a gap of $\sim 8000 \text{ cm}^{-1}$ between the 6D multiplet and the levels of the next highest multiplets. Above this energy the density of states becomes quite high and there is a considerable breakdown of LS coupling with the result that only J remains a good quantum number for the free Gd^{3+} ion. The states of a given J follow the Wigner statistical distribution⁶² quite closely.

IV. GROUND-STATE G-FACTOR

The measurement of the g -factor for the ground-state of trivalent gadolinium in various host crystals has been the subject of numerous paramagnetic resonance experiments. In particular, Hutchison *et al.*¹³ have found $g = 1.991 \pm 0.001$ in GdCl_3 diluted in LaCl_3 while Bleaney *et al.*^{28,29} find $g = 1.990 \pm 0.002$ for $\text{Gd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ diluted in $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. In both cases the Gd^{3+} ion was presumed to be at a site of C_{3h} symmetry and the g factor was found to be highly isotropic.

Theoretically we find $g = 1.99454$ which is substantially larger than the experimental value. Increasing the magnitude of the spin-orbit coupling constant ζ decreases the discrepancy as is evident from Table III. However, complete agreement can only be attained by adapting an unrealistically large value of ζ . Judd and

⁵³ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

⁵⁴ W. A. Runciman and B. G. Wybourne, *J. Chem. Phys.* **31**, 1149 (1959).

⁵⁵ J. Sugar, *Phys. Rev. Letters* **14**, 731 (1964).

⁵⁶ K. Rajnak and B. G. Wybourne, *Phys. Rev.* **132**, 280 (1963).

⁵⁷ B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963).

⁵⁸ R. Trees, *J. Opt. Soc. Am.* **54**, 651 (1964).

⁵⁹ K. Rajnak, *J. Opt. Soc. Am.* **55**, 126 (1965).

⁶⁰ K. Rajnak, University of California Lawrence Radiation Laboratory Report UCRL-10460, 1962 (unpublished).

⁶¹ E. Y. Wong, *J. Chem. Phys.* **38**, 976 (1963).

⁶² C. E. Porter, *Statistical Theories of Spectral Fluctuations* (Academic Press, Inc., New York, 1965).

Lindgren⁶³ have estimated the relativistic and diamagnetic corrections to the $^8S_{7/2}$ ground state of the neutral europium atom and found the Schwinger corrected g factor to be reduced by 0.00175. The inclusion of the relativistic and diamagnetic corrections should likewise have the effect of reducing the g factor in Gd^{3+} . The actual correction should be somewhat larger than for neutral europium since relativistic corrections will certainly be larger in an ion of higher atomic number and nuclear charge. It is difficult to obtain a reliable estimate of the relativistic and diamagnetic corrections without having relativistic Hartree-Fock wave functions to compute the necessary integrals.

Fidone and Stevens⁶⁴ have noted that the presence of covalent bonding can lead to additional contributions, of either sign, to the g -factor. Low and Rubins⁶⁵ have found rather convincing evidence for changes in the g -factors attributable to covalent effects for several rare earths. Title²⁶ has noticed similar effects for $^8S_{7/2}$ ions in CdSe and CdTe while Baker *et al.*⁶⁶ have found the g -factor of $Tb^{4+} 4f^7(^8S_{7/2})$ in ThO_2 single crystals

TABLE II. Eigenvectors obtained for the 8S and $^6(PDI)$ levels of Gd^{3+} .

SLJ Designation	Eigenvector ^a
$^8S_{7/2}$	$0.9866 {}^8_7S\rangle+0.1618 {}^6_5P\rangle-0.0123 {}^6_7D\rangle$
$^6P_{7/2}$	$0.8514 {}^6_5P\rangle-0.1503 {}^8_7S\rangle-0.4038 {}^6_7D\rangle+0.0713 {}^6_5F\rangle$ $+0.1799 {}^4_3D_{30}\rangle+0.1936 {}^4_7D_{22}\rangle$
$^6P_{5/2}$	$0.8911 {}^6_5P\rangle-0.4176 {}^6_7D\rangle+0.0638 {}^6_5F\rangle$ $+0.1002 {}^4_3D_{30}\rangle+0.1088 {}^4_7D_{22}\rangle$
$^6P_{3/2}$	$0.9341 {}^6_5P\rangle-0.3231 {}^6_7D\rangle-0.1088 {}^4_7S_{22}\rangle$
$^6I_{7/2}$	$-0.9644 {}^6_7I\rangle-0.1884 {}^4_5H_{21}\rangle-0.1579 {}^4_5H_{30}\rangle$
$^6I_{9/2}$	$-0.9738 {}^6_7I\rangle-0.1563 {}^4_5H_{21}\rangle-0.1316 {}^4_5H_{30}\rangle$ $+0.0604 {}^6_5H\rangle$
$^6I_{17/2}$	$0.9800 {}^6_7I\rangle-0.1448 {}^4_5K_{21}\rangle-0.1312 {}^4_5K_{30}\rangle$
$^6I_{11/2}$	$-0.9811 {}^6_7I\rangle-0.1197 {}^4_5H_{21}\rangle-0.0996 {}^4_5H_{30}\rangle$ $+0.0685 {}^6_5H\rangle$
$^6I_{13/2}$	$-0.9855 {}^6_7I\rangle+0.0695 {}^6_5H\rangle-0.0769 {}^4_5H_{21}\rangle$ $-0.0613 {}^4_5H_{30}\rangle$
$^6I_{15/2}$	$-0.9862 {}^6_7I\rangle+0.1033 {}^4_5K_{21}\rangle+0.0952 {}^4_5K_{30}\rangle$ $+0.0602 {}^6_5H\rangle$
$^6D_{9/2}$	$0.9604 {}^6_7D\rangle-0.1938 {}^6_5F\rangle+0.0660 {}^6_7G\rangle$ $+0.1742 {}^4_5F_{30}\rangle$
$^6D_{1/2}$	$0.9929 {}^6_7D\rangle-0.0681 {}^6_5F\rangle-0.0752 {}^4_5P_{11}\rangle$
$^6D_{7/2}$	$-0.8696 {}^6_7D\rangle-0.3940 {}^6_5P\rangle+0.1974 {}^6_5F\rangle$ $+0.1142 {}^4_5D_{21}\rangle+0.0559 {}^8_7S\rangle$
$^6D_{3/2}$	$0.9287 {}^6_7D\rangle+0.3237 {}^6_5P\rangle-0.1262 {}^6_5F\rangle$
$^6D_{5/2}$	$0.8755 {}^6_7D\rangle+0.4208 {}^6_5P\rangle-0.1708 {}^6_5F\rangle$ $-0.1175 {}^4_5D_{21}\rangle$

^a The left-hand subscript associated with the SL quantum numbers is the seniority number. The right-hand subscripts were used in Racah's (Ref. 42) U designation for distinguishing states having the same SL quantum numbers.

⁶³ B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

⁶⁴ J. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **73**, 116 (1959).

⁶⁵ W. Low and R. S. Rubins, Phys. Rev. **131**, 2527 (1963).

⁶⁶ J. M. Baker, J. R. Chadwick, G. Garton, and J. P. Hurrell, Proc. Roy. Soc. (London) **A286**, 352 (1965).

TABLE III. Eigenvectors and g factors for the $^8S_{7/2}$ ground state for $\zeta=1480, 1520, 1560, \text{ and } 1600 \text{ cm}^{-1}$.

ζ	Eigenvector	Intermediate coupling g
1480	$0.98655 {}^8_7S\rangle+0.16176 {}^6_5P\rangle-0.01232 {}^6_7D\rangle$ $+0.0010 {}^6_5F\rangle-0.00014 {}^6_7G\rangle$	1.99454
1520	$0.98581 {}^8_7S\rangle+0.16604 {}^6_5P\rangle-0.01299 {}^6_7D\rangle$ $+0.0011 {}^6_5F\rangle-0.00015 {}^6_7G\rangle$	1.99410
1560	$0.98505 {}^8_7S\rangle+0.17032 {}^6_5P\rangle-0.01368 {}^6_7D\rangle$ $+0.0012 {}^6_5F\rangle-0.00017 {}^6_7G\rangle$	1.99365
1600	$0.98426 {}^8_7S\rangle+0.17459 {}^6_5P\rangle-0.01438 {}^6_7D\rangle$ $+0.0013 {}^6_5F\rangle-0.00019 {}^6_7G\rangle$	1.99319

to be *larger* than the spin only value showing clearly the existence covalent bonding or configuration mixing. Unfortunately, it is extremely difficult to estimate the magnitude of covalent effects without a detailed knowledge of the interaction of the Gd^{3+} ion with the lattice. Changes in the ground-state g factor can also arise as a result of configuration mixing either via the electrostatic interaction or by the crystal field interaction. These mechanisms may be represented schematically as

$$\langle {}^8S_{7/2} | V_E | {}^8X_J \rangle \langle L + 2S | {}^8X_J \rangle \langle {}^8X_J | V | {}^8S_{7/2} \rangle, \quad (3)$$

where V_E is the configuration mixing interaction and 8X_J is a state of the excited configuration. The electrostatic interactions will only couple states of the same S and L and hence will not change the magnitude of the g factor unless there is also spin-orbit interaction. Crystal field mixing of configurations will result in the coupling of states of different L and hence may lead to changes in the g factor. Octets with $g({}^8X_J) > g({}^8S_{7/2})$ will lead to an *increase* in the ground-state g factor while those with $g({}^8X_J) < g({}^8S_{7/2})$ will result in a *decrease* in the ground-state g factor. Actually, there can only be four octets (${}^8P_{5/2}$, ${}^8D_{5/2}$, ${}^8D_{3/2}$, and ${}^8F_{1/2}$) with $g(X_J) > g({}^8S_{7/2})$, all other octets have smaller g factors. Thus we might well expect this mechanism to *decrease* the calculated g factor for the ground state of Gd^{3+} . Again, there is considerable difficulty in obtaining a reliable estimate for the corrections to the g factor due to a lack of knowledge of the necessary radial integrals.

We have indicated four mechanisms that can lead to departures from the LS coupling ground-state g factor of 2.00232. To recapitulate, they are (1) spin-orbit interaction with excited states; (2) relativistic and diamagnetic effects; (3) covalency effects; (4) configuration mixing. It seems most unlikely that (1) can, by itself, explain the observed values of $g=1.991$. Furthermore, the relativistic and diamagnetic corrections appear to be somewhat too small to completely overcome the discrepancy. Thus it appears inevitable that a complete theory of the ground-state g factor must give cognizance to mechanisms (3) and (4). We might note that mechanism (4) would be essentially contained

in the complete molecular orbital treatment of mechanism (3).

V. GROUND-STATE SPLITTING CONTRIBUTIONS FROM WITHIN $4f^7$

Bleaney *et al.*^{26,27} have measured the ground-state splitting of gadolinium ethyl sulfate at 20°K by the technique of paramagnetic resonance. They find that at zero field the four Kramers pairs lie at 0, 0.049, 0.132, and 0.245 cm^{-1} , the $\pm\frac{7}{2}$ pair being *uppermost*. The crystal structure studies of Ketelaar⁶⁷ indicate that the Gd^{3+} ion is in a local crystal field of D_{3h} symmetry.

If we assume that the entire crystal field splitting comes from interactions within the f^7 configuration we may write the crystal field potential for D_{3h} symmetry as an expansion in tensor operators of the type $C_q^{(k)}$ to give⁴⁴

$$V_c = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_0^6 C_0^{(6)} + B(C_{-6}^{(6)} + C_6^{(6)}). \quad (4)$$

The quantities B_q^k are the crystal field parameters. The tensor operators appearing in Eq. (4) are of *even* rank and hence can only couple states of the f^7 configuration that are of different class. Thus if the ground-state splitting arises from interactions within the f^7 configuration the mechanism must in most cases involve at least fourth-order perturbations.

The simplest fourth-order perturbation to consider may be schematically represented as¹³

$$\langle {}^8S_{7/2} | \Lambda | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | \Lambda | {}^6D_{7/2} \rangle \langle {}^6D_{7/2} | V_c | {}^6P_{7/2} \rangle \times \langle {}^6P_{7/2} | \Lambda | {}^8S_{7/2} \rangle, \quad (5)$$

where Λ represents the spin-orbit interaction. The crystal field matrix elements will vanish except for the term in B_0^2 . If we write the ground-state eigenvector as

$$| {}^8S_{7/2} \rangle = a | {}^8S_{7/2} \rangle + b | {}^6P_{7/2} \rangle + c | {}^6D_{7/2} \rangle \quad (6)$$

then we have for the mechanism of Eq. (5) that,^{44,68}

$$\langle {}^8S_{7/2} M | V | {}^8S_{7/2} M' \rangle = \delta(M, M') (5^{1/2}/210) \times [4M^2 - 21] bc B_0^2. \quad (7)$$

Comparison with other rare-earth ethylsulfates indicates that B_0^2 is positive and $\sim 200 \text{ cm}^{-1}$ while considerations of perturbation theory lead to the conclusion that the product bc is necessarily *negative*. Thus this mechanism, while correctly predicting highly isotropic g values, gives the $\pm\frac{7}{2}$ Kramers pair as *lowest*, in contrast to the experimental result^{28,29} that it is *uppermost*. Using the values of b and c from Table II we calculate the ground-state splittings to be

$$0(\pm\frac{7}{2}), \quad 0.102(\pm\frac{5}{2}), \quad 0.170(\pm\frac{3}{2}), \quad \text{and} \quad 0.203(\pm\frac{1}{2}) \text{ cm}^{-1}. \quad (8)$$

⁶⁷ J. A. A. Ketelaar, *Physica* 4, 619 (1937).

⁶⁸ We note that the phase factor of Eq. (6-5) of Ref. 44 should be $(-1)^{S+L'+J+k}$.

TABLE IV. Intermediate coupling reduced matrix elements for the ${}^8S_{7/2}$ ground state using $\zeta = 1480, 1520, 1560,$ and 1600 cm^{-1} .

ζ	$\langle \psi_g \mathbf{U}^{(2)} \psi_g \rangle$	$\langle \psi_g \mathbf{U}^{(4)} \psi_g \rangle$	$\langle \psi_g \mathbf{U}^{(6)} \psi_g \rangle$
1480	0.0018617	0.0000544	0.0000021
1520	0.0020185	0.0000623	0.0000026
1560	0.0021840	0.0000710	0.0000031
1600	0.0023585	0.0000806	0.0000037

Considering the parameters B_0^2 and ζ_f are not optimized, the over-all splitting, and the relative spacings of the Kramers pairs, would be in reasonable agreement with the observed values were it not for the discrepancy in sign.

The calculation of the ground-state splitting produced by the mechanism of Eq. (5) was refined by using the complete intermediate coupling eigenvectors (all 50 components) to compute the crystal field matrix elements for the ground state using the results of Table IV. As would be expected, the contributions from the B_0^6 and B_6^6 terms are wholly negligible. Assuming the interpolated value of $B_0^4 = 550 \text{ cm}^{-1}$ and $\zeta_f = 1480 \text{ cm}^{-1}$ we obtained the ground-state splitting as

$$0(\pm\frac{7}{2}), \quad 0.114(\pm\frac{5}{2}), \quad 0.180(\pm\frac{3}{2}), \quad \text{and} \quad 0.120(\pm\frac{1}{2}). \quad (9)$$

Again the wrong sign is obtained. It is apparent that the observed ground-state splitting cannot be explained by simply considering the reflection of the splittings of excited states of f^7 into the ground state via the spin-orbit interaction.

Judd^{12,13} has proposed an additional fourth-order mechanism that may be schematically represented as

$$\langle {}^8S_{7/2} | \Lambda | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | V_c | V^6 L_{J''} \rangle \langle {}^6L_{J''} | V_c | {}^6P_{7/2} \rangle \times \langle {}^6P_{7/2} | \Lambda | {}^8S_{7/2} \rangle. \quad (10)$$

Restricting ourselves to states within $4f^7$ we see that L is limited to the states $D, G,$ and I and that the total contribution from this mechanism will be obtained by summing up the contributions from all of them. Equation (10) may be rewritten as

$$= -b^2 \sum_{k,q,q'} \sum_{L,J'',M''} \langle {}^6P_{7/2} M | B_{q^k} C_{q^k} | {}^6L_{J''} M'' \rangle \times \langle {}^6L_{J''} M'' | B_{q^k} C_{q^k} | {}^6P_{7/2} M' \rangle / E({}^6L_{J''} M'' - {}^8S_{7/2}) \quad (11)$$

where b is the ${}^6P_{7/2}$ component of the ground-state eigenvector. The detailed computation of Eq. (11) is a formidable problem unless some simplifying approximations are made. Since the spin-orbit and crystal field splittings of the excited states are small compared with their energy separations from the ground state, and the crystal field splittings are small compared to the sextet separations, it is a reasonable assumption to perform a closure over the $J''M''$ states of the 6L multi-

plets. This summation may be readily performed using the identity:

$$\begin{aligned} \Omega(M, M') &= \sum_{J''M''} \langle SLJM | \mathbf{U}_q^{(k)} | SL''J''M'' \rangle \\ &\quad \times \langle SL''J''M'' | \mathbf{U}_{q'}^{(k)} | SLJM' \rangle \\ &= (-1)^{s+L'+J} (2J+1) (SL \| \mathbf{U}^{(k)} \| SL')^2 \sum_x \\ &\quad \times (2x+1) \begin{pmatrix} J & J & x \\ M-M' & -(q+q') & \end{pmatrix} \begin{pmatrix} kk & x \\ qq' & -(q+q') \end{pmatrix} \\ &\quad \times \begin{Bmatrix} L L x \\ k k L' \end{Bmatrix} \begin{Bmatrix} L L x \\ J J S \end{Bmatrix} (-1)^{J-M'}. \quad (12) \end{aligned}$$

For the case of immediate interest $L=1$ and we have $2 \geq x \geq 0$ and hence for D_{3h} symmetry $q+q'=0$ and $M=M'$. The term with $x=0$ is independent of M and thus will not contribute to the *relative* separation of the ground-state Kramers' pairs. Furthermore, when we consider the summation of q and q' in Eq. (11) it is apparent that the *odd* terms in x will cancel out in pairs. Hence as long as we are only interested in relative separations we may write for the case of interest.

$$\begin{aligned} \Omega'(M) &= \sum_{J''M''} \langle {}^6P_{7/2M} | \mathbf{U}_{\pm q}^{(k)} | SL''J''M'' \rangle \\ &\quad \times \langle SL''J''M'' | \mathbf{U}_{\pm q}^{(k)} | {}^6P_{7/2M} \rangle \\ &= 40({}^6P \| \mathbf{U}^{(k)} \| {}^6k)^2 \begin{pmatrix} \frac{7}{2} & \frac{7}{2} & 2 \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} k & k & 2 \\ \pm q & \mp q & 0 \end{pmatrix} \\ &\quad \times \begin{Bmatrix} k & k & 2 \\ 1 & 1 & k \end{Bmatrix} \begin{Bmatrix} \frac{7}{2} & \frac{7}{2} & 2 \\ 1 & 1 & \frac{3}{2} \end{Bmatrix} (-1)^{M+1/2}, \quad (13) \end{aligned}$$

where we omit a constant term. Upon explicitly evaluating the $3-j$ and $6-j$ symbols, noting that

$$({}^6P \| \mathbf{U}^{(k)} \| {}^6k)^2 = k(k+1)/28 \text{ for } f^7, \quad (14)$$

and dropping a further constant term we obtain

$$\Omega_R'(M) = \frac{M^2[3q^2 - k(k+1)][3 - 4k(k+1)]}{1176(2k-1)(2k+1)(2k+3)}. \quad (15)$$

Using this expression in Eq. (11) and noting Eq. (7) we obtain the total ground-state splitting $T(M)$ from the combined effect of the mechanisms of Eq. (5) and (10) as

$$\begin{aligned} T(M) &= \frac{bM^2}{21} \left[\frac{2(5)^{1/2}}{5} c B_0^2 - b \left(\frac{(B_0^2)^2}{25E_D} + \frac{5(B_0^4)^2}{99E_G} \right. \right. \\ &\quad \left. \left. + \frac{25[7(B_0^6)^2 - 22(B_6^6)^2]}{1859E_I} \right) \right] \quad (16) \end{aligned}$$

where E_D , E_G , and E_I are the average energies of the 6D , 6G , and 6I multiplets, respectively. We note that

this expression has the same M -dependence as Eq. (7) and hence the ratios of the spacings of the successive Kramers' pairs remains the same. Whereas the contribution from the mechanism of Eq. (5) are linear in the crystal field parameters the mechanism of Eq. (5) is linear in the crystal field parameters the mechanism of Eq. (10) is a quadratic function of the parameters. The quadratic term is dominated by the sixth-order terms of the crystal field potential and since we generally have $22(B_6^6)^2 > 7(B_0^6)^2$ the net quadratic contribution has the opposite sign to the linear contribution.

To obtain a semiquantitative estimate of the combined mechanisms let us assume that $E_D=40320$, $E_G=5000$, and $E_I=36360 \text{ cm}^{-1}$ and that $B_0^2=200$, $B_0^4=-550$, $B_0^6=-550$, and $B_6^6=550 \text{ cm}^{-1}$. Using these values in Eq. (16) we obtain

$$T(M) = (bM^2/21)[178.89c + 1.3151b], \quad (17)$$

where c is negative with respect to b . The combination of these two mechanisms will only yield the $\pm \frac{7}{2}$ Kramers pair uppermost if $b/c > 144$. However, this requirement cannot be satisfied by any reasonable choice of ζ as is apparent from Table III. Thus we are forced to conclude that the zero-field splitting of Gd^{3+} in the ethyl sulfate cannot be accounted for by the combination of the linear and quadratic mechanisms of Eqs. (5) and (10) as long as we restrict our attention to states within the $4f^7$ configuration. Using the values of b and c from Table II in Eq. (17) we obtain the ground-state splitting as

$$0(\pm \frac{7}{2}), \quad 0.091(\pm \frac{5}{2}), \quad 0.153(\pm \frac{3}{2}), \quad 0.183(\pm \frac{1}{2}) \text{ cm}^{-1}. \quad (18)$$

VI. CONTRIBUTIONS FROM SPIN-SPIN INTERACTIONS WITHIN f^7

There is a third-order mechanism involving the spin-spin interaction (V_{ss}) which may be schematically represented as

$$\langle {}^8S_{7/2} | V_{ss} | {}^6D_{7/2} \rangle \langle {}^6D_{7/2} | V_c | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | \Lambda | {}^8S_{7/2} \rangle. \quad (19)$$

The spin-spin interaction matrix element may be evaluated using Eq. (2-135) of Ref. 44 to give⁶⁹

$$\begin{aligned} \langle {}^8S_{7/2} | V_{ss} | {}^6D_{7/2} \rangle \\ = -(2(42)^{1/2}/42) \left(M^0 + 2M^2 + \frac{25}{11} M^4 \right), \quad (20) \end{aligned}$$

where the M^k 's are the Marvin radial integrals.⁷⁰ These integrals have been computed by Blume *et al.*⁷¹ using

⁶⁹ The last $6-j$ symbol appearing in Eq. (2-135) of Ref. 44 should be $\begin{Bmatrix} L' & L & 2 \\ k-1 & k+1 & L'' \end{Bmatrix}$.

⁷⁰ H. Marvin, Phys. Rev. **71**, 102 (1947).

⁷¹ M. Blume, A. J. Freeman, and R. E. Watson, Phys. Rev. **134**, A320 (1964).

Hartree-Fock wave functions. Using their values in Eq. (20), and evaluating the matrix elements of Eq. (19) we find that the spin-spin mechanism contribution to the ground-state splitting has the right sign but is only $\sim 10^{-3} \text{ cm}^{-1}$ and hence cannot explain the observed splitting.

VII. PRYCE'S SECOND-ORDER SPIN-SPIN MECHANISM

Pryce² has proposed a second-order spin-spin mechanism involving interaction with the $4f^6p$ configuration. His mechanism may be schematically represented as

$$\langle 4f^7 {}^8S_{7/2}M | V_{ss} | 4f^7({}^7F)6p^8D_{7/2}M \rangle \\ \times \langle 4f^6({}^7F)6p^8D_{7/2}M | V_c | 4f^7 {}^8S_{7/2}M' \rangle \quad (21)$$

Dieke and Crosswhite⁷² have indicated that the $4f6p$ configuration is $\sim 150\,000 \text{ cm}^{-1}$ above the $4f^7$ configuration and hence this mechanism will only be important if the M -dependent portion of the product of the two matrix elements of Eq. (21) is $\sim 50\,000 \text{ cm}^{-1}$. The crystal field matrix elements may be evaluated to give

$$\langle 4f^7({}^7F)6p^8D_{7/2}M | V_c | 4f^7 {}^8S_{7/2} \rangle \\ = ((105)^{1/2}/700)[4M^2 - 21]B_0^2(\langle r^2 \rangle_{4f6p}/\langle r^2 \rangle_{4f4f}). \quad (22)$$

Rajnak⁶⁰ has calculated the ratio $(\langle r^2 \rangle_{4f6p}/\langle r^2 \rangle_{4f4f})$ to be ~ 0.7 . Using her result in Eq. (22), together with $B_0^2 = 200 \text{ cm}^{-1}$, we find the M -dependent part of Eq. (22) to be only $8M^2 \text{ cm}^{-1}$. Thus for Pryce's mechanism to be dominant we would require that the spin-spin matrix element between $4f^7({}^8S_{7/2})$ and $4f^6({}^7F)6p^8D_{7/2}$ be $\sim 500 \text{ cm}^{-1}$. This is considerably larger than even the typical electrostatic matrix elements which connect the two configurations and which are necessarily considerably larger than the spin-spin matrix elements. Unfortunately, the relevant Marvin integrals are not available and hence it is not possible to make a detailed numerical estimate of the contribution from Pryce's mechanism. An additional contribution would arise from spin-spin interaction with the $5p^54f^8$ configuration, but again this contribution can be expected to be negligible.

VIII. SECOND-ORDER RELATIVISTIC CONTRIBUTION

The crystal field matrix element between states of different spin vanish in the nonrelativistic limit and hence the matrix element coupling the ${}^8S_{7/2}$ state to the ${}^6P_{7/2}$ state of the $4f^7$ configuration is normally assumed to vanish. It has recently been pointed out that if relativistic effects are taken into account this matrix element is no longer zero.⁷³ Thus we can obtain a second-

order contribution to the ground-state splitting of Gd^{3+} which may be written as

$$S(M) = -2A_2^0 \zeta_{4f} \langle {}^8S_{7/2}M | \sum_{i=1} (\mathbf{s} \cdot \mathbf{I})_i | {}^6P_{7/2}M \rangle \\ \times \langle {}^6P_{7/2}M | b_2(11)\mathbf{W}_0^{(11)2} | {}^8S_{7/2}M \rangle / \Delta E \quad (23)$$

where $\Delta E = |E({}^8S) - E({}^6P)|$ and

$$b_2(11) = 4(21)^{1/2}[-5R_{++}^2 + 3R_{+-}^2 + 2R_{--}^2]/245. \quad (24)$$

with R_{++}^2 , R_{+-}^2 , and R_{--}^2 being relativistic radial integrals.⁷³ Upon evaluating the matrix elements Eq. (23) reduces to

$$S(M) = 8A_2^0 \zeta_{4f} (-5R_{++}^2 + 3R_{+-}^2 + 2R_{--}^2)M^2 / 245\Delta E. \quad (25)$$

Using the radial integrals of Waber and Cromer^{74,75} we find the contribution to be⁷³

$$0(\pm \frac{7}{2}), 0.156(\pm \frac{5}{2}), 0.260(\pm \frac{3}{2}), 0.312(\pm \frac{1}{2}) \text{ cm}^{-1} \quad (26)$$

This mechanism produces a calculated splitting which is *larger* than the observed splitting and of the *opposite* sign.

IX. CRYSTAL FIELD CONFIGURATION MIXING

The crystal field operators $\mathbf{C}^{(k)}$ are one-particle operators and hence they can only couple to f^7 configurations differing by at most one particle. It is natural to consider second-order mechanisms of the type

$$-\sum_x \langle f^7SLJM | V_c | X \rangle \langle X | V_c | f^7SL'J'M' \rangle / \Delta E_x, \quad (27)$$

where X is a state belonging to an excited configuration and ΔE_x is the positive excitation energy. However, Rajnak and Wybourne⁷⁶ have shown that the averaged effect of Eq. (27) is simply proportional to the matrix elements

$$\langle f^7SLJM | V_c | f^7SL'J'M' \rangle,$$

and also gives rise to a uniform shift of the crystal field levels without changing the zero-order spacings. Thus this mechanism will, at the best, correspond to a linear shielding of the B_q^k parameters and since we are already using empirically derived parameters we may regard these contributions as already incorporated in the mechanisms discussed in Sec. V.

X. ELECTROSTATICALLY CORRELATED CRYSTAL FIELD CONTRIBUTIONS

Rajnak and Wybourne⁷⁶ have discussed the effects produced by electrostatically correlated crystal field interactions that may be represented as

$$(-2/\Delta E_{Av}) \sum_x \langle nL^N \psi | V_c | X \rangle \langle X | V_B | L^N \psi' \rangle, \quad (28)$$

⁷² G. H. Dieke and H. M. Crosswhite, Appl. Optics **2**, 675 (1963).

⁷³ B. G. Wybourne, J. Chem. Phys. **43**, 4506 (1965).

⁷⁴ J. T. Waber and D. T. Cromer, J. Chem. Phys. **42**, 4116 (1965).

⁷⁵ J. T. Waber (private communication).

⁷⁶ K. Rajnak and B. G. Wybourne, J. Chem. Phys. **41**, 565 (1964).

where V_c and V_B are the crystal field and Coulomb potentials, respectively, X is an excited state of a perturbing configuration of parity $(-1)^{lN}$, and ΔE_{Av} is positive average energy of excitation. Since ΔE_{Av} is greater than 10^5 cm^{-1} for the lowest connected configuration ($4f^6 6p$) we can expect conventional perturbation to give a reasonable representation. Rajnak and

Wybourne have shown that excitations of the type $n'l^{4l'+2}n^{lN} \rightarrow n'l^{4l'+1}n^{lN+1}$ or $n^{lN} \rightarrow n^{lN-1}n'l'$ are of special interest because even in the case of a half-filled shell they lead to an effective interaction between states of the same class. We are particularly interested in the effective interaction, V_{eff} , for the 6P state of f^7 . Following Eq. (13) of Rajnak and Wybourne we may write⁷⁷

$$\begin{aligned} \langle n f^7 {}^6P | V_{\text{eff}} | n f^7 {}^6P \rangle &= -\frac{2}{\Delta E_{Av}} \sum_{6P'} A_2^0 \langle n f^7 {}^6P || r^2 C^2 || {}^6P' \rangle \langle {}^6P' || \sum_k \frac{r^{<k}}{r^{>k+1}} \sum_{i>j} (\mathbf{C}_i^{(k)} \cdot \mathbf{C}_j^{(k)}) || n f^7 {}^6P \rangle \\ &= -\frac{2(5)^{1/2}}{5\delta E_{Av}} \langle l' || \mathbf{C}^{(2)} || 3 \rangle B_0^2 \frac{\langle n'l' | r^2 | n f \rangle}{\langle n f | r^2 | n f \rangle} \sum_{k \leq 0} [k] \begin{Bmatrix} k k 2 \\ 3 l' 3 \end{Bmatrix} \langle f^7 {}^6P || \sum_{i,j} \{ \mathbf{u}_i^{(k)} \mathbf{u}_j^{(k)} \}^{(2)} || f^7 {}^6P \rangle \\ &\quad \times \langle 3 || \mathbf{C}^{(k)} || 3 \rangle \langle 3 || \mathbf{C}^{(k)} || l' \rangle R^k(n f n f n' l'), \quad (29) \end{aligned}$$

where ${}^6P'$ belongs to the perturbing configuration ($n'l^{4l'+1}n^{f8}$ or $n f^6 n' l'$), the $R^k(n f n f n' l')$'s are the usual Slater radial integrals and the JM dependence of the matrix elements of V_{eff} has been removed.

We may obtain a fourth-order contribution to the ground state splitting of the form

$$\zeta_{n f^2} \left[\frac{\langle n f^7 {}^8S_{7/2} | \sum_{i=1} (\mathbf{s} \cdot \mathbf{l})_i | n f^6 {}^6P_{7/2} \rangle}{E({}^8S) - E({}^6P)} \right] \times \langle n f^7 {}^6P_{7/2} M | V_{\text{eff}} | n f^7 {}^6P_{7/2} M \rangle. \quad (30)$$

Evaluating the spin-orbit matrix element, extracting the JM dependence and retaining only the M dependent part of the resultant expression we obtain the contribution

$$S(M) = \frac{(30)^{1/2} \zeta_{n f^2} M^2}{15 |E({}^8S) - E({}^6P)|^2} \langle n f^7 {}^6P || V_{\text{eff}} || n f^7 {}^6P \rangle. \quad (31)$$

For $n f \leftrightarrow n' p$ excitations we find

$$\begin{aligned} \langle n f^7 {}^6P || V_{\text{eff}} || n f^7 {}^6P \rangle &= \frac{-2(30)^{1/2}}{35\Delta E_{Av}} B_0^2 \frac{\langle n' p | r^2 | n f \rangle}{\langle n f | r^2 | n f \rangle} \\ &\quad \times \left[\frac{9R^2}{25} (n f n f n' p) + \frac{R^4(n f n f n' p)}{2} \right], \quad (32a) \end{aligned}$$

and for $n f \leftrightarrow n' f$

$$\begin{aligned} \langle n f^7 {}^6P || V_{\text{eff}} || n f^7 {}^6P \rangle &= \frac{+(30)^{1/2}}{15\Delta E_{Av}} B_0^2 \frac{\langle n' f | r^2 | n f \rangle}{\langle n f | r^2 | n f \rangle} \\ &\quad \times \left[\frac{11R^2(n f n f n' f)}{75} - \frac{R^4(n f n f n' f)}{11} \right. \\ &\quad \left. - \frac{875}{429} R^6(n f n f n' f) \right]. \quad (32b) \end{aligned}$$

Rajnak⁶⁰ has estimated the magnitude of the integrals and energy denominators appearing in Eqs. (32a) and (32b) for $4f \rightarrow 6p$ and $4f \rightarrow 5f$ excitations by interpolation from her results for Pr^{3+} and Tm^{3+} . Using her results we find

$$\begin{aligned} \langle 4f^7 {}^6P || V_{\text{eff}} || 4f^7 {}^6P \rangle_{4f \rightarrow 6p} &= +1.026 \text{ cm}^{-1}, \\ \langle 4f^7 {}^6P || V_{\text{eff}} || 4f^7 {}^6P \rangle_{4f \rightarrow 5f} &= +3.850 \text{ cm}^{-1}. \end{aligned}$$

Putting these values in Eq. (31) we find a total contribution to the ground state splitting of $\sim 0.05 \text{ cm}^{-1}$ with the $\pm \frac{7}{2}$ level highest. The excitations $5p \rightarrow 4f$ should yield a contribution of opposite sign to those just considered and probably more than annul them.

XI. FIFTH-ORDER CONFIGURATION INTERACTION MECHANISM

The $4f^7({}^8S_{7/2})$ ground state of Gd^{3+} is perturbed by electrostatic interaction with the two ${}^8S_{7/2}$ levels of the $4f^5 5d^2$ configuration. The unnormalized perturbed ground-state wave function may be written as

$$|{}^8S_{7/2}\rangle = |4f^7 {}^8S_{7/2}\rangle + b |4f^5 {}^6P 5d^2; {}^8S_{7/2}\rangle + c |4f^5 {}^6F 5d^2; {}^8S_{7/2}\rangle,$$

where

$$b = -(210)^{1/2} [2G_1(4f5d) + 3G_3(4f5d) - 33G_5(4f5d)] / W_{6p}$$

and

$$c = -(105)^{1/2} [3G_1(4f5d) - 8G_3(4f5d) - 11G_5(4f5d)] / W_{6f}.$$

Rajnak⁶⁰ has obtained estimates of the $G_k(4f5d)$ integrals and the energy denominators W_{6p} and

⁷⁷ Note that in the above reference the quantity

$$\begin{aligned} &[k]^{-1/2} \begin{Bmatrix} \kappa & k & \kappa \\ l & l & l' \end{Bmatrix} \\ &\text{should be replaced by} \\ &[k]^{-1/2} \begin{Bmatrix} \kappa & k & \kappa' \\ l & l & l' \end{Bmatrix}. \end{aligned}$$

H'_{6x} . Using her values we find the coefficients b and c to be ~ 0.08 . Bearing in mind these admixtures we may obtain a fifth-order contribution to the ground-state splitting which may be schematically represented as

$$\begin{aligned} \langle f^7 \ ^8S | V_E | f^5 \ ^6X5d^2 \ ^8S \rangle & \langle f^5 \ ^6X5d^2 \ ^8S | \Lambda | f^5 \ ^6X'5d^2 \ ^{2S+1}P \rangle \\ & \times \langle f^5 \ ^6X'5d^2 \ ^{2S+1}P | V_0^2 | f^5 \ ^6X''5d^2 \ ^{2S+1}P \rangle \\ & \times \langle f^5 \ ^6X''5d^2 \ ^{2S+1}P | \Lambda | f^5 \ ^6X5d^2 \ ^8S \rangle \\ & \times \langle f^5 \ ^6X5d^2 \ ^8S | V_E | f^7 \ ^8S \rangle. \quad (33) \end{aligned}$$

These contributions will be approximately proportional to the inverse *fourth* power of W_{6x} . We may infer from the work of Dieke *et al.*⁷² that W_{6x} is $\sim 200\,000\text{ cm}^{-1}$ while the matrix elements of spin-orbit and crystal field interaction are less than $\sim 10\,000\text{ cm}^{-1}$. It is apparent that this mechanism could not account for more than a few percent of the observed splitting. This would appear to be generally the case for high-order perturbations produced by excited configurations. The energy denominators involved are much too large to give any significant contributions to the ground-state splitting.

XII. SUMMARY OF CONTRIBUTIONS TO THE GROUND-STATE SPLITTING

In the course of this paper we have examined several mechanisms that can lead to a splitting of the ground-state of the Gd^{3+} ion in the ethyl sulfate crystal. It appears that none of these mechanisms, or any combination of them, can give an adequate explanation of the result of Bleaney *et al.*^{28,29} that the $\pm \frac{7}{2}$ Kramers doublet is uppermost. It might be objected that we have made an unfortunate choice of B_0^2 , especially since the value computed from a point charge model is ~ 10 times larger than the value used here. However, changing the value of B_0^2 will mainly just scale the different contributions and not alter the *sign* of the over-all splitting. There appears to be no valid reason for supposing that B_0^2 changes sign between Eu^{3+} and Tb^{3+} .

Several of the mechanisms discussed can be regarded as simply mechanisms that reflect a portion of the splitting of the ${}^6P_{7/2}$ excited state into the ${}^8S_{7/2}$ ground state. Dieke and Leopold⁴⁶ have shown that in the hydrated trichloride the arrangement of the Kramers doublets for the excited ${}^6P_{7/2}$ state is $\pm \frac{7}{2}$, $\pm \frac{5}{2}$, $\pm \frac{3}{2}$, $\pm \frac{1}{2}$ with the $\pm \frac{7}{2}$ doublet *lowest*. A similar situation appears in the ethylsulfate.⁷⁸ However, any mechanism that reflects the ${}^6P_{7/2}$ splitting into the ground state must yield the $\pm \frac{7}{2}$ Kramers doublet of the ground state *lowest* in contradiction to the experimental result of Bleaney *et al.* Thus we are forced to conclude that mechanisms that are, in effect, simply a reflection of a portion of the ${}^6P_{7/2}$ excited state crystal field splitting cannot explain the observed splitting in the ground-state. There appears to be no difficulty in explaining the

major part of the crystal field splitting of the 6P excited states using a *positive* value of B_0^2 .

If the crystal field were to be over-shielded in the excited states of Gd^{3+} we would expect the B_0^2 deduced from the excited state splittings to be *negative*. The degree of shielding in the ground state could be expected to be smaller than in the excited states due to the larger energy denominators. Since B_0^2 is *positive* in the excited states we conclude that B_0^2 should also be positive in the ground state.

The relativistic, spin-spin, and configuration mixing mechanisms do not depend directly on the splitting of the ${}^6P_{7/2}$ excited state and hence might have been expected to be the important mechanisms. However, it is clear that these mechanisms, important as they are, cannot account for the observed splitting. We note that for Cm^{3+} the ground state $5f^7({}^8S_{7/2})$ also has the $\pm \frac{1}{2}$ Kramers doublet *lowest*⁷⁹ and we might at first think that the mechanisms discussed here would again yield the wrong sign giving the $\pm \frac{7}{2}$ Kramers doublet *lowest*. However, the splitting of the ground state of Cm^{3+} should be⁸⁰ $\sim 3-5\text{ cm}^{-1}$ and the sign of B_0^2 , for the actinides, is apparently *negative*,⁸¹ and hence, the major portion of the ground-state splitting can probably be accounted for by the mechanisms discussed herein. That fact that B_0^2 is negative probably means that the screening in the actinides produced by $6s \rightarrow 6d$ excitations is larger than that produced by the $5s \rightarrow 5d$ excitations in the corresponding lanthanides.

Our major conclusion concerning the origin of the ground-state splitting of Gd^{3+} in lanthanum ethyl sulfate is simply that the basically ionic mechanisms that have been frequently mentioned in the literature in a qualitative manner do not yield the correct quantitative agreement with experiment even when the numerical calculation is carried out in considerable detail. Thus it would appear that mechanisms that separate the Gd^{3+} ion from the host crystal cannot explain the observation of Bleaney *et al.*^{28,29}

Future developments in the theory of the ground-state splitting of gadolinium in lanthanum ethyl sulfate will probably require the detailed molecular orbital treatment of the $\text{Gd}(\text{H}_2\text{O})_9^{3+}$ complex. It should be noted that while our discussion has been entirely devoted to the ground-state splitting of Gd^{3+} in the lanthanum ethyl sulfate, for most of the host crystals that have been studied, especially the lanthanum trihalides, the sign of the splitting is calculated to be opposite to the experimental measurements. The marked sensitivity of the splitting in LaCl_3 to temperature¹³ would seem to indicate that the mechanisms we have discussed are closely competing with another

⁷⁸ A. Piskis (private communication).

⁷⁹ M. Abraham, B. R. Judd, and H. H. Wickham, *Phys. Rev.* **130**, 611 (1963).

⁸⁰ W. T. Carnall and B. G. Wybourne, *J. Chem. Phys.* **40**, 3428 (1965).

⁸¹ J. G. Conway (private communication).

mechanism which actually dominates all other contributions.

XIII. INTENSITIES IN Gd³⁺ CRYSTAL AND SOLUTION SPECTRA

Judd⁸² and Ofelt⁸³ have developed a theory of the intensities of rare-earth solution and crystal spectra. Their result for solution absorption spectra may be written as

$$P = \sum_{\lambda \text{ even}} T_{\lambda} \sigma(\psi_{\sigma} J \| U^{(\lambda)} \| \psi_{\sigma} J')^2 / (2J+1),$$

where P is the oscillator strength, T_{λ} is a parameter that depends on the nature of the crystal field, and σ is the wave number of the transition from the ground state $\psi_{\sigma} J$ to the excited state $\psi_{\sigma} J'$. Our notation, in general, follows Carnall *et al.*⁸⁴ The reduced matrix elements in intermediate coupling are listed in Table V for the excited states below 45 000 cm⁻¹. Carnall *et al.* have deduced values of T_{λ} ($\lambda=2, 4,$ and 6) for Pr³⁺, Nd³⁺, Er³⁺, and Tm³⁺ in aqueous solution. Using their values and interpolating for Gd³⁺ we find

$$T_2 \cong 1.6 \times 10^{-9}, \quad T_4 \cong 3 \times 10^{-9}, \quad \text{and} \quad T_6 \cong 5 \times 10^{-9}.$$

Considering these values together with the experimental values of σ from Table I and the reduced matrix elements of Table V we compute the oscillator strengths shown in Table VI.

The oscillator strengths for the transitions to the ⁶ P and ⁶ D levels are evidently dominated by T_2 while

TABLE V. Intermediate coupling reduced matrix elements of $(\psi_{\sigma} \| U^{(k)} \| \psi_{\sigma})$ ($k=2, 4,$ and 6) between the ground state ψ_{σ} and the excited states ψ_{σ} below 45 000 cm⁻¹.

ψ_{σ}	$(\psi_{\sigma} \ U^{(2)} \ \psi_{\sigma})$	$(\psi_{\sigma} \ U^{(4)} \ \psi_{\sigma})$	$(\psi_{\sigma} \ U^{(6)} \ \psi_{\sigma})$
⁶ $P_{7/2}$	0.03644	0.00276	0.00119
⁶ $P_{5/2}$	-0.02367	-0.00070	0.00005
⁶ $P_{3/2}$	0.00515	-0.00025	0
⁶ $I_{7/2}$	-0.00049	0.00181	0.06503
⁶ $I_{9/2}$	-0.00110	-0.00339	-0.10300
⁶ $I_{17/2}$	0	0	0.14801
⁶ $I_{11/2}$	-0.00009	0.00393	0.13445
⁶ $I_{13/2}$	0	-0.00291	-0.15719
⁶ $I_{15/2}$	0	-0.00122	0.16593
⁶ $D_{9/2}$	0.07624	0.01043	-0.00181
⁶ $D_{11/2}$	0	-0.00063	0
⁶ $D_{7/2}$	0.06525	0.00665	-0.00045
⁶ $D_{3/2}$	-0.02890	0.00048	0
⁶ $D_{5/2}$	0.04893	0.00202	-0.00008

⁸² B. R. Judd, Phys. Rev. **127**, 750 (1962).

⁸³ G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

⁸⁴ W. T. Carnall, P. R. Fields, and B. G. Wybourne, J. Chem. Phys. **42**, 3797 (1965).

TABLE VI. Oscillator strengths computed for Gd³⁺ in an aqueous solution.

Transition	10 ⁹ P
⁸ $S_{7/2} \rightarrow$ ⁶ $P_{7/2}$	8.62
⁶ $P_{5/2}$	3.66
⁶ $P_{3/2}$	0.018
⁶ $I_{7/2}$	95.0
⁶ $I_{9/2}$	240
⁶ $I_{17/2}$	536
⁶ $I_{11/2}$	445
⁶ $I_{13/2}$	610
⁶ $I_{15/2}$	681
⁶ $D_{9/2}$	62.1
⁶ $D_{11/2}$	0.006
⁶ $D_{7/2}$	34.6
⁶ $D_{3/2}$	6.81
⁶ $D_{5/2}$	19.6

those to ⁶ I are dominated by T_6 . Unfortunately, there has been no quantitative work published on the oscillator strengths of Gd³⁺ in either solutions or crystals. In the original study by Dieke and Leopold⁴⁶ of Gd³⁺ spectra in crystals the ⁶ $P_{3/2}$ levels was not observed due evidently to its extreme weakness. Cook and Dieke⁴⁷ subsequently observed it as two very weak transitions. Their result is in accord with the expectations of Table VI.

XIV. CONCLUDING REMARKS

In the present paper we have attempted to interpret some of the spectroscopic properties of the Gd³⁺ ion in crystals. While some progress has been made in estimating the role of several mechanisms that lead to a splitting of the ground state of Gd³⁺ it is apparent that we still lack an adequate explanation of the observed splitting. The agreement between the calculated and experimental g factor is not as good as might be expected and we suspect that the reason for this discrepancy is the same as for the discrepancy in the calculated and experimental crystal field splitting, namely, the failure to include the overlap of the ligand orbitals with those of the central ion.

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