

Magnetic Ordering Properties of Rare-Earth Ions in Strong Cubic Crystal Fields*

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A theoretical discussion of some of the effects resulting from the interplay between strong crystalline-field torques and weaker exchange torques acting on rare-earth ions is given. The crystalline field is supposed to have cubic symmetry. A semiclassical discussion of the effect of the crystalline field in determining easy directions, anisotropy, and the depression of ground-state ordered moment values for the rare-earth series is given and used to interpret the results of the exact calculations. It is shown that for some of the rare earths the crystalline field may be so large that no long-range magnetic order is possible at low temperatures. The theory is applied to the case of the rare-earth phosphides. Adjusting the exchange and crystalline-field parameters to yield the observed ordered moment values (and moment directions) of TbP and ErP, one predicts the HoP moment in agreement with the experimental value, and predicts that TmP will not order at all. The "holmium flopside" moment pattern is explained as being due to magnetic dipole forces. The ratio of the sixth-order component of the crystalline potential to the fourth-order component must be increased some five times over the naively computed value in order to reach agreement with experiment; however, an experimental indication of a possibly important noncubic component of the crystalline potential may change this value appreciably.

I. INTRODUCTION

MAGNETICIANS have long found the study of the rare earths interesting and instructive. The work of Van Vleck¹ and co-workers on the high-temperature paramagnetic susceptibilities of various rare-earth salts established that the magnetic moments of the rare-earth ions were closely the same as that expected for the free 3^+ ion coupled according to Hund's rule with L - S coupling, and that the principal effect of the chemical environment could be understood as due to the "crystal fields" exerting torques on the asymmetric $4f$ shell electrons. The integrity of the $4f$ shell electrons was regarded as being due to the deep embedment of the $4f$ shell in the ion which reduced to negligibility its direct overlap with the electron shells of neighboring atoms, and at the same time made the intrashell exchange forces and spin-orbit forces sufficiently strong such that the remaining interactions with the environment could not disrupt the free-ion coupling.

Further evidence of the essential correctness of this view of the rare earths was provided by the analysis of Elliot and Stevens² of the paramagnetic resonance studies of various rare-earth salts conducted by Bleaney and co-workers.^{3,4} These workers found that the results could be explained in terms of the Van Vleck model if the strengths of the crystalline potentials were given

values in rough accord with that suggested by simple electrostatic considerations of the fields due to the surrounding ions. However, these naive values were sometimes found to differ considerably from those revealed by experiment, in particular, the quadrupole component of the potential was in some cases found to be remarkably low.⁵

The magnetic properties of the rare-earth metals have been investigated by Spedding *et al.*⁶ by the "classical" means of susceptibility and specific heat measurements, and by Cable *et al.*⁷ using neutron diffraction techniques. The principal features of the unusual magnetic behavior disclosed by these studies seem to be well accounted for by theories advanced by Elliot,⁸ Kaplan,⁹ and Miwa and Yosida,¹⁰ who attribute the ordering to the polarization of the conduction band electrons by the $4f$ electrons.

Child *et al.*¹¹ have recently begun a study of the rare-

⁵ B. R. Judd, Proc. Roy. Soc. (London) **232**, 458 (1955).

⁶ F. Spedding, S. Legvold, J. Doane, and L. Jennings, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 368.

⁷ J. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, J. Appl. Phys. **32**, 49S (1961); W. C. Koehler, *ibid.* **32**, 20S (1961); M. K. Wilkinson, W. C. Koehler, E. O. Wollan, and J. W. Cable, *ibid.* **32**, 48S (1961); W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, *ibid.* **33**, 1124 (1962); J. Phys. Soc. Japan **17**, Suppl. B III, **32** (1962), Proceedings of Third International Conference on Magnetism and Crystallography, 1961 (unpublished); M. K. Wilkinson, H. R. Child, W. C. Koehler, J. W. Cable and E. O. Wollan, J. Phys. Soc. Japan **17**, Suppl. B III, **27** (1962), Proceedings of Third International Conference on Magnetism and Crystallography, 1961 (unpublished); W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **126**, 1672 (1962); J. W. Cable, H. R. Child, W. C. Koehler, M. K. Wilkinson and E. O. Wollan, "Neutron-Diffraction Studies of Rare-Earth Metals and Compounds," reprinted from *Pile Neutron Research in Physics*, International Atomic Energy Agency, (Vienna, 1962), pp. 379-390.

⁸ R. J. Elliot, Phys. Rev. **24**, 346 (1961).

⁹ T. A. Kaplan, Phys. Rev. **124**, 329 (1961).

¹⁰ H. Miwa and K. Yosida, Prog. Theoret. Phys. (Kyoto) **26**, 693 (1961).

¹¹ H. R. Child, M. K. Wilkinson, J. W. Cable, W. C. Koehler, and E. O. Wollan, preceding paper, Phys. Rev. **131**, 922 (1963).

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† This work was begun and much of it performed while the author was employed at the Oak Ridge National Laboratory.

¹ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), Chap. IX.

² R. J. Elliot and K. W. H. Stevens, Proc. Phys. Soc. (London) **A64**, 205 (1951); Proc. Roy. Soc. (London) **218**, 553 (1953); **219**, 387 (1953).

³ B. Bleaney and H. E. D. Scovil, Proc. Phys. Soc. (London) **A63**, 1369 (1951); **64**, 204 (1951).

⁴ Further references to and a summary of the theoretical and experimental results may be found in W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2, Sec. 20.

earth intermetallic compounds (anion in the nitrogen column) by neutron diffraction methods. While not so bizarre as the metals, these compounds also exhibit interesting magnetic behavior,¹¹ which it is our purpose to try to elucidate.

Unlike the metals, the ordered component of the magnetic moments of the rare-earth ions in these materials was found to be considerably smaller than the maximum free-ion value, while the total moment was the same (to within a few percent) as that appropriate to the free ion. The critical ordering temperatures are a few tens of degrees Kelvin. On the other hand, it is known, from crude theoretical estimates and from the properties of rare-earth ions in similar materials, that the crystalline fields will remove the spatial orientation degeneracy of the $4f$ shell by introducing an over-all splitting of order of 100 cm^{-1} (except for the nearly spherical Gd^{3+} ion, of course). The strong crystalline torques, then, inhibit the full alignment of the moments in the ground state, accounting for the observations. In the case of TmN the crystalline splittings are sufficiently large relative to the exchange energy to lead to the theoretical prediction that it will not exhibit long-range order at all, and no ordering has been found down to 1.4°K .

While the "strong" crystalline torques complicate the theoretical analysis, their interplay with the weak exchange torques lead to some interesting effects.

In Sec. II the basic assumptions and formulas are stated and a discussion of their consequences given. Section III contains a semiclassical discussion of crystal-field effects. Section IV contains the eigenfunctions and eigenvalues of second-half rare ions in fields of cubic symmetry. In Sec. V a discussion of the crystalline ground state with exchange and crystalline fields effects included is given. In Sec. VI the theory of Sec. V is applied to the rare-earth phosphides. Then, in Sec. VII, we consider the effects of magnetic dipole and electric quadrupole and the possible indication of a noncubic distortion which might severely modify the K_6/K_4 estimate made in Sec. VI.

II. BASIC FACTS AND ASSUMPTIONS

The neutron diffraction results¹¹ are on the second-half (more than half-filled $4f$ shell) rare-earth compounds. We assume the $4f$ shell configuration is that of the free 3^+ ion and that the $4f$ electrons are coupled in the Russell-Saunders manner and are in the Hund ground state. That is, the total orbital angular momentum (L), the total spin angular momentum (S), and the total angular momentum (J) are good quantum numbers; S is the maximum possible, L is the maximum possible consistent with this S , and $J=L+S$ (for second-half rare earths). Van Vleck,¹ Elliot and Stevens,² and Low,⁴ may be consulted for data and arguments attesting to the accuracy of these assumptions. In short, this assignment leads to values of the magnetic moments

within a few percent of the measured values, and values of the various electric moments probably⁶ not more than 10% in error.

With a somewhat larger error, we shall assume that the effective exchange interaction between two rare-earth ions is isotropic. The direct-exchange energy resulting from the direct overlap of the $4f$ shells of neighboring rare-earth ions may be estimated to be less than 1 cm^{-1} if the separation distance is greater than $3A^\circ$.¹² The principle exchange interaction is then via the outer electrons. The isotropic exchange could be justified if the interaction is via the $6s$ electrons, but the exchange via $5d$ and $6p$ electrons will result in an anisotropic exchange contribution. Liu¹³ has considered this effect but has made no quantitative estimates. In any case, the major source of anisotropy in the intermetallics are the spin-independent crystalline fields. A possible indication of a nonisotropic exchange term is discussed in Sec. VII.

The exchange energy between electrons in the $4f$ shells of different rare-earth atoms may, in principle, be calculated in second-order perturbation theory, and the result be represented in the Dirac-Van Vleck^{14,15} manner as a dot product between the spin vectors of the electrons occupying the $4f$ orbitals in the two rare-earth atoms. The energy of the collection of rare-earth atoms in the crystal may then be represented by

$$H = \sum_i V_{ei} - \frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \dots, \quad (1)$$

where V_{ei} is that part of the energy of the rare-earth atom " i " which does not depend on the spin directions of the other rare earths. The second term in Eq. (1) represents the isotropic part of the exchange interaction, and the dots indicate the nonisotropic exchange terms, the magnetic dipole, electric quadrupole, etc., interactions between the rare-earth atoms.

The rare-earth intermetallic compounds have a cubic rock salt structure. An x-ray analysis of¹¹ HoN showed that any noncubic distortion was less than about 2×10^{-4} . According to Sec. VII Eq. (56), such a distortion would introduce only about 1% correction to the crystalline potential energy, V_c , and could then be neglected. One might expect similarly small distortions in the other intermetallics, however, a close analysis of the diffraction data¹¹ has given an indication of the existence of perhaps a 20% noncubic component in the V_c of HoP (Sec. VII). A recomputation of the phosphides along the lines of Sec. VI, but including V_2 , is now underway. The dominant crystal field terms in any case are those showing cubic point symmetry and in this paper we neglect the noncubic terms.

With these assumptions and dropping the spherically

¹² This was estimated using the Hartree-Fock results of Freeman and Watson (Ref. 20).

¹³ S. H. Liu, Phys. Rev. **121**, 451 (1961).

¹⁴ P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, New York, 1947), 3rd ed., Chap. IX.

¹⁵ J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

symmetric part of V_c we have

$$V_c = V_4 + V_6 + \dots, \quad (2)$$

where

$$\begin{aligned} V_4 &= (8/35) \sum v_4(r) [P_4(z/r) + P_4(x/r) + P_4(y/r)] \\ &= \sum v_4(r) r^{-4} [x^4 + y^4 + z^4 - \frac{3}{2}r^4] \\ &= \sum v_4(r) r^{-4} \{ (1/20)(35z^4 - 30z^2r^2 + 3r^4) \\ &\quad + \frac{1}{8}[(x+iy)^4 + (x-iy)^4] \}, \quad (3) \end{aligned}$$

and

$$\begin{aligned} V_6 &= (16/21) \sum v_6(r) [P_6(z/r) + P_6(x/r) + P_6(y/r)] \\ &= \sum v_6(r) r^{-6} [11(x^6 + y^6 + z^6) - 15(x^4 + y^4 + z^4)r^2 \\ &\quad + (30/7)r^6] \\ &= \frac{3}{8} \sum v_6(r) r^{-6} \{ [11z^6 - 15z^4r^2 + 5z^2r^4 - (5/21)r^6] \\ &\quad - \frac{1}{2}(x+iy)^4(11z^2 - r^2) - \frac{1}{2}(11z^2 - r^2)(x-iy)^4 \}. \quad (4) \end{aligned}$$

In Eq. (2) the potential energy of the charge distribution in the crystal field is expanded in the multipole expansion, account being taken of the cubic point symmetry of the rare-earth sites, and in Eqs. (3) and (4) we give V_4 and V_6 in terms of sums over the coordinates (x, y, z) of the $4f$ electrons of a given rare-earth atom, the P 's are Legendre polynomials. Charge distributions of f electrons have no electric multipole moments higher than 2^6 pole.²

The matrix elements of the right-hand side of Eq. (1) (among states of good J), according to the Wigner-Eckart theorem, are the same as those of^{2,16}

$$H = \sum_i \mathcal{U}_{ci} - \frac{1}{2} \sum_{i,j} \mathcal{G}_{ij} \mathbf{J}_i \cdot \mathbf{J}_j, \quad (5)$$

where

$$\mathcal{U}_c = \mathcal{U}_4 + \mathcal{U}_6, \quad (6)$$

with

$$\begin{aligned} \mathcal{U}_4 &= (8/35) K_4 [\mathcal{O}_4(J_z) + \mathcal{O}_4(J_x) + \mathcal{O}_4(J_y)] \div \mathcal{O}_4(J) \\ &= K_4 [J_z^4 + J_y^4 + J_x^4 \\ &\quad - \frac{1}{5}J(J+1)(3J^2 + 3J - 1)] \div \mathcal{O}_4(J) \\ &= K_4 \{ (1/20)[35J_z^4 - 30J(J+1)J_z^2 \dots] \\ &\quad + \frac{1}{8}(J_+^4 + J_-^4) \} \div \mathcal{O}_4(J), \quad (3') \end{aligned}$$

$$\begin{aligned} \mathcal{U}_6 &= (16/21) K_6 [\mathcal{O}_6(J_z) + \mathcal{O}_6(J_x) + \mathcal{O}_6(J_y)] \div \mathcal{O}_6(J) \\ &= K_6 [11(J_x^6 + J_y^6 + J_z^6) \\ &\quad - 15J(J+1)(J_x^4 + J_y^4 + J_z^4) \dots] \div \mathcal{O}_6(J) \\ &= (3/8) K_6 \{ [11J_z^6 - 15J(J+1)J_z^4 \dots] \\ &\quad - \frac{1}{2}J_+^4 [11J_z(J_z+4) + 50 - J(J+1)] \\ &\quad - \frac{1}{2} [11J_z(J_z+4) + 50 - J(J+1)] J_-^4 \} \div \mathcal{O}_6(J), \quad (4') \end{aligned}$$

where

$$K_4 = \langle v_4(r) \rangle \langle \sum P_4(z/r) \rangle_J, \quad (7)$$

$$K_6 = \langle v_6(r) \rangle \langle \sum P_6(z/r) \rangle_J, \quad (8)$$

and the expectation values refer to the $4f$ shell electrons in the state with $M_J = J$. The multipole moments, $\langle \sum P_i(z/r) \rangle_J$, may be obtained from the β and γ

coefficients of Stevens¹⁶ by using

$$\begin{aligned} \langle \sum P_4(z/r) \rangle_J &= \beta \mathcal{O}_4(J), \\ \langle \sum P_6(z/r) \rangle_J &= \gamma \mathcal{O}_6(J). \end{aligned} \quad (9)$$

The \mathcal{O} 's are the operator equivalents of the Legendre polynomials which are given by Stevens.¹⁶ (The terms in Eqs. (3') and (4') which are indicated by dots, for brevity, are easily filled in by comparing with Stevens' operator equivalents expressions.) The values of β , γ , $\mathcal{O}_4(M)$, $\mathcal{O}_6(M)$ are given by Stevens for all of the rare earths. Finally, in Eq. (5), $\mathcal{G}_{ij} = (g-1)^2 \mathcal{G}_{ij}'$, where g is the Landé g factor. For the second-half rare earths $(g-1) = S/J$.

It is useful to make some preliminary comments concerning the magnetic behavior of these materials. If the exchange forces tending to align the spins of neighboring ions are, at first, neglected, then the $(2J+1)$ degenerate free-ion states are split by V_c into various states which form bases of the irreducible representations of the cubic rotation group¹⁷ (with an expected over-all splitting of the order of 100 cm^{-1}). These states are usually not eigenfunctions of any component of \mathbf{J} , of course; so to form the state, for example, having the component, J , along some direction would generally require a superposition of states from several of the cubic symmetry types with concomitant energy spread of the order of 100 cm^{-1} . Exchange energies of only a few tens of wave numbers will generally cause a mixture of just a few low-lying cubic symmetry types which will lead to ground-state ordered moment values less than J . Of course, it must not be concluded that if the exchange energy is much less than the over-all crystalline splitting then the ground-state ordered moment will be *much* less than J . The classical effect of the crystal field is to yield certain directions of minimum potential energy along which \mathbf{J} may have a time-average value equal to J ; it is a quantum-mechanical effect due to the finite size of J and quantum-mechanical tunneling which reduces this value along the "easy" directions. It is only in the off-"easy" directions where the crystalline potential energy and torques are large that it necessarily requires large exchange fields to attain time-average moment values near J .

If the ordered moment, induced by exchange energies which are small compared to the over-all crystal splitting, is near J , then one may be sure that the material is very anisotropic; i.e., the exchange energy required to obtain the same ordered moment in off-easy directions would have to be of the order of the total crystalline splitting. (This follows from the fact that the expected value of the anisotropy energy for a state having a definite component of angular momentum along some direction when averaged over all directions is the average crystalline-field splitting). For the large ordered moment cases (large anisotropy), then, the

¹⁶ K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

¹⁷ The classic paper on the splitting of atomic levels in crystals is H. A. Bethe, Ann. Physik **3**, 133 (1929).

magnetic domain boundaries are expected to be sharp, the moment switching abruptly from one easy direction to another. The anisotropy may be small, on the other hand, if the ordered moment is considerably less than J , as we shall discuss more fully in Sec. V.

For rare earths with an odd number of $4f$ electrons the ground state in the crystalline field will be either doubly or quadruply degenerate,¹⁷ and there will be a magnetically ordered ground state.

If the $4f$ shell contains an even number of electrons, then the stationary states in the cubically symmetrical crystal field are of the cubic symmetry types $\Gamma_1, \dots, \Gamma_5$ in Bethe's notation,¹⁷ the first two types being singlets, the third a doublet, and the last two triplets. If the ground state is of the type Γ_4 or Γ_5 , then exchange coupling will give a magnetically ordered ground state for the crystal as a whole. If the ground state is of type Γ_1, Γ_2 , or Γ_3 , on the other hand, one may or may not get ordering under the exchange forces, depending, of course, on their strengths relative to the crystalline splittings. As an example (see below), in the nitrides both Tb^{3+} and Tm^{3+} have crystalline ground states of type Γ_1 , extrapolating the crystal field and exchange parameters which give the observed moment for Tb to Tm, one finds, as mentioned earlier, that TmN should not be expected to exhibit long range magnetic order.

As final general comments on the effects of strong crystal fields one may notice that if a given ion has an expected moment $\langle \mathbf{J} \rangle$ in the ground state, then it has a mean-square fluctuating moment $J(J+1) - \langle \mathbf{J} \rangle \cdot \langle \mathbf{J} \rangle$. Exchange forces will cause a partial correlation in the fluctuating moments of neighbors, and in the ground state there will be a short-range moment correlation superposed on the long-range order.

The final generality, spin waves in these substances are peculiar. If one considers the stationary states of a given ion in the crystalline field and the average exchange field of its neighbors, then several of the excited states will have matrix elements of \mathbf{J} to the ground state, and there will be several spin-wave modes. Further, there will be modes of oscillation of the moment of a given ion involving the oscillation of a single component of \mathbf{J} , for example, the component parallel to $\langle \mathbf{J} \rangle$; when these oscillating moments from the various ions are coupled together the result is the same as for spring-coupled linear oscillators: ferromagnetic spin waves with frequencies proportional to the wave number rather than to its square.¹⁸

III. SEMICLASSICAL DISCUSSION OF THE CRYSTAL FIELD

It is, first of all, necessary to get an idea of the relative sizes and signs of the multipole moments of the second-

¹⁸ This peculiar effect of anisotropy has been recently pointed out by Kaplan (Ref. 9), by G. Trammell, Suppl. J. Appl. Phys. **31S**, 362S (1960), and in an unpublished summary and amplification of the material covered in the talk from which the present paper is largely taken.

TABLE I. Electric multipole moments of the second-half earths. The P 's are Legendre polynomials, the sum is over the $4f$ electrons, and the expected value is for the state indicated with $J_z=J$.

		$\langle \Sigma P_2(\theta) \rangle_J$	$\langle \Sigma P_4(\theta) \rangle_J$	$\langle \Sigma P_6(\theta) \rangle_J$
$\text{Tb}^{3+}(4f)^8$	7F_6	-1/3	1/11	-5/429
$\text{Dy}^{3+}(4f)^9$	${}^6H_{15/2}$	-1/3	-4/33	25/429
$\text{Ho}^{3+}(4f)^{10}$	6I_8	-2/15	-1/11	-50/429
$\text{Er}^{3+}(4f)^{11}$	${}^4I_{15/2}$	2/15	1/11	50/429
$\text{Tm}^{3+}(4f)^{12}$	3H_6	1/3	+4/33	-25/429
$\text{Yb}^{3+}(4f)^{13}$	${}^2F_{7/2}$	1/3	-1/11	5/429

half rare earths. These may be obtained from the tables of Stevens.¹⁶ We give the indicated quantities in Table I and shall often call them for short the quadrupole, hexadecapole, and the 2^6 -pole moments (the moments are actually $\langle r^l \rangle$ times the tabulated quantities). We note that the moments are antisymmetric about the $10\frac{1}{2}$ electron ($3\frac{1}{2}$ hole) position. The hexadecapole moment shows only a 30% variation (however, $\langle r^4 \rangle$ will exhibit a systematic decrease down the table) in magnitude, while the 2^6 -pole moment of Tb^{3+} is a factor of 10 smaller than that of Ho^{3+} and Er^{3+} . The quadrupole moment is actually irrelevant in pure cubic fields.

We now imagine that \mathbf{J} is a classical vector and consider the dependence of \mathcal{U}_c as given by Eqs. (6), (3'), and (4'), on the direction of \mathbf{J} . Actually the direction of \mathbf{J} may be fixed at best to within $\theta = \tan^{-1}(J^{-1/2})$, of course. For Ho^{3+} and Tb^{3+} we have $\theta = 20^\circ$ and 22° , respectively, showing that the directional uncertainties are not negligible even for these large J 's. To take this indeterminacy partially into account, we take as the classical analog of the potential energy for \mathbf{J} pointing in a certain direction the expected value of the potential energy for the state of maximum component of \mathbf{J} along that direction. Making use of the addition theorem for the P 's we have from Eqs. (6), (3'), and (4')

$$\begin{aligned} \langle \mathcal{U}_c \rangle &= K_4(x^4 + y^4 + z^4 - \frac{2}{3}) \\ &\quad + K_6[11(x^6 + y^6 + z^6) - 15(x^4 + y^4 + z^4) + 30/7], \\ &= \langle \mathcal{U}_4 \rangle + \langle \mathcal{U}_6 \rangle, \end{aligned} \quad (10)$$

where K_4 and K_6 are given in Eqs. (7) and (8), and $\langle \mathcal{U}_c \rangle$ is the expected value of \mathcal{U}_c for the state of maximum $xJ_x + yJ_y + zJ_z$, with $x^2 + y^2 + z^2 = 1$.

The values of Eq. (10) in the [100], [111], and [110] directions are

$$\begin{aligned} \langle \mathcal{U}_c \rangle_{100} &= (2/5)K_4 + (2/7)K_6, \\ \langle \mathcal{U}_c \rangle_{111} &= -(4/15)K_4 + (32/63)K_6, \\ \langle \mathcal{U}_c \rangle_{110} &= -(1/10)K_4 - (13/28)K_6. \end{aligned} \quad (11)$$

The maxima and minima of $\langle \mathcal{U}_c \rangle$ are always in one of these directions. {The values of $\langle \mathcal{U}_c \rangle$ in the direction $[\alpha\beta\gamma]$ is the same as in the direction $[|\alpha'|\beta'|\gamma'|]$, where $[\alpha'\beta'\gamma']$ is a permutation of $[\alpha\beta\gamma]$.} From Eqs. (10) and (11) we see that $\langle \mathcal{U}_4 \rangle / K_4$ has a peak at [100], a bottom at [111], and a pass at [110]. $\langle \mathcal{U}_6 \rangle / K_6$ has a peak at [111] and a bottom at [110].

It is now convenient to make an estimate of the magnitudes of K_4 and K_6 . $\langle \sum P_4 \rangle_J$ and $\langle \sum P_6 \rangle_J$ are given in Table I. We make the rough approximation that the crystalline potential is that due to six ($-q$) point charges situated at the nearest anion positions to a given rare-earth ion, we then obtain

$$\begin{aligned}\langle v_4(r) \rangle &= (q/3)(105e^2/4a^5)\langle r^4 \rangle, \\ \langle v_6(r) \rangle &= (q/3)(63e^2/8a^7)\langle r^6 \rangle,\end{aligned}\quad (12)$$

where e is the electronic charge, a is one-half the lattice spacing, and the expected values are for a $4f$ electron of the rare earth considered. It was found¹⁹ that a moderately good fit to the neutron form factor of Er^{3+} could be obtained by using hydrogenic wave functions for the $4f$ electrons with an effective charge $Z-S=23$. This gives $\langle r^4 \rangle = 0.7a_0^4$, $\langle r^6 \rangle = 0.9a_0^6$, where a_0 is the Bohr radius.

Freeman and Watson²⁰ have recently determined the Hartree-Fock wave functions for the various rare earths. Their results for Er^{3+} are $\langle r^4 \rangle_{\text{Er}} = 1.1a_0^4$, $\langle r^6 \rangle_{\text{Er}} = 4.0a_0^6$, as is to be expected the hydrogenic wave functions underestimate $\langle r^6 \rangle / \langle r^4 \rangle$ ratios. Although, according to Blume, Freeman, and Watson²¹ there still seems to be about a 10% discrepancy in the "size" of the $4f$ shell as given by their calculation and that given by the neutron diffraction results of Koehler and Wollan, on the oxides of Nd and Ho, indicating a possible expansion of the $4f$ shell in the crystal, their results are sufficiently accurate for our purposes. Interpolating in Table VII of Ref. 20, we obtain $\langle r^4 \rangle_{\text{Tb}} = 1.4a_0^4$, $\langle r^6 \rangle_{\text{Tb}} = 5.6a_0^6$; $\langle r^4 \rangle_{\text{Ho}} = 1.2a_0^4$, $\langle r^6 \rangle_{\text{Ho}} = 4.5a_0^6$.

Taking $a = 2.8A^\circ$ for ErP (and neglecting the variation of a) and substituting Freeman and Watson's values of $\langle r^4 \rangle$ and $\langle r^6 \rangle$ into Eq. (12), we obtain

$$\begin{aligned}\langle v_4(r) \rangle &= 1.9 \times 10^8 (q/3) \text{ cm}^{-1} (\text{TbP}) \\ &= 1.6 \times 10^8 (q/3) \text{ cm}^{-1} (\text{HoP}) \\ &= 1.5 \times 10^8 (q/3) \text{ cm}^{-1} (\text{ErP}), \\ \langle v_6(r) \rangle &= 73 (q/3) \text{ cm}^{-1} (\text{TbP}) \\ &= 59 (q/3) \text{ cm}^{-1} (\text{HoP}) \\ &= 52 (q/3) \text{ cm}^{-1} (\text{ErP}).\end{aligned}\quad (13)$$

K_4 and K_6 may now be estimated from Eqs. (7), (8), (13), and the values of the multipole moments given in Table I.

If the values so obtained are now substituted into Eq. (11), then it is seen that the V_6 terms are at least an order of magnitude smaller than the V_4 terms in the three principle directions indicated. In Sec. VI, however, we shall present evidence indicating that Eq. (13) severely underestimates the value of $\langle v_6(r) \rangle$ relative to

that of $\langle v_4(r) \rangle$,²³ and so it is desirable to have the positions of the peaks and bottoms of $\langle v_c \rangle$ for all ratios of K_6/K_4 .

From Eq. (11) we obtain that if (a) $K_4 > 0$, $K_6 > 0$, then the peak is at $[100]$ if $|K_6| < 3|K_4|$, otherwise it is at $[111]$, the bottom is at $[111]$ if $|K_6| < 6/35|K_4|$, otherwise it is at $[110]$; (b) $K_4 > 0$, $K_6 < 0$, then the peak is at $[100]$ if $|K_6| < \frac{2}{3}|K_4|$, otherwise it is at $[110]$, the bottom is at $[111]$. If $K_4 < 0$, $K_6 < 0$, or $K_4 < 0$, $K_6 > 0$ we interchange peaks and bottoms in (a) or (b), respectively.

The positions of the extremas of $\langle \mathcal{U}_c \rangle$ may be more succinctly expressed by rewriting Eq. (10) in the form

$$\langle \mathcal{U}_c \rangle = a_4(x^4 + y^4 + z^4) + a_6(x^6 + y^6 + z^6) + a_0. \quad (10')$$

If $a_4 > 0$, $a_6 > 0$, $[100]$ is a peak, $[111]$ is a bottom, and $[110]$ is a pass, there are no other extrema. If $a_4 < 0$, $a_6 < 0$, the peaks and bottoms are interchanged. If we define $|a_4/a_6| \equiv \zeta$, then if $a_4 > 0$, $a_6 < 0$, the peaks, bottoms, and passes are given in Table II. If $a_4 < 0$, $a_6 > 0$, the peaks and bottoms of Table II are interchanged.

The bottoms of the $\langle \mathcal{U}_c \rangle$ plot are the easy directions of magnetization for the case of very large exchange forces acting on the rare-earth atoms, and we expect them to usually be the easy directions (directions of maximum susceptibility) in the weak-exchange force case.

Classically, \mathbf{J} would move along the equipotentials of $\langle \mathcal{U}_c \rangle$, precessing clockwise around the bottoms or counterclockwise around the peaks. Very near a peak or bottom the equipotentials are circles which become progressively distorted as one moves away from the peak or bottom, the distortion exhibiting the rotational symmetry of the peak or bottom to which the contour belongs.

We may now draw some conclusions concerning the quantum states in the semiclassical case. Consider one of the peaks or bottoms of $\langle \mathcal{U}_c \rangle$, call this direction Z' . Now let J be very large. Then, for large $J_{Z'}$ the stationary states will be states of pretty good $J_{Z'}$ [if for

TABLE II. The position of the peaks (P or p) bottoms (B or b), and passes (s) of the right-hand side of Eq. (9') for $a_4 > 0$, $a_6 < 0$, and $|a_4/a_6| = \zeta$. The highest peaks and lowest bottoms are indicated by capital letters. $[1\alpha\alpha]$ and $[11\beta]$ are itinerant passes, α going from zero to one as ζ goes from $3/2$ to 1 , and β going from 1 to 0 as ζ goes from 1 to $3/4$.

	[100]	[110]	[111]	[1 $\alpha\alpha$]	[11 β]
$\zeta > 3/2$	P	s	B		
$4/3 < \zeta < 3/2$	b	P	B	s	
$1 < \zeta < 4/3$	B	P	b	s	
$5/6 < \zeta < 1$	B	p	P		s
$3/4 < \zeta < 5/6$	B	p	P		s
$0 < \zeta < 3/4$	B	s	P		

¹⁹ G. T. Trammell, Phys. Rev. **92**, 1387 (1953).

²⁰ A. J. Freeman and R. E. Watson, Materials Research Laboratory Report No. 118, Ordnance Materials Research Office, Watertown Arsenal, Watertown, Massachusetts, 1962 (unpublished).

²¹ M. Blume, A. J. Freeman, and R. E. Watson (to be published).

²² W. C. Koehler and E. O. Wollan, Phys. Rev. **92**, 1380 (1953).

²³ This is with the assumption of negligible noncubic distortion; see Sec. VII.

angles $\theta < \delta$ the distortion of the equipotentials from circles is negligible, then for $(J - J_{z'})/J < (\delta^2/2)$ we may neglect the admixture of different $J_{z'}$ states], with spacings about equal to the classical precession rate, $(\partial \langle \mathcal{U}_e \rangle / \partial \theta) \div J\theta$. As $(J - J_{z'})/J$ increases into the region of appreciable distortion $J_{z'}$ ceases to be stationary, an appreciable admixture of $J_{z'} \pm p, J_{z'} \pm 2p$, etc., resulting where p is the symmetry index of Z' ($p=4$ for [100], etc.). In the region where the classical equipotentials from different bottoms or peaks join, these considerations become useless. Returning to the very low (or very high) states with $J_{z'} \doteq J$ these are still not stationary, in first-order perturbation theory there will be mixed into them the states of $J_{z'} \pm p$, however, more importantly they are not correct zero-order states because the similar states built around the directions Z'' (into which Z' is carried under the operations of the cubic group) are degenerate with them. The zero-order states are linear combinations of these similar states belonging to the different directions Z', Z'', \dots (in fact, they are basis functions of the irreducible representations of the group) with splittings proportional to overlap integrals (of the nondiagonal-in- $J_{z'}$ part of \mathcal{U}_e) of the similar states belonging to Z', Z'', \dots . Speaking roughly, a very low (or high) lying state (actually at least two states to make up the wave packet) would precess "rapidly" in a circle about a direction Z' , but after a while it would have "jumped" to the neighborhood of $Z'' \dots$. The jumping rate vanishes relative to the precession rate as J becomes very large, and, other things being equal, the jumping rate, if $Z' = [100]$, is less than that if $Z' = [111]$, which is less than that if $Z' = [110]$ because of the increasing overlaps. For very large J the over-all splitting may be obtained from Eq. (11), the low- and high-lying states may be grouped into multiplets with the degeneracies of the peaks or bottoms to which they belong. The spacing between multiplets decreases roughly as $1/J$ as J becomes large, the intramultiplet splitting for the very high and very low lying states decrease exponentially with J .

In this limit then, exchange energies only of the order of the intramultiplet splitting are sufficient to attain a ground state with $J_{z'} = J$ if the exchange field is applied in the easy direction, whereas exchange energies of the order of the over-all splitting are necessary to attain $J_{z'} \doteq J$ in off-easy directions.

These semiclassical considerations have only a heuristic value for the ions dealt with in practice ($J \leq 8$) and it is unprofitable to elaborate this picture further. We shall find these considerations of some aid in understanding the results of our quantum-mechanical calculations in the succeeding sections.

IV. THE CRYSTALLINE SPLITTINGS

In this section we give the eigenfunctions and eigenvalues of \mathcal{U}_6 [Eqs. (6), (7), and (8)] for the second-half rare earths. The notations and methods are explained

TABLE III. Tb^{3+} and Tm^{3+} . a 's and b 's [Eq. (14)] for the states of Eq. (15).

	(5/2) a	(7/2) b
$(\gamma^1, v_e \gamma^1)$	-14/11	8/11
$(\gamma^2, v_e \gamma^2)$	22/33	8
$(\gamma^3, v_e \gamma^3)$	38/33	-24/11
$(\gamma^4, v_e \gamma^4)$	-32/33	4/11
$(\gamma^5(6), v_e \gamma^5(6))$	1	1
$(\gamma^5(2), v_e \gamma^5(2))$	-59/99	-32/11
$(\gamma^5(2), v_e \gamma^5(6))$	(5/99) $^{1/2}$	-7(5/11) $^{1/2}$

in a previous paper²⁴ along with references to earlier work. Of this earlier work, only that of Ebena and Tsuya²⁵ gives the eigenfunctions and eigenvalues of rare-earth ions, in general, cubically symmetric potentials. We give our results because it is desirable to have an independent check of these complicated computations²⁶; but more importantly, it is not easy to transcribe their representations of the eigenfunctions into that which we have used for all of our computations and discussions.

The eigenfunctions of \mathcal{U}_6 are cubic symmetry functions. The number of times each cubic symmetry type is represented in the $(2J+1)$ states of given J is obtained by reduction of the character and is given by Bethe¹⁷ (or Table IV of Ref. 24). We give only one member of each symmetry type occurring in the reduction, the other members may be obtained from Tables I or III of Ref. 24. In Tables III to VI we give the non-vanishing matrix elements of \mathcal{U}_6 among the symmetry functions. If a symmetry type appears in the reduction only once, this gives the eigenvalue directly. If a symmetry type appears M times, one must diagonalize the $M \times M$ matrix to get the eigenvalues (and eigenfunctions). We don't perform this diagonalization since it would complicate the tables. Except for Er^{3+} and Dy^{3+}

TABLE IV. Ho^{3+} . a 's and b 's [Eq. (14)] for the states of Eq. (16).

	(5/2) a	(7/2) b
$(\gamma^1, v_e \gamma^1)$	14/13	-8/13
$(\gamma^3(6), v_e \gamma^3(6))$	-3/4	-3/4
$(\gamma^3(2), v_e \gamma^3(2))$	47/52	127/52
$(\gamma^3(6), v_e \gamma^3(2))$	(1/4)(165/91) $^{1/2}$	-(11/4)(105/143) $^{1/2}$
$(\gamma^4(8), v_e \gamma^4(8))$	1	1
$(\gamma^4(4), v_e \gamma^4(4))$	-6/13	16/13
$(\gamma^4(8), v_e \gamma^4(4))$	(1/2)(5/91) $^{1/2}$	-(3/2)(35/13) $^{1/2}$
$(\gamma^5(6), v_e \gamma^5(6))$	-3/4	-3/4
$(\gamma^5(2), v_e \gamma^5(2))$	-1/4	-125/52
$(\gamma^5(6), v_e \gamma^5(2))$	(1/4)(165/91) $^{1/2}$	-(11/4)(105/143) $^{1/2}$

²⁴ G. T. Trammell, J. Math. Phys. 4, 431 (1963).

²⁵ Y. Ebena and N. Tsuya, Sci. Rep. Res. Inst. Tohoku Univ. Ser. B 12, Nos. 1, 3, and 4 (1960).

²⁶ Our computation, which was carried out before we were aware of Ebena and Tsuya's, was found to contain a few errors when we compared with their results.

TABLE V. Er^{3+} , Dy^{3+} . a 's and b 's [Eq. (14)] for the states of Eqs. (17) and (19).

	(5/2) a	(7/2) b
$(\gamma^6, v_c \gamma^6)$	1.08	-0.615
$(\gamma^7, v_c \gamma^7)$	-0.095	-4.80
$(u_1, v_c u_1)$	0.961	1.82
$(u_2, v_c u_2)$	-0.904	0.120
$(u_3, v_c u_3)$	-0.546	0.753
$(u_1, v_c u_2)$	0.10	-2.10
$(u_1, v_c u_3)$	0.11	-2.38
$(u_2, v_c u_3)$	0.14	-0.58

there are only the trivial 2×2 matrices to diagonalize, for Er^{3+} and Dy^{3+} there is a 3×3 matrix.

We write

$$(u, \mathcal{U}_c v) = aK_4 + bK_6, \quad (14)$$

where K_4 and K_6 are given in Eqs. (7) and (8). We give the a 's and b 's in Tables III to VI.

We conclude this section by a brief discussion of the results along the lines of the preceding section.

Tb^{3+} and Tm^{3+} . $J=6$. $13 \rightarrow \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$.

The symmetry functions may be taken,

$$\begin{aligned} \gamma^1 &= (2^{3/2}/3)(O_x + O_y + O_z), \\ \gamma^2 &= [4/3(10)^{1/2}](6_z + 6_{-z} - 6_x - 6_{-x} + 6_y + 6_{-y}), \\ \gamma^3 &= [4/(66)^{1/2}](6_z + 6_{-z} - 6_y - 6_{-y}), \\ \gamma^4 &= 2^{-1/2}(4_z - 4_{-z}), \\ \gamma_1^5(6) &= 2^{-1/2}(6_z - 6_{-z}), \\ \gamma_1^5(2) &= 2^{-1/2}(2_z - 2_{-z}). \end{aligned} \quad (15)$$

The a 's and b 's are given in Table III.

Ho^{3+} . $J=8$. $17 \rightarrow \Gamma_1 + 2\Gamma_3 + 2\Gamma_4 + 2\Gamma_5$. We may take as symmetry functions

$$\begin{aligned} \gamma' &= 6^{-1/2}(64/65)^{1/2}(8_z + 8_{-z} + 8_x + 8_{-x} + 8_y + 8_{-y}), \\ \gamma_1^3(6) &= 6^{-1/2}(6_z + 6_{-z} + 6_y + 6_{-y}), \\ \gamma_1^3(2) &= 6^{-1/2}(2_x + 2_{-x} + 2_y + 2_{-y}), \\ \gamma_1^4(8) &= 2^{-1/2}(8_z - 8_{-z}), \\ \gamma_1^4(4) &= 2^{-1/2}(4_z - 4_{-z}), \\ \gamma_1^5(6) &= 2^{-1/2}(6_z - 6_{-z}), \\ \gamma_1^5(2) &= 2^{-1/2}(2_z - 2_{-z}). \end{aligned} \quad (16)$$

The a 's and b 's are given in Table IV.

Rather than the mathematically convenient γ^3 func-

TABLE VI. Yb^{3+} . a 's and b 's [Eq. (14)] for the states of Eq. (20).

	(5/2) a	(7/2) b
$(\gamma^6, v_c \gamma^6)$	2	-20
$(\gamma^7, v_c \gamma^7)$	-18/7	-12
$(\gamma^8, v_c \gamma^8)$	2/7	+16

tions given in Eq. (16), there is a physical significance in introducing a γ^3 function based on the 8_i functions. We have

$$\gamma_1^3(8) = (128/127 \times 3)^{1/2} \times [8_z + 8_{-z} - \frac{1}{2}(8_x + 8_{-x} + 8_y + 8_{-y})], \quad (17)$$

and from Table V and Eq. (5) of Ref. 24 for the d matrix,²⁷ we obtain

$$\begin{aligned} \gamma_1^3(8) &= (1/32)(128/127)^{1/2} \\ &\quad \times [(15)^{1/2}\gamma_1^3(6) + (1001)^{1/2}\gamma_1^3(2)], \quad (18) \\ \bar{\gamma}_1^3(8) &= (1/32)(128/127)^{1/2} \\ &\quad \times [(1001)^{1/2}\gamma_1^3(6) - (15)^{1/2}\gamma_1^3(2)], \end{aligned}$$

where $\bar{\gamma}_1^3$ is the γ_1^3 function orthogonal to $\gamma_1^3(8)$. For the matrix elements we have

$$\begin{aligned} [\gamma_1^3(8), \mathcal{U}_c \gamma_1^3(8)] &= (8 \times 127)^{-1} [15\mathcal{U}_{66} + 1001\mathcal{U}_{22} \\ &\quad + 2(15 \times 1001)^{1/2}\mathcal{U}_{62}], \\ (\bar{\gamma}_1^3, \mathcal{U}_c \bar{\gamma}_1^3) &= (8 \times 127)^{-1} [1001\mathcal{U}_{66} + 15\mathcal{U}_{22} \\ &\quad - 2(15 \times 1001)^{1/2}\mathcal{U}_{62}], \quad (19) \\ [\gamma_1^3(8), \mathcal{U}_c \bar{\gamma}_1^3] &= (8 \times 127)^{-1} [(15 \times 1001)^{1/2}\mathcal{U}_{66} \\ &\quad - (15 \times 1001)^{1/2}\mathcal{U}_{22} + 986\mathcal{U}_{62}], \end{aligned}$$

where in Eq. (19) we use the notation

$$[\gamma_1^3(6), \mathcal{U}_c \gamma_1^3(6)] = \mathcal{U}_{66}, \text{ etc.}$$

Dy^{3+} and Er^{3+} . $J=15/2$. $16 \rightarrow \Gamma_6 + \Gamma_7 + 3\Gamma_8$. We may take as symmetry functions for Γ_6 and Γ_7

$$\begin{aligned} \gamma_1^6 &= 3^{-1/2}(64/65)^{1/2} [(15/2)_{-z} + 2^{-1/2}F(\pi/4, 15/2)], \\ \gamma_1^7 &= (64/33)^{1/2} [(11/2)_{-z} - 2^{-1/2}F(-3\pi/4, 11/2)]. \end{aligned} \quad (20)$$

Three linearly independent and normalized Γ_8 functions are

$$\begin{aligned} \gamma_1^8(15/2) &= \frac{1}{2}(128/127)^{1/2}F(3\pi/4, 15/2), \\ \gamma_1^8(11/2) &= 16(543)^{-1/2} \\ &\quad \times [(11/2)_z + 2^{-3/2}F(3\pi/4, 11/2)], \quad (21) \\ \gamma_1^8(9/2) &= 4(2/185)^{1/2}F(3\pi/4, 9/2). \end{aligned}$$

The three spinors of Eq. (21) are not orthogonal; to avoid the inconvenience of the use of nonorthogonal functions we introduce spinors u_1 , u_2 , and u_3 which are orthonormal. These are linearly independent combinations of the spinors of Eq. (21) and take them to be

$$\begin{aligned} u_1 &= \gamma_1^8(15/2), \\ u_2 &= 1.007\gamma_1^8(11/2) - 0.118\gamma_1^8(15/2), \\ u_3 &= 1.367\gamma_1^8(9/2) + 0.920\gamma_1^8(11/2) \\ &\quad - 0.298\gamma_1^8(15/2). \end{aligned} \quad (22)$$

The a 's and b 's are given in Table V.

²⁷ Which in this case is $d_{mj}^i(\pi/2) = 2^{-i} \binom{2j}{j+m}^{1/2}$.

Yb^{3+} , $J=7/2$, $8 \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8$. The cubic symmetry spinors we may take as

$$\begin{aligned} \gamma_1^6(7/2) &= [2/(15)^{1/2}][(7/2)_{-z} + 2^{-1/2}F(\pi/4, 7/2)], \\ \gamma_1^7(5/2) &= [2/(27)^{1/2}] \\ &\quad \times [(5/2)_z - 2^{-1/2}F(-3\pi/4, 5/2)], \\ \gamma_1^8(7/2) &= (2/7)^{1/2}F(3\pi/4, 7/2). \end{aligned} \quad (23)$$

The a 's and b 's are given in Table VI.

Discussion

If at first the effect of V_6 is neglected then, according to Eq. (11), in the extreme classical limit there should be six highest (let $K_4 > 0$) states with $(5/2)a=1$, Eq. (14), and eight lowest states with $(5/2)a=-\frac{2}{3}$. In the semiclassical case these multiplets should be split, the lowest states being split more because of larger overlap integrals. In Ho^{3+} (Table IV) there is a singlet, doublet, and triplet with $(5/2)a=1.08, 0.97,$ and 1.01 , respectively, and these states are constructed from the six 8_i functions with a 1% admixture of other states. There is a doublet and two triplets with $(\frac{5}{2})a=-0.812, -0.471,$ and -0.918 , respectively, and finally there is a triplet with $(5/2)a=-0.08$. Even in this largest J state the octet constructed from [111] functions is split considerably, however, for the sextet states the splittings are only 5% of the over-all splitting. The situation for Er^{3+} and Dy^{3+} is not much different.

For Tb^{3+} and Tm^{3+} there is a singlet, a doublet, and triplet with $(\frac{5}{2})a=0.67, 1.15, 1,$ respectively; and a singlet and two doublets with $(\frac{5}{2})a=-1.3, -0.97,$ and -0.6 , respectively. The "multiplets" are appreciably split. Finally, the multiplet structure has, of course, disappeared in the case of Yb^{3+} ($J=\frac{7}{2}$), where one has two doublets and a quartet with $(\frac{5}{2})a=2, -2.6,$ and 0.29 , respectively.

Because of the increasing importance of overlap integrals as J decreases, the over-all splitting [of $(\frac{5}{2})a$] has increased from the infinite J limit of 1.7 to 2.0 for Ho^{3+} ($J=8$) and 4.6 for Yb^{3+} ($J=\frac{7}{2}$).

In the extreme classical limit V_6 , according to Eq. (11), would give a highest octet with $(\frac{7}{2})b$ equal 1.8, and a twelve-fold lowest multiplet with $(\frac{7}{2})b=-1.6$. For Ho^{3+} there is a doublet and two triplets with $(\frac{7}{2})b=3.9, 3.6,$ and 1.2 ; a singlet, a doublet, and two triplets with $(\frac{7}{2})b=-0.615, -2.1, -1.3, -4.3$. The semiclassical considerations have little relevance for a pure V_6 potential for $J \leq 8$.

Cases in which V_4 and V_6 both contribute importantly to the splitting will be considered in the practical cases encountered below.

V. THE EFFECT OF EXCHANGE

We may now investigate the ground state of a crystal with H given by Eq. (5).

Let us first find the best product wave function

approximation to the ground state,

$$\phi_0 = \prod_i w_{0i}, \quad (24)$$

where the product is over the various rare earths and w_{0i} is the yet to be determined ground-state vector (in this approximation) of the i th rare earth.

The condition that H of Eq. (5) be minimum then gives

$$[\mathcal{U}_{ci} - \sum_j \mathcal{J}_{ij} \langle \mathbf{J}_j \rangle_0 \cdot \mathbf{J}_i] w_{0i} = e_{0i} w_{0i}, \quad (25)$$

where

$$\langle \mathbf{J}_j \rangle_0 = (w_{0j}, \mathbf{J}_j w_{0j}). \quad (26)$$

In this approximation the ground-state energy is

$$\begin{aligned} (\phi_0, H \phi_0) &= \sum_i (\phi_0, \mathcal{U}_{ci} \phi_0) - \frac{1}{2} \sum_{i,j} \mathcal{J}_{ij} \langle \mathbf{J}_j \rangle_0 \cdot \langle \mathbf{J}_i \rangle_0 \\ &= \sum e_{0i} + \frac{1}{2} \sum_{i,j} \mathcal{J}_{ij} \langle \mathbf{J}_j \rangle_0 \cdot \langle \mathbf{J}_i \rangle_0. \end{aligned} \quad (27)$$

For a given \mathcal{J}_{ij} the self-consistent equations (25) and (26) generally admit many solutions, but we mean by the w_{0i} functions those solutions of Eqs. (25) and (26) which minimize Eq. (27). In terms of these "ground-state" wave functions (we use "wave function" in a loose sense—we mean state vectors), we define

$$\mathbf{B}_i = \sum_j \mathcal{J}_{ij} \langle \mathbf{J}_j \rangle_0, \quad (28)$$

and the orthonormal functions w_{ni} which satisfy

$$[\mathcal{U}_{ci} - \mathbf{B}_i \cdot \mathbf{J}_i] w_{ni} = e_{ni} w_{ni}, \quad (29)$$

may be used to specify any state of the i th atom. The functions

$$\phi_{n_1, n_2, \dots} = \prod_i w_{n_i i}, \quad (30)$$

constitute a complete orthonormal set of states for the crystal. We may now rewrite H , Eq. (5), in the form

$$H = H_0 + H_1, \quad (31)$$

where

$$H_0 = \sum_i [\mathcal{U}_{ci} - \sum_j \mathcal{J}_{ij} \langle \mathbf{J}_j \rangle_0 \cdot \mathbf{J}_i] + \frac{1}{2} \sum_{ij} \mathcal{J}_{ij} \langle \mathbf{J}_j \rangle_0 \cdot \langle \mathbf{J}_i \rangle_0, \quad (32)$$

and

$$H_1 = -\frac{1}{2} \sum_{ij} \mathcal{J}_{ij} (\mathbf{J}_i - \langle \mathbf{J}_i \rangle_0) \cdot (\mathbf{J}_j - \langle \mathbf{J}_j \rangle_0). \quad (33)$$

H_0 is diagonal in the states Eq. (30), and its eigenvalue for the state ϕ_0 is the self-consistent approximation to the energy of the ground state. H_1 has zero expectation value for the state ϕ_0 but it does have matrix elements between ϕ_0 and ϕ_n 's where two of the n_i 's are different from zero. H_1 causes a short-range correlation in the ground-state moments which will be discussed in a future paper along with a discussion of the low-lying excited states (spin waves) of Eq. (31).²⁸

²⁸ A short account of an investigation of the effects of short-range correlations and of the spin-wave spectrum in the rare-earth nitrides was given by the author in the reference of 18.

TABLE VII. The nonzero matrix elements of $(\gamma^i, \mathbf{J}\gamma^j)$ are represented by 1's for the cubic symmetry functions corresponding to Γ_1 to Γ_6 .

$i \backslash j$	1	2	3	4	5
1	0	0	0	1	0
2	0	0	0	0	1
3	0	0	0	1	1
4	1	0	1	1	1
5	0	1	1	1	1

In this paper we shall ignore the effect of the mixing in of the higher ϕ_{n_i}, \dots into ϕ_0 and shall assume that the ground state is adequately described by ϕ_0 [Eqs. (24), (25), and (26)] with the right-hand side of Eq. (27) minimum.

If \mathcal{U}_c is negligible relative to the exchange forces then $|\langle \mathbf{J}_i \rangle_0| = J$, and Yoshimori²⁹ and Villain³⁰ have shown that in the ground state the spins are parallel in layers and turn by a certain angle as one goes from layer to layer, the screw pattern (this includes the ferromagnetic and antiferromagnetic arrangements as special cases). If \mathcal{U}_c is small relative to the exchange terms, Yoshimori²⁹ has shown how the screw is distorted, hurrying over the hard directions and lingering in the easy directions.

In our case we assume that the exchange energy is small compared to the over-all crystalline splitting. We then expect that the effect of exchange is just to cause an intermixture of several of the low-lying states of \mathcal{U}_c in the formation of the w_0 's. It, thus, is expedient to use the crystal symmetry functions as bases for the expression of the w 's, and it is then necessary to obtain the matrix elements of \mathbf{J} between the cubic symmetry function.

Since the components of \mathbf{J} transform like Γ_4 , $(\gamma^\alpha, \mathbf{J}\gamma^\beta)$ is zero unless $\Gamma_4 \times \Gamma_\beta$ contains Γ_α in its reduction. The reduction may be readily accomplished by means of the character tables, and we give the results in Tables VII and VIII. In Table VIII the 2 represents the fact that Γ_8 occurs twice in the reduction of $\Gamma_4 \times \Gamma_8 (= \Gamma_6 + \Gamma_7 + 2\Gamma_8)$.

One sees from Tables VII and VIII that if the ground level of \mathcal{U}_c is of one of the five types $\Gamma_4 \dots \Gamma_8$ then one can take a linear combination of the degenerate ground states for which $\langle \mathbf{J} \rangle$ does not vanish and, therefore, for no matter how small g_{ij} 's the crystal ground state will

TABLE VIII. The nonzero matrix elements of $(\gamma^i, \mathbf{J}\gamma^j)$ are represented by 1's and a 2 for the cubic symmetry functions corresponding to Γ_6 , Γ_7 , and Γ_8 .

$i \backslash j$	6	7	8
6	1	0	1
7	0	1	1
8	1	1	2

²⁹ A. Yoshimori, J. Phys. Soc. Japan 14, 807 (1959).

³⁰ J. Villain, J. Phys. Chem. Solids 11, 303 (1959).

be magnetically ordered. The question comes up concerning the anisotropy of these moments, among these states how do the eigenvalues of $\mathbf{J} \cdot \boldsymbol{\tau}$ depend upon the direction of the unit vector $\boldsymbol{\tau}$? The answer is that except for Γ_8 the eigenvalues are independent of $\boldsymbol{\tau}$, i.e., if the ground level of \mathcal{U}_c is $\Gamma_4 \dots \Gamma_7$ then for sufficiently small g_{ij} 's the crystalline ground state exhibits the same ordered pattern as if \mathcal{U}_c were zero, except the ordered moment is reduced.

To show this, and for other purposes as well, we must get the matrix elements $(\gamma^i, \mathbf{J}\gamma^j)$. Koster and Statz³¹ obtained these for all the point groups. If $|w_i^\lambda\rangle$ and $|u_j^\mu\rangle$ are state vectors transforming according to the irreducible representations Γ_λ and Γ_μ of a group, and Θ_k^ν is an operator which transforms according to Γ_ν , then if in the reduction of $\Gamma_\nu \times \Gamma_\mu$, Γ_λ occurs once then

$$(w_i^\lambda, \Theta_k^\nu u_j^\mu) = (w^\lambda | | \Theta^\nu | | u^\mu) C_{ikj}^{\lambda\nu\mu},$$

if Γ_λ occurs twice,³¹

$$(w_i^\lambda, \Theta_k^\nu u_j^\mu) = (w^\lambda | | \Theta^\nu | | u^\mu) {}_1 C_{ikj}^{\lambda\nu\mu} + (w^\lambda | | \Theta^\nu | | u^\mu) {}_2 C_{ikj}^{\lambda\nu\mu}, \text{ etc.}$$

This is an expression of the generalized Wigner-Eckart³² theorem. The Clebsch-Gordan coefficients (the C 's) do not depend on w , Θ , or u : That dependence is in the "reduced matrix elements" $(a||b||c)$. The Clebsch-Gordan coefficients for the cubic group and for $\nu=4$ (\mathbf{J} transforms according to Γ^4) may be obtained from Koster, or directly by making use of the prototype symmetry functions of the cubic rotation group. One obtains for the nonzero matrix elements of \mathbf{J} among γ^1 to γ^5

$$\begin{aligned} (\gamma^1, J_1 \gamma^1) &= (\gamma^1, J_2 \gamma^2) = (\gamma^1, J_3 \gamma^3), \\ (\gamma^2, J_1 \gamma^1) &= (\gamma^2, J_2 \gamma^2) = (\gamma^2, J_3 \gamma^3), \\ (\gamma^1, J_3 \gamma^3) &= (\gamma^2, J_1 \gamma^1) = -2(\gamma^1, J_2 \gamma^2) = -2(\gamma^1, J_1 \gamma^1) \\ &= -2(\gamma^2, J_3 \gamma^3) = -2(\gamma^2, J_2 \gamma^2), \\ (\gamma^1, J_1 \gamma^1) &= (\gamma^2, J_2 \gamma^2) = -(\gamma^1, J_2 \gamma^2) \\ &= -(\gamma^2, J_3 \gamma^3), \\ (\gamma^1, J_2 \gamma^3) &= (-)^P (\gamma^\lambda, J_\mu \gamma^\nu), \\ (\gamma^1, J_2 \gamma^3) &= (\gamma^\lambda, J_\mu \gamma^\nu), \\ (\gamma^1, J_2 \gamma^3) &= (-)^P (\gamma^\lambda, J_\mu \gamma^\nu). \end{aligned} \quad (34)$$

In the last three equations (λ, μ, ν) is a permutation of $(1, 2, 3)$ and P is the number of interchanges required to get (λ, μ, ν) from $(1, 2, 3)$. The significance of the subscripts on the γ 's may be manifested by giving the prototypes:

$$\begin{aligned} (\gamma^1, \gamma^2) &= [z^2 - \frac{1}{2}(x^2 + y^2); x^2 - \frac{1}{2}(z^2 + y^2)], \\ (\gamma^1, \gamma^2; \gamma^3) &= (x, y, z), \quad (\gamma^1, \gamma^2, \gamma^3) = (yz, zx, xy). \end{aligned}$$

³¹ G. F. Koster and H. Statz, Phys. Rev. 115, 1568 (1959); 113, 445 (1959); G. F. Koster, *ibid.* 109, 227 (1958).

³² E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959); C. Eckart, Rev. Mod. Phys. 2, 304 (1930).

We take as prototype spinors for $\Gamma_6, \Gamma_7, \Gamma_8^{24}$:

$$\begin{aligned} (\gamma_{1/2}^6; \gamma_{-1/2}^6) &= \left[\left| \frac{1}{2}, \frac{1}{2} \right\rangle; \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right]; \\ (\gamma_{\alpha^7}; \gamma_{\beta^7}) &= \left[xyx \left| \frac{1}{2}, \frac{1}{2} \right\rangle; xyz \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right]; \\ [\gamma_{3/2}^8; \gamma_{1/2}^8; \gamma_{-1/2}^8; \gamma_{-3/2}^8] &= \left[\left| \frac{3}{2}, \frac{3}{2} \right\rangle; \left| \frac{3}{2}, \frac{1}{2} \right\rangle; \dots \right]. \end{aligned}$$

Then the nonvanishing matrix elements of \mathbf{J} are

$$\begin{aligned} (\gamma_{1/2}^6, J_z \gamma_{1/2}^6) &= -(\gamma_{-1/2}^6, J_z \gamma_{-1/2}^6) = \frac{1}{2}(\gamma_{1/2}^6, J_+ \gamma_{-1/2}^6) \\ &= \frac{1}{2}(\gamma_{-1/2}^6, J_- \gamma_{1/2}^6), \\ (\gamma_{1/2}^6, J_z \gamma_{1/2}^8) &= (\gamma_{-1/2}^6, J_z \gamma_{-1/2}^8) = (\gamma_{1/2}^6, J_+ \gamma_{-1/2}^8) \\ &= -(\gamma_{-1/2}^6, J_- \gamma_{1/2}^8) = 3^{-1/2}(\gamma_{-1/2}^6, J_+ \gamma_{-3/2}^8) \\ &= -3^{-1/2}(\gamma_{1/2}^6, J_- \gamma_{3/2}^8), \\ (\gamma_{\alpha^7}, J_z \gamma_{\alpha^7}) &= -(\gamma_{\beta^7}, J_z \gamma_{\beta^7}) = (1/2)(\gamma_{\alpha^7}, J_+ \gamma_{\beta^7}) \\ &= (1/2)(\gamma_{\beta^7}, J_- \gamma_{\alpha^7}), \\ (\gamma_{\alpha^7}, J_z \gamma_{-3/2}^8) &= (\gamma_{\beta^7}, J_z \gamma_{3/2}^8) \\ &= (\gamma_{\alpha^7}, J_+ \gamma_{3/2}^8) = -(\gamma_{\beta^7}, J_- \gamma_{-3/2}^8) \quad (35) \\ &= 3^{-1/2}(\gamma_{\alpha^7}, J_- \gamma_{-1/2}^8) = -3^{-1/2}(\gamma_{\beta^7}, J_+ \gamma_{1/2}^8), \\ (\gamma_{3/2}^8, J_z \gamma_{3/2}^8) &= -(\gamma_{-3/2}^8, J_z \gamma_{-3/2}^8) \equiv a, \\ (\gamma_{1/2}^8, J_z \gamma_{1/2}^8) &= -(\gamma_{-1/2}^8, J_z \gamma_{-1/2}^8) = (1/3)(a+4b), \\ (\gamma_{3/2}^8, J_+ \gamma_{1/2}^8) &= (\gamma_{-3/2}^8, J_- \gamma_{-1/2}^8) = (2/3)(a+b), \\ (\gamma_{1/2}^8, J_- \gamma_{3/2}^8) &= (\gamma_{-1/2}^8, J_+ \gamma_{-3/2}^8) = (2/\sqrt{3})(a+b), \\ (\gamma_{3/2}^8, J_- \gamma_{-3/2}^8) &= (\gamma_{-3/2}^8, J_+ \gamma_{3/2}^8) \equiv -2b, \\ (\gamma_{1/2}^8, J_+ \gamma_{-1/2}^8) &= -(\gamma_{-1/2}^8, J_- \gamma_{1/2}^8) = (2/3)(2a-b). \end{aligned}$$

In Eq. (35), $J_+ = J_x + iJ_y$, $J_- = J_x - iJ_y$, and the matrix elements given (and their complex conjugates) are the only nonvanishing ones of J_x, J_+ , and J_- .

Among the four γ^8 states the eigenvalues of $\mathbf{J} \cdot \boldsymbol{\tau} = xJ_x + yJ_y + zJ_z$ are determined by a characteristic equation whose coefficients involve $x^2 + y^2 + z^2 = 1$, and $x^4 + y^4 + z^4$ (the irreducible representations Γ^i , $i < 8$, involve only $x^2 + y^2 + z^2$ and, hence, the eigenvalues are independent of $\boldsymbol{\tau}$). Since $x^4 + y^4 + z^4$ has its extreme values along the cube edge and the body diagonal, the maximum $\mathbf{J} \cdot \boldsymbol{\tau}$ value will occur for one of these directions. The secular equation is rather clumsy, so we just give the eigenvalues in these two directions.

$$J_{100} = \pm a, \pm \frac{1}{3}(a+4b), \quad (36)$$

$$\begin{aligned} (J_{111}/a)^2 &= \frac{1}{2}[1 + (1+4p)^2/9] \pm \frac{1}{2}\{[1 - (1+4p)^2/9]^2 \\ &\quad + (64/27)p(2+3p-p^3)\}^{1/2}. \quad (37) \end{aligned}$$

where a and b are given in the last few lines of Eqs. (35) and $p = b/a$.

Γ_1, Γ_2 , or Γ_3 *Ground State*. If the ground level of \mathcal{U}_c is of type Γ_1, Γ_2 , or Γ_3 then according to Table VII the expected value of $\mathbf{J} \cdot \boldsymbol{\tau}$ in the ground state is zero, and we can show that for sufficiently small g_{ij} the ground state will not exhibit long-range order. For simplicity, we shall assume that $g_{ij} > 0$ so that in the ground state all the atoms are equally aligned, then the self-consistent

Eqs. (24) to (27) become

$$[\mathcal{U}_c - \mathbf{B}_n \cdot \mathbf{J}] w_n = e_n w_n, \quad (38)$$

$$\mathbf{B}_n = g(\mathbf{J})_n, \quad (39)$$

$$E_n = e_n + \frac{1}{2} \mathbf{B}_n \cdot \langle \mathbf{J} \rangle_n, \quad (40)$$

and to compute $\langle \mathbf{J}_n \rangle$ from e_n we have

$$-de_n/dB_n = \langle \mathbf{J} \rangle_n. \quad (41)$$

In Eq. (39) $g = \sum_j g_{ij}$, and we are interested in the solution $n=0$ for which E_n is minimum.

Call the direction of \mathbf{B}_0 the Z direction, a ground state function of \mathcal{U}_c , u_1 , an excited state function of \mathcal{U}_c , u_2 . Let $(u_1, \mathcal{U}_c u_1) = 0$, $(u_2, \mathcal{U}_c u_2) = \Delta$, $(u_1, J_z u_1) = (u_2, J_z u_2) = 0$, $(u_1, J_x u_2) = j$. We then have among these states,

$$e_0 = \Delta/2 - \frac{1}{2}[\Delta^2 + 4B_0^2 j^2]^{1/2}, \quad (42)$$

$$\langle J_z \rangle_0 = 2g \langle J_z \rangle_0 j^2 [\Delta^2 + 4g^2 \langle J_z \rangle_0^2 j^2]^{-1/2}. \quad (43)$$

Equation (43) has solutions

$$\langle J_z \rangle_0 = 0 \quad (44a)$$

or

$$\langle J_z \rangle_0 = j[1 - \Delta^2/(4g^2 j^2)]^{1/2}, \quad (44b)$$

where it is clear that (44b) can hold only if $2gj^2 > \Delta$, and if this condition holds this gives the lowest energy.

In this simple example, $\Delta/2$ is the crystalline energy in the fully aligned case, $\frac{1}{2}gj^2$ is the exchange energy in the fully aligned case, and we get alignment only if $\frac{1}{2}gj^2 > \frac{1}{2}(\Delta/2)$.

Thus, if the ground state of \mathcal{U}_c has $\langle \mathbf{J} \rangle = 0$, then for given exchange integrals there is a critical value of \mathcal{U}_c above which no long-range order exists in the ground state. In a sense, \mathcal{U}_c plays the role for the ground state that the temperature does for ordinary materials. The interesting question of whether at higher temperatures there might exist long-range order and none at lower temperatures is left open here. We shall see later that TmN seems to be a realization of a nonordered zero temperature system.

Concerning anisotropy in these cases, to the extent that the ground state consists of just a mixture of Γ_1 and Γ_4 , or Γ_2 and Γ_5 there is no anisotropy as may easily be shown from Eqs. (34). However, if in \mathcal{U}_c , Γ_3 lies lowest then one always has an anisotropy as may be seen from Eq. (34). This result is in contradiction with the often made statement that the (weak field) susceptibility of paramagnetic ions in cubic crystals is isotropic, and it seems worthwhile to pause and elaborate on this point.

Suppose the ground state of \mathcal{U}_c is a Γ_3 doublet, and consider the effect of an external field in lowering the energy of the ground state by mixing in, for example, a Γ_4 state. Let $H = \mathcal{U}_c - \mathbf{B} \cdot \mathbf{J}$ and consider the energy of the ground state as a function of \mathbf{B} for small B . Using the relation Eq. (34), we easily obtain in second-order per-

turbation theory

$$E_{100} = -B^2 |(\gamma_1^3, J_z \gamma_z^4)|^2 \div \Delta, \quad (45a)$$

$$E_{111} = -B^2 |(\gamma_1^3, J_z \gamma_z^4)|^2 \div 2\Delta, \quad (45b)$$

$$E_{110} = -3B^2 |(\gamma_1^3, J_z \gamma_z^4)|^2 \div 4\Delta, \quad (45c)$$

as the lowering of the energy of the ground state for B in the $[100]$, $[111]$, and $[110]$ directions, respectively. This yields a susceptibility twice as great in the $[100]$ direction as in the $[111]$.

The argument is sometimes given that $E(\mathbf{B})$ is a quadratic function of \mathbf{B} , and since it is also invariant under the group of the cube it must be of the form $E = -C(B_x^2 + B_y^2 + B_z^2)$; this, however, follows only in the case the ground state of \mathcal{U}_c is nondegenerate. The energy of the ground state need not be an analytic function of B_x , B_y , B_z , it is also allowed that

$$E = -C(B_x^2 + B_y^2 + B_z^2) + D(|B_x B_y| + |B_x B_z| + |B_y B_z|),$$

if we take $D=C/2$ we get agreement with Eq. (45).

Rather than further general discussion we turn in the next section to the problem of understanding the magnetic properties of the rare-earth phosphides in terms of these results.

VI. ANALYSIS OF THE PHOSPHIDES

Our knowledge of the magnetic ordering properties of the rare-earth nitrides, phosphides, arsenides, and antimonides, comes mainly from the neutron diffraction results on powdered crystalline samples of Child *et al.*¹¹ In this paper we shall concentrate primarily on their 1.4°K data for the rare-earth phosphides; however, we first make some more general remarks.

In the first place, in the compounds of Tb, Dy, and Ho the ground-state ordered moments are in the directions predicted on the basis of the results of Sec. III with K_4 and K_6 having the (point charge) values of Eq. (31), i.e., the Tb moment points along the $[111]$ direction, whereas the Ho and Dy moments point along $[100]$ directions. The Er moments are perpendicular to $[111]$ directions and we shall discuss them subsequently. These Tm compounds are not found to order at all.

Although the moment directions are correctly given (for Tb, Dy, and Ho) on the basis of a simple ionic model these are certainly not simple ionic compounds. According to Pauling's ideas and electronegativity values³³ the single rare-earth-nitrogen bond is expected to be about 60% ionic, whereas the rare-earth phosphide, etc., bonds are expected to be only 20% ionic. Furthermore, Miller and Himes³⁴ give the room-temperature resistivity values for ErSb as $\rho = 0.5 \times 10^{-4}$

Ω -cm, whereas $\rho = 10^{-4}$ Ω -cm for Er metal; $\rho = 2.4 \times 10^{-6}$ Ω -cm for LaN, whereas $\rho = 62 \times 10^{-6}$ Ω -cm for La metal (in addition, LaN becomes superconducting at low temperatures). Thus, these substances seem to be as good conductors at room temperature as the metals. Whether at low temperatures these materials turn out to be true conductors or semiconductors it seems quite likely that the outer electron distribution on a given rare-earth ion will exhibit an appreciable departure from spherical symmetry and substantially alter the values of the crystal-field parameters from those computed on the basis of the naive, simple ionic model.

We find in this section that the magnitude and directions of the ground-state moments in the phosphides of Tb, Ho, and Er can be accounted for on the basis of a crystal field of cubic symmetry if the ratio of the strengths of the sixth-order to fourth-order potential is increased by a factor of 5.5 beyond that predicted by the naive value. In view of our preceding remarks this result does not appear unduly surprising and could probably be accounted for on the basis of a partial occupation of the Γ_3 or Γ_5 $5d$ orbitals. However, in the next section we mention evidence for the existence of a noncubic distortion in the phosphides, which until properly taken into account in the crystal field calculations, leaves the K_6/K_4 ratio uncertain.

The rare-earth phosphides (except HoP), antimonides, and arsenides, exhibit a simple antiferromagnetic ordering¹¹ which can be accounted for on the basis of appreciable exchange interactions among the nearest and next-nearest neighbors only. The HoN moment configuration,¹¹ on the other hand, seems to involve blocks of about seven planes with parallel spins alternating between the cubic edge directions. The stability of this structure would seem to require alternating exchange integrals of an appreciable magnitude out to about seven nearest neighbor distances. This provides some evidence for the existence of a conduction band at these low temperatures filled up to a Fermi level corresponding to a wavelength of about seven $[111]$ spacings via which the exchange is affected by a Ruderman-Kittel³⁵ mechanism. Because of the small size of the nitrogen atoms it is to be expected that the properties of the nitrides will be considerably different from those of the phosphides, etc.; the inter-rare-earth ion distances in the nitrides are within a few percent of those in the metal, the small nitrogens fit in the metal lattice interstices, whereas in the phosphides, etc., these distances have increased some 0.54° and on the basis of the Hartree-Fock calculation³⁰ the direct overlap of $6s$ (and $5d$) orbitals of neighboring rare earths will be much less than in the case of the metals or nitrides.

We now proceed to apply the theory of the preceding sections to the phosphides, neglecting magnetic dipole-dipole, electric quadrupole-quadrupole forces, and non-cubic distortions, which effects are discussed in the

³³ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., Chap. 3.

³⁴ J. F. Miller and R. C. Hines, *Rare Earth Research*, edited by E. V. Kleber (The Macmillan Company, New York, 1961), p. 232.

³⁵ M. A. Ruderman and C. Kittel, *Phys. Rev.* **96**, 99 (1954).

following section. The nitrides will be discussed at a later date.

TbP. TbP exhibits a simple antiferromagnetic ordering, the moments lying along a [111] direction with ordered moment values $|\langle \mu_{111} \rangle| = 6.2 \pm 0.3 \mu_B$, as compared to a maximum possible value of $gJ = 9 \mu_B$. Putting $g = \frac{3}{2}$ we get $|\langle J_{111} \rangle| = 4.1 \pm 0.2$ as the expected value of the [111] component of \mathbf{J} in the ground state. According to Table I, Tb has a positive 2^4 pole moment and a negative 2^6 pole moment. If we take $\langle v_4 \rangle$ and $\langle v_6 \rangle$ positive in accordance with the naive model, Eq. (12), we get [Eqs. (7) and (8)] $K_4 > 0, K_6 < 0$. From Eqs. (10) the minima of \mathcal{U}_e are in the [111] direction and according to the arguments of Sec. II, we expect the ground-state ordered moments to point in these directions, as they do.

Our procedure now is to find the smallest B such that the ground state of

$$H_0 = \mathcal{U}_e - \mathbf{B} \cdot \mathbf{J} \quad (46)$$

has the observed moment [compare with Eqs. (29) and (32)]. According to Eqs. (1), (5), and (28)

$$\mathbf{B} = (S/J)^2 g' \langle \mathbf{J} \rangle_0, \quad (47)$$

where

$$g' = \sum_j g_{ij}' \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \quad (48)$$

and $\boldsymbol{\tau}_i$ is a unit vector in the direction of spin of the i th rare-earth ion. Because of the small 2^6 pole moment of Tb (Table I), \mathcal{U}_6 is negligible, the ratio of K_4 to g' is then determined by the above procedure. By extrapolating these values to Ho and Er we then determine K_6/K_4 .

The eigenfunctions and eigenvalues of \mathcal{U}_e are given by Eq. (15) and Table III. From Table III $\gamma^5(2)$ has a 10% admixture of $\gamma^5(6)$ in the eigenfunctions of \mathcal{U}_e , this is negligible for our purposes. In arbitrary units the eigenvalues of \mathcal{U}_e are $\Gamma_1(-126), \Gamma_4(-96), \Gamma_5(2)(-59), \Gamma_2(62), \Gamma_5(6)(99), \Gamma_3(114)$. If the admixtures of $\gamma^5(2)$ and $\gamma^5(6)$ were taken account of $\Gamma_5(2)$ would be lowered to -62 , and the separation of the (Γ_4, Γ_1) and (Γ_5, Γ_4) levels would be 30 and 34, respectively (possibly indicating that the traveling of J among the [111] directions has a nearly simple harmonic time dependence).

For small \mathbf{B} , Γ_1 would be lowered by an admixture with Γ_4 , but since γ^1 is connected only to γ^4 by \mathbf{J} [Eq. (34)] and since there is only one Γ_4 here the maximum moment of such a state would be $(J(J+1)/3)^{1/2} = (14)^{1/2} = 3.7$, which is too small, and furthermore with Γ_1 and Γ_4 the moment value is independent of the direction of \mathbf{B} . B must be sufficiently large then to cause Γ_5 to be admixed into the ground state, which takes place via the coupling of Γ_4 to Γ_5 [Eq. (34)]. From Eq. (34) we easily obtain that $(\gamma^4, J_{111}\gamma^5) = (2/\sqrt{3}) \cdot (\gamma_1^4, J_2\gamma_3^5)$, whereas in the [110] and [100] directions the $2/\sqrt{3}$ factor is replaced by one (for the [100] direction the γ^5 states having the same symmetry as γ^1 are not coupled to γ^4 by $J_{[100]} = J_3$). Thus, it is the admixture of γ^5 which makes [111] the easy direction. γ^1 has the same sym-

metry around the [111] directions as the state $6_{[111]}$, the ground state of Tb for $B=0$ then goes over continuously into the ground state for $B=\infty$ if B is in the [111] direction. If B is the [100] direction the ground state for $B=0$ is of different symmetry than that for $B=\infty$ and is crossed twice by other levels as B becomes large [$\gamma^1(B=0) \rightarrow 4_z(B=\infty)$]. This expected behavior is confirmed by the results of White and Andelin.³⁶

We set $j_1 = (\gamma^1, J_{111}\gamma^4) = (14)^{1/2}$, $j_2 = (\gamma^4, J_{111}\gamma^5) = (5/2)^{3/2}$, and the secular equation of the 3×3 submatrix of Tb corresponding to γ^1, γ^4 , and $\gamma^5(2)$ becomes

$$y(y - \Delta_1 - \Delta_2) - B^2(j_1^2 + j_2^2) + B^2(j_2^2\Delta_1 - j_1^2\Delta_2)(\Delta_1 - y)^{-1} = 0, \quad (49)$$

where $\Delta_1 = E(\Gamma_4) - E(\Gamma_1)$, $\Delta_2 = E(\Gamma_5) - E(\Gamma_4)$, and $y = E - E(\Gamma_1)$. The last term in Eq. (48) is negligible for the ground state y , and we obtain

$$2y = \Delta_1 + \Delta_2 - [(\Delta_1 + \Delta_2)^2 + 4B^2(j_1^2 + j_2^2)]^{1/2}, \quad (50)$$

$$\langle J_{111} \rangle = \frac{\partial y}{\partial B} = (j_1^2 + j_2^2)^{1/2} (1 + x^2)^{-1/2}, \quad (51)$$

where $x = (\Delta_1 + \Delta_2) \div 2B[j_1^2 + j_2^2]^{1/2}$. Putting $[j_1^2 + j_2^2]^{1/2} = 5.4$ and $\langle J_{111} \rangle = 4.1 \pm 0.2$, Eq. (50) gives $x = 0.9 \pm 0.1$. The contribution of the other levels may be estimated by perturbation methods and are still negligible for $x \approx 1$. From Eq. (47) we obtain for these values of x

$$g' = (0.10 \pm 0.01)[E(\Gamma_5) - E(\Gamma_1)], \quad (\text{Tb}). \quad (52)$$

HoP. HoP exhibits a peculiar magnetic order in its ground state¹¹ in which the moments in (111) planes are in, say, the $+z$ or $+x$ directions, and the moment directions in adjacent (111) planes are mutually perpendicular (the moment direction "flops" from $+z$ to $+x$ to $+z$, etc., hence, "holmium flopside"). The spin arrangement may be thought of as a superposition of a ferromagnetic pattern with moments along [101] directions and an antiferromagnetic pattern with moments along $[\bar{1}01]$ directions. Since it is clear that, on the assumption of isotropic exchange interactions, the exchange energy for the configuration is the average of the ferromagnetic and the antiferromagnetic (of the TbP type) exchange energies, this actual ground state can only be understood as due to effects so far neglected. In the next section we shall argue that magnetic interactions are responsible for this peculiar ordered arrangement, but since even in these cases the magnetic interactions are small compared to exchange interactions, we shall argue that the difference in the exchange energies for the ferromagnetic, antiferromagnetic, or the "flopside" configurations are relatively small. We then assume that g' , Eq. (48), for HoP is negligibly different from that of TbP, Eq. (52). We also assume that $\langle v_4 \rangle$ and $\langle v_6 \rangle$ are reduced in going from Tb to Ho in approximately the ratios indicated by

³⁶ R. L. White and J. P. Andelin, Phys. Rev. **115**, 1435 (1959).

TABLE IX. Estimated parameters for HoP based on extrapolations from TbP results. C is an adjustable parameter.

K_4	K_6	g'	$\langle J_{100} \rangle$	B
$-0.84K$	$-0.04CK$	$(0.027 \pm 0.003)K$	7 ± 0.25	$(0.012 \pm 0.001)K$

Eqs. (13), although our conclusions are not very sensitive to the assumption. We then find that $\langle v_6 \rangle / \langle v_4 \rangle$ must be appreciably increased over that given by Eq. (13) in order to obtain the observed expected moment value for Ho.

If we let $K_4(\text{TbP}) \equiv K$ then, with the assumptions stated, the HoP parameters are given in Table IX.

In the table C is an adjustable parameter which has the value one if K_6/K_4 is given by the naive model Eq. (13). The uncertainty indicated in the value of g' (and B) is just that coming from the uncertainty of the TbP moment, there is an additional uncertainty not indicated arising from the extrapolation from TbP to HoP.

For convenience we shall take $K=100$ then in Table X we give the crystalline splittings obtained from Table IV and Eqs. (16) and (19) [it is desirable to use $\gamma^3(8)$ and $\tilde{\gamma}^3$]. As mentioned in Sec. IV the six states Γ_1 and the lowest Γ_4 and Γ_3 states are split very little (for C of the order of one) relative to the over-all splitting; furthermore, Γ_4 and Γ_3 are almost purely $\gamma^4(8)$ and $\gamma^3(8)$, these states constitute the semiclassical ground multiplet. In Table XI we give the energy levels for these states.

From Table XI it is seen that as C increases Γ_4 and Γ_3 remain low and close together but Γ_1 moves up. From Table IX, $\langle J_z \rangle = 84-90\%$ of J and $B \approx 1.2$. Now $(\gamma^4(8), J_z \gamma^1(8)) = J/\sqrt{3}$, $(\gamma^4(8), J_z \gamma^3(8)) = (2/3)^{1/2}J$. Taking $B=1.2$ and $C=1$ we obtain $\langle J_z \rangle \approx 97\%J$, it is necessary to increase C to 5-7 in order to account for $\langle J_z \rangle = 7 \pm 0.25$. The results are given in Table XII. In the last column of the table we give the result of including the $\gamma^4(4)$ and $\tilde{\gamma}^3$ admixtures in the wave functions. We think it unlikely that g' for Ho is much less than that for Tb, a crude estimate based on their critical temperatures would indicate that it might be 20% less (see Sec. VII). We then estimate that $C = (K_6/K_4)$ must be some 5-7 times the naive estimate. If $\langle J_z \rangle$ actually is as low as 6.75, C would have to be increased to about 10 to account for that value.

ErP. The ground state exhibits the TbP-type anti-ferromagnetic order. The neutron diffraction results determine that the moment direction is perpendicular to [111]. Making the same type of extrapolations from TbP as were made for HoP we obtain the results of Table XIII. Again letting $V=100$ and inserting the values of K_4 and K_6 from Table XIII into Eq. (14) and making use of Table V, we obtain the results of Table XIV for the matrix elements of \mathcal{U}_o among the various states indicated [see Eqs. (20) and (22)].

We see from Table XIV that for $C=1$, the states arising from u_2 [Eq. (22)] are lowest, and there is a considerable admixture of u_3 . From the semiclassical considerations of Sec. III we might expect that the largest moment would be attained along the [111] direction. The calculation is rather tedious because of the admixture of u_3 ; if that admixture is neglected then the largest moment (for state u_2) is along [100] and of magnitude $(11/2) \cdot (493/543) = 5.0$, with the moment along [110] and [111] being 10% smaller. u_2 alone then gives a nearly isotropic moment but with [100] direction largest, whether the admixture of u_3 will make the maximum moment along [111], or whether the semiclassical considerations are a completely unreliable guide in this case, is unknown.

From the considerations of Sec. III the lowest bottoms in \mathcal{U}_c switch from the [111] directions to the [110] directions as K_6 becomes larger than $(1/6)K_4$, i.e. (Table XIII) when $C > 4$. From Table XIV we see that Γ_7 falls rapidly with increasing C , crossing the lowest Γ_8 level at $C \approx 5$. For $C \approx 5$ the admixture of u_3 and u_1 into the lowest Γ_8 level may be neglected and since u_2 is nearly pure $\gamma^8(11/2)$ [Eq. (22)] the six lowest states $\Gamma_7 + \Gamma_8$ are the six states $(11/2)_i$. From a crude geometrical argument one might expect these states to give the largest moment along [110]. In fact this is found to be the case, the maximum moment becoming 5.9g in the [110] direction compared to 5.5g in the [100] direction.

In the region of interest here, C in the range 4-8 say, $B \approx 0.5$, only Γ_7 and the $\gamma^8(11/2)$ states are of appreciable importance in making up the ground state. Let $E(\Gamma_7) - E(\Gamma_8) = \Delta$; we can now say that if $\Delta > 0$ then for sufficiently large B ($5B \gg \Delta$) the ground state will have a [110] moment direction and its value will be greater than 5g (which is the value attainable from

TABLE X. The crystalline splittings for Ho³⁺.

Γ_1	Γ_4	Γ_3
V_{88}	V_{44}	V_{88}
$-36.1 + 0.71C$	$+15.5 - 1.42C$	$-32.2 - 2.1C$
Γ_3	Γ_5	
V_{--}	V_{66}	V_{62}
$27.1 + 0.154C$	$25.1 + 0.86C$	$-11.3 + 2.7C$

TABLE XI. Ho³⁺. V_{38} for the low levels and various C 's, the values $6'$ are the correct levels for $c=6$.

C	0	1	2	4	6	$6'$
Γ_1	-36.1	-35.4	-34.7	-33.3	-31.8	-31.8
Γ_4	-33.6	-34.7	-36	-38.2	-40.5	-44
Γ_8	-32.2	-34.3	-36.4	-40.6	-44.8	-47.2

$\gamma^8(11/2)$, alone, in the [100] direction). For smaller values of B/Δ the moment will be in the [100] direction (and have a value greater than 5g).

When Γ_7 lies below Γ_8 , $\Delta < 0$, the ground-state moment is always in the [110] direction. This is made plausible by the fact that for the state of maximum moment the fraction of Γ_7 is 1/17 for the [100] moment direction, and 1/(2.8) for the [110] moment direction; thus, aside from the effect of the larger moment the [110] state will lie $2\Delta/3$ below the [100] state in this case. This effect persists for smaller ($B/|\Delta|$) values. If then $\Delta < 0$ the ground-state moment will be in the [110] direction and have a value lying between 2.9g (Γ_7 alone) and 5.9g.

 TABLE XII. $\langle J_z \rangle$ for the ground state of HoP for two values of B and various values of C . The column $6'$ refers to $C=6$ with $\gamma^4(4)$ and $\tilde{\gamma}^3$ admixtures included.

C	4	5	6	7	$6'$
1.2	7.3	7.05	7.2
0.9	7.6	7.25	7.0	...	6.9

The experimental facts so far known are consistent with the moment being in a [110] direction, but not with a [100] or [111] direction. Furthermore, the moment value is likely a little less than 5g and with our assumptions this indicates that Γ_7 is a little lower than Γ_8 . We get in this way a rather close estimate of C .

We give in Table XV the matrix elements of \mathbf{J} which are relevant here (the ones not given explicitly follow from symmetry considerations).

In the table

$$F_z = \gamma_1^8(11/2), \quad (53a)$$

$$\phi_z = -\gamma_2^7(11/2), \quad (53b)$$

where $\gamma_1^8(11/2)$ is given in Eq. (21) and ϕ_z is the mate

 TABLE XIII. Estimated parameters for ErP based on extrapolations from TbP, C is an adjustable parameter.

K_4	K_6	g'	$\langle J_i \rangle$	B
0.79V	0.035CV	(0.027±0.003)V	4.75±0.25	(0.005±0.001)V

of the function given in Eq. (20), obtained by replacing $(11/2)_{-z}$ by $(11/2)_z$, and $-3\pi/4$ by $+3\pi/4$ in Eq. (20).²⁴ F_z and F_{-z} are obtained by rotating F_z by $\pi/2$ and π , respectively, around the y axis.²⁴

The ground state for the moment in the z direction is a linear combination of ϕ_z and F_z and is easily obtained from the table. If the moment is in the [101] direction the ground state is a linear combination of

$$u_1 = (2+1/\sqrt{2})^{-1/2}(F_z+F_x), \quad (54a)$$

$$u_2 = (2-1/\sqrt{2})^{-1/2}(F_{-z}-iF_{-x}), \quad (54b)$$

$$u_3 = (2-\sqrt{2})^{-1/2}(\phi_z+\phi_x), \quad (54c)$$

all of which are of the same symmetry type relative to rotations about the [101] axis. $u_2 = (6/5)^{1/2}(u_3 - 6^{-1/2}u_1)$ is orthogonal to u_1 .

The secular equation for the ground state in the [101] direction is obtained from Eqs. (54) with the aid of Table XV and is a cubic. In Table XVI we give the energy value and the ground-state moment value for various values of $5.0B/\Delta$, where $5.0 = (\gamma^8(11/2), J_z \gamma^8(11/2))$ and $\Delta = E(\Gamma_8) - E(\Gamma_7)$ is the amount Γ_7 is below Γ_8 in the absence of the exchange forces ($B=0$).

Since $\langle J_{101} \rangle = 4.5 - 5$ (Table XIII), we see from Table XVI that $x \doteq 5 - 6$, or $\Delta \doteq B = 0.5$ (Table XIII), and this gives (Table XIV) $C = 5.5 - 5.7$. The moment value is very sensitive to variations of C here; hence, the close estimate.

This value of C is consistent with that determined above from the HoP data.

VII. NONCUBIC DISTORTIONS AND ELECTRO-MAGNETIC INTERACTIONS AMONG THE RARE EARTHS

Distortion

In the preceding section we have neglected the effects of noncubic crystalline distortions and the magnetic dipole-dipole and electric quadrupole-quadrupole interactions among the rare earths.

An x-ray diffraction study of HoN revealed that there was less than about 10^{-4} noncubic distortion in these

 TABLE XIV. The crystalline splittings for Er³⁺.

Γ_6	Γ_7	V_{11}	V_{22}	V_{33}	Γ_8	V_{12}	V_{13}	V_{23}
34.2-0.62C	-3.0-4.8C	30.4+1.8C	-28.6+0.12C	-17.2+0.753C		3.2-2.1C	3.5-2.4C	4.4-0.58C

TABLE XV. Matrix elements of J for Er^{3+} or Dy^{3+} for the states of Eqs. (53). The entries should be multiplied by $(11/2)$.

$(F_{z_1}J_zF_z)$	$(\phi_{z_1}J_z\phi_z)$	$(F_{z_1}J_z\phi_z)$	$(F_{z_1}J_zF_{-z})$	$(F_{z_1}J_zF_y)$
493/543	-17/33	$50[99 \times 181]^{-1/2}$	117/543	$-i259/(1086\sqrt{2})$

substances in the magnetically ordered state. If we consider a strain along the z axis then there will be introduced into the potential of Eq. (2) a term V_2 ,

$$V_2 \doteq -72qea^{-3}r^2(\sum P_2(\theta))\delta, \quad (55)$$

where q is the charge on the adjacent anions, a is the lattice spacing, and we have included the effect of only the six nearest anions. Taking $a=5.7A^\circ$, $\langle r^2 \rangle_{4f}=0.7a_0^2$ (Freeman and Watson²⁰), and $\langle \sum P_2 \rangle_J = \frac{1}{3}$ (Table I) we obtain a contribution to the energy

$$\delta E \doteq -10^4 \delta \text{ cm}^{-1}. \quad (56)$$

In (56) we have used wave-number units (multiply by hc to get energy). For $\delta \doteq 10^{-4}$ Eq. (56) gives a contribution to the energy which is less than about 1% of the over-all crystalline splitting but of the same order as the dipole-dipole and quadrupole-quadrupole contributions.

According to Eq. (56) the distortion will cause a lowering of the energy per unit volume by an amount $-4 \times 10^{10} \delta$ ergs cm^{-3} but to this must be added the increase in the elastic energy $\frac{1}{2}Y\delta^2$ where Y is the Young's modulus. The energy minimum requirement then gives for equilibrium $\delta=4 \times 10^{10}Y^{-1}$, or $Y=4 \times 10^{14}$ dyn/ cm^2 for $\delta=10^{-4}$. This value of the Young's modulus is surely one or two orders magnitude too high. Therefore, (55) and (56) give too great a lowering of the energy under distortion by one or two orders of magnitude, according to our assumptions. If this is true, then the distortion effects are completely negligible. It is difficult to understand why K_2 should be so much less than (55) would indicate; however, in the preceding section we already found that ascribing the crystalline field to charge distributions centered on the neighboring anions led to too large a ratio of K_4/K_6 by about a factor of 6, so any estimate of K_2 based on the same model is very uncertain. We then neglect distortion and find that we can find a satisfactory explanation of the observations made

TABLE XVI. The energy and moment values for the $[101]$ ground state of Er^{3+} for various assumed values of $(5.0B/\Delta) \equiv x$ where $\Delta = E(\Gamma_8) - E(\Gamma_7)$. The first entry is the depression of the energy below $E(\Gamma_8)$ in units of Δ , the second is the expected moment value in units \hbar .

$x=1$	4	6	10
-1.8, 3.2	-5.0, 4.3	-7.4, 4.9	-12.1, 5.8

³⁷ See, however, the discussion at the end of this section concerning evidence for the existence of noncubic distortion in the phosphides.

so far.³⁷ The need for further experimental observations should be clear.

Magnetic Effects

The magnetic energy per dipole is

$$E^D = \frac{1}{2} \sum_j [\mathbf{u}_i \cdot \mathbf{u}_j - 3(\mathbf{u}_i \cdot \mathbf{r}_{ij})(\mathbf{u}_j \cdot \mathbf{r}_{ij})r_{ij}^{-2}]r_{ij}^{-3}. \quad (57)$$

In the ferromagnetic case we have the well-known result, $E_F^D = \frac{1}{2}N\mu^2(-4\pi/3 + \mathfrak{N})$, where N is the number of dipoles per unit volume, and \mathfrak{N} , the demagnetization factor, may be neglected for an unmagnetized sample. We are interested in E^D for antiferromagnetic patterns of the dipoles wherein all the dipole moments of atoms in a given (111) plane are parallel, but are antiparallel to those in the two adjacent (111) planes. For these patterns we see from symmetry that if $\pm(k, l, m)$ are the direction cosines of the moments then E^D is given by

$$E_A^D(k, l, m) = -3\mu^2(kl + km + lm) \sum_j \pm x_{ij} z_{ij} r_{ij}^{-5}, \quad (58)$$

where the plus or minus sign is chosen depending on whether the moment of atom " j " is parallel or antiparallel to that of atom " i ". The lattice sum in Eq. (58) has been given by Cohen and Keffer³⁸ (along with many more lattice sums) who give its value as

$$NS^{13}(444) = \sum \pm x_{ij} z_{ij} r_{ij}^{-5} = -1.20N. \quad (59)$$

Therefore Eq. (58) becomes

$$E_A^D(k, l, m) = 3.6(kl + km + lm)N\mu^2, \quad (60)$$

and for comparison purposes we give the ferromagnetic energy

$$E_F^D = -2.1N\mu^2. \quad (61)$$

According to (60), E_A^D attains its maximum value of $3.6N\mu^2$ when the dipoles are in the $\pm[111]$ direction, and its minimum value of $-1.8N\mu^2$ when the dipoles are perpendicular to the $[111]$ direction.

It is clear for the "flopside" arrangement in which the moments are alternately in the $+Z$ and $+X$ direction that E^D is the mean of the ferromagnetic value and $E_A^D(1/\sqrt{2}, 0, -1/\sqrt{2})$,

$$E_{11}^D = -1.95N\mu^2. \quad (62)$$

For the second-half rare-earth phosphides we may neglect the small differences in lattice spacings and we have

$$N\mu^2 = 10^{-2}(\mu/\mu_B)^2 \text{ cm}^{-1}, \quad (63)$$

where μ_B is the Bohr magneton, and we have expressed energy in (63) in wave-number units (multiply by hc for other units).

It is convenient for our discussion to write the exchange energy per particle as

$$E^{\text{ex}} = -\frac{1}{2} \sum_j \mathcal{J}_{ij}' \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle, \quad (64a)$$

$$= -\frac{1}{2} (a_e \mathcal{J}_e' + a_0 \mathcal{J}_0') \langle \mathbf{S}_i \rangle^2, \quad (64b)$$

³⁸ M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955).

where g_e' is the sum of g_{ij}' over all atoms "j" lying in even numbered (111) planes (the plane containing "i" being zero, adjacent planes, ± 1 , etc.) and g_o' is the corresponding sum over the odd planes. We now write $E^{\text{ex}} + E^D$ for HoP having the flopside pattern, E_{fi} , the antiferromagnetic pattern, E_A , and the ferromagnetic pattern, E_F ,

$$E_{fi} = -\frac{1}{2}g_e'\langle \mathbf{S}_i \rangle^2 - 1.95N\mu^2, \quad (65a)$$

$$E_A = -\frac{1}{2}g_e'\langle \mathbf{S}_i \rangle^2 + \frac{1}{2}g_o'\langle \mathbf{S}_i \rangle^2, \quad (65b)$$

$$E_F = -\frac{1}{2}g_e'\langle \mathbf{S}_i \rangle^2 - \frac{1}{2}g_o'\langle \mathbf{S}_i \rangle^2 - 2.1N\mu^2. \quad (65c)$$

We shall show later that the quadrupole-quadrupole interaction will not substantially affect our results. The condition that (65a) be less than (65b) or (65c) now gives

$$0.15N\mu^2 < -\frac{1}{2}g_o'\langle \mathbf{S}_i \rangle^2 < 1.95N\mu^2. \quad (66)$$

Thus $g_o' < 0$ (antiferromagnetic coupling), and from (63) using $\mu = 8.8\mu_B$,¹¹

$$0.1 \text{ cm}^{-1} < -\frac{1}{2}g_o'\langle \mathbf{S}_i \rangle^2 < 1.5 \text{ cm}^{-1}. \quad (\text{HoP}) \quad (66)$$

Now using the rough estimate $\frac{1}{2}g_e'\langle \mathbf{S}_i \rangle^2 \doteq \frac{3}{2}kT_c = 6 \text{ cm}^{-1}$, we see that it is only necessary to assume that g_o' is negative and less than about a fourth of g_e' to understand the flopside pattern of the HoP ground state. It is easy to see that the antiferromagnetic pattern of ErP would still lie lowest since its magnetic energy already has the low value $-1.8N\mu^2$ and so it can only lower by $0.3N\mu^2$ in going to the ferromagnetic state.

TbP is in the state with maximum magnetic energy, $+3.6N\mu^2$. If its spins were aligned $\pm[1, 1, -1]$, the magnetic energy (60) would be lowered to $-1.2N\mu^2$. The crystalline energy (preceding section) and its quadrupole-quadrupole energy would be unaffected by such a transition. Hence, except possibly for a crystalline distortion effect which we have argued is probably very small³⁷ the observed alignment along $[111]$ must be due to anisotropic exchange integrals. With this assumption we have

$$\frac{1}{2}\langle \mathbf{S}_i \rangle^2 [g_e'(111) - g_o'(111) - g_e(11-1) + g_o'(11-1)] > 4.8N\mu^2. \quad (67)$$

Inserting $\mu = 6.2\mu_B$ the right-hand side of (67) is 2 cm^{-1} , as compared with the estimate

$$\frac{1}{2}\langle \mathbf{S}_i \rangle^2 [g_e'(111) - g_o'(111)] = 9.5 \text{ cm}^{-1}.$$

Thus, (67) would imply possibly about 20% anisotropy in g' for Tb.

From the failure of TbP to be ferromagnetic we have

$$-g_o'(111)\langle \mathbf{S}_i \rangle^2 > 5.7N\mu^2 \quad (\text{TbP}). \quad (68)$$

Equation (68) gives $-g_o'(111) > 0.5 \text{ cm}^{-1}$ (TbP) when we insert $\mu = 6.2\mu_B$ and $|\langle \mathbf{S}_i \rangle| \doteq 2$; whereas (66) gives $-g_o'(100) < 1.0 \text{ cm}^{-1}$ (HoP). Thus, the same value of g_o' could account for the TbP and HoP patterns.

In terms of the simple model in which we assume that

appreciable interactions exist only between nearest neighbors, g_n' , and next-nearest neighbors, g_{nn}' , we have $g_e' = 6g_n'$, $g_o' = 6g_n' + 6g_{nn}'$. It is only necessary to assume that g_n' is ferromagnetic, g_{nn}' antiferromagnetic and slightly larger in magnitude than g_n' to account for our results. The estimates above lead to $-1.0 \text{ cm}^{-1} < 6(g_{nn}' + g_n') < -0.5 \text{ cm}^{-1}$, $6g_n' \doteq 4 \text{ cm}^{-1}$, $g_n' \doteq 0.8g_{nn}'$.

It is of interest to see how large an external magnetic field is required to stabilize the ferromagnetic state. If \mathfrak{B} is the component of the field in the moment direction then for the ferromagnetic state to lie lowest for TbP \mathfrak{B} must be larger than the value determined by

$$-g_o'(111) = [3.6N\mu^2 + \mathfrak{B}\mu] \div \langle \mathbf{S}_i \rangle^2, \quad (\text{TbP}) \quad (69a)$$

$$= (0.33 + 0.7\mathfrak{B}) \text{ cm}^{-1}, \quad (\text{TbP}) \quad (69b)$$

where in (69b) \mathfrak{B} is in units of 10^4 G , and in (69) we have assumed that the crystallites are of roughly spherical shape. Similarly, for HoP and ErP we obtain

$$-g_o'(100) = 2(\mathfrak{B}\mu - 1.95N\mu^2) \div \langle \mathbf{S}_i \rangle^2, \quad (\text{HoP}) \quad (70a)$$

$$= (2.6\mathfrak{B} - 1.0) \text{ cm}^{-1} \quad (\text{HoP}) \quad (70b)$$

$$-g_o'(110) = (\mathfrak{B}\mu - 1.8N\mu^2) \div \langle \mathbf{S}_i \rangle^2, \quad (\text{ErP}) \quad (71a)$$

$$= (2.9\mathfrak{B} - 0.65) \text{ cm}^{-1}. \quad (\text{ErP}) \quad (71b)$$

If $-g_o' \doteq 1 \text{ cm}^{-1}$ then according to (71b) it would require a magnetic field only of the order of 6 kG applied along a $[110]$ axis to bring about the ferromagnetic state in ErP, and fields of the order of 8 and 20 kG to make HoP and TbP ferromagnetic. Since the quadrupole energy of the "flopside" pattern is somewhat higher than that of the ferromagnetic pattern there is a small correction to (70b).

The electric quadrupole-quadrupole contribution to the energy is not completely negligible relative to that of the magnetic dipole-dipole. It is sufficient for our purposes to consider the interaction of quadrupoles having common symmetry axes or perpendicular symmetry axes. From elementary electrostatics the interaction energy per quadrupole in the former case is

$$E_{11}^Q = (1/8)Q^2 \sum_j 3r_{ij}^{-5} [35(z_{ij}/r_{ij})^4 - 30(z_{ij}/r_{ij})^2 + 3], \quad (72a)$$

and in the latter case

$$E_{11}^Q = (1/8)Q^2 \sum_j 3r_{ij}^{-5} [35(z_{ij}x_{ij}/r_{ij}^2)^2 - 5(z_{ij}^2 + x_{ij}^2)/r_{ij}^2 + 1], \quad (72b)$$

where Z and X indicate the symmetry axes of the quadrupoles and

$$Q = e\langle r^2 \rangle_{4f} \langle \sum P_2(\theta) \rangle, \quad (73)$$

is the expected value of the quadrupole moment of a given rare earth in the crystal. The expected value indicated in Eq. (57) refers to the actual state of the ion in the crystal, not that for $M_J = J$ given in Table I. Summing the contributions of (72a) or (72b) gives

$$E^Q = (Q^2/8)(\sqrt{2}/a)^5 F, \quad (74)$$

where a is the lattice spacing. Summation over the sets of three nearest neighbors gives an estimate of F for quadrupoles along the $[100]$, $[111]$, and $[110]$ axes of -31 , $+20$, and $+19$, respectively, and for the "flopside" pattern $F_{11} = -18.5$. The neglect of further neighbors introduces about a 10% error in the value of F . We see that the flopside pattern has a higher quadrupole energy than the (100) parallel quadrupoles. Freeman and Watson²⁰ give $\langle r^2 \rangle_{4f} = 0.75, 0.70, 0.67$ for the tripositive ions of Tb, Ho, and Er, respectively. Inserting these values and the lattice constant for the phosphides yield

$$(Q^2/8)(\sqrt{2}/a)^5 = 0.6 \langle \sum P_2(\theta) \rangle^2 \text{ cm}^{-1}. \quad (75)$$

Inserting $\langle \sum P_2(\theta) \rangle^2 = (2/15)^2$ as an overestimate for Ho (Table I) we obtain for the difference of the "flopside" and the antiferromagnetic (or ferromagnetic) quadrupole energies for HoP, $E_{11}^Q - E_{11}^Q(100) = 0.24 \text{ cm}^{-1}$, which is small in comparison with the dipole contribution $E_F^D - E_A^D = 1.5 \text{ cm}^{-1}$, Eq. (66), justifying our neglect of E^Q in our previous discussion.

Finally, we come back to the question of distortion. A careful examination of the data by Wilkinson *et al.* yielded an indication that the moments in HoP may not be strictly along the z or x axes, say, but rather that the angle between the spin directions in adjacent (111) planes has been decreased to about 87° . It is easy to show that with the assumption of cubic symmetry and isotropic exchange interactions this angle should be slightly increased beyond 90° in HoP. If we assume the reality of this decreased angle then it provides rather clear-cut evidence for not inappreciable non-cubic distortion in these substances.³⁹

The powder data does not indicate in which direction the moments are tipped with respect to the cube edge. However, the assumption that in the phosphides there is a distortion along the $[111]$ direction is attractive for several reasons. Such a distortion (a) will yield a tip of the HoP moments away from the cube edges towards the $[111]$ direction, (b) in accord with observation, will leave the moments of TbP and ErP in the $[111]$ direction and the (111) plane, respectively, (c) will lower the crystalline energy in the $[111]$ direction

³⁹ Nonisotropic exchange could also lead to such a result; however, such effects are probably not sufficiently large to yield a tip angle of the order of 2° .

relative to that of the $[1\bar{1}1]$ direction in TbP, making it unnecessary to invoke a sizable nonisotropic exchange as in Eq. (67), and (d) it is very likely to reduce the anomalously large V_6/V_4 ratio which was found necessary in the preceding section to account for the moment values and directions of the phosphides when distortion was neglected.

If we assume such a distortion then we must add a term $V_2 = \sum v_2(r) P_2(\theta_{111})$ to the right-hand side of Eq. (2), where θ_{111} is the angle between the radius vector of a $4f$ electron and the $[111]$ direction. In Eq. (10) there will be added a term $K_2(xy+xz+yz)$, where $K_2 = \langle v_2(r) \rangle \times \langle \sum P_2(\theta) \rangle_f$. K_2 must be taken to be negative in HoP, and since according to Table I the quadrupole moment of Ho^{3+} is negative we conclude that $\langle v_2(r) \rangle$ is positive. If we assume that the sign of the quadrupole potential is correctly given by considering only the nearest neighbor anions then the distortion is an elongation along the $[111]$ direction. With the addition of the V_2 term to Eq. (10) the bottom (in the case of HoP) will be shifted away from the $[001]$ direction an angle $\theta = K_2 \div (2\sqrt{2}K_4)$, where we have neglected V_6 . For $\theta = \sqrt{2}/40$ we get $K_2 \doteq (1/10)V_4$, and an over-all V_2 splitting roughly 20% of that due to V_4 .

A recomputation of the crystalline field parameters along the lines of Sec. VII but including V_2 is now being carried out in collaboration with F. Specht, and we expect to report on the results in the near future.

VIII. CONCLUSION

We have presented a theory of the effect of strong crystalline fields of cubic symmetry on the magnetic ordering properties of rare-earth compounds. In the last two sections we have applied the theory to the rare-earth phosphide data, obtaining satisfactory agreement except for an indication that noncubic terms in the crystalline potential, which we discuss briefly, may be of importance.

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