

Phenomenological Discussion of Magnetic Ordering in the Heavy Rare-Earth Metals

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The rare-earth metals Gd-Tm have similar crystal structures and their magnetic properties have been partially evaluated by a number of techniques. The magnetic order is complicated, showing several phases in some cases and differing considerably in the various elements. These various orderings can be explained on a molecular field (Bragg-Williams) model if a long-range oscillatory exchange interaction whose minimum Fourier component $J(\mathbf{q})$ is at $q \neq 0$, small quadrupole-quadrupole interaction, and anisotropy are included. A crystal field calculation gives axial and hexagonal anisotropies which vary along the series in a way which accounts for the observed structures. In Tb, Dy, and Ho the moment is forced into the basal plane and the order is a spiral at high T , becoming ferromagnetic at low T because of the hexagonal anisotropy. The quadrupole-quadrupole interaction determines the change of pitch with T . In Er and Tm the moment is forced along the c axis and the observed order, with sinusoidal variation of this moment, is found to have lowest free energy at high T . As T is lowered, transitions to an anti-phase domain structure and then to ferromagnetism are predicted.

I. INTRODUCTION

FROM recent measurements on single crystals of Dy, Ho, and Er the actual nature of the rather complicated magnetic properties of these metals has become apparent. There are noticeable similarities in the properties of all the elements from Gd to Tm in the second half of the rare-earth series which crystallize in a simple hcp structure. From the little data available on Ce¹ and Nd² at the beginning of the series it appears that these metals have rather different ordering properties. The f shells are markedly bigger than those in the second half of the series, and it is therefore likely that the effects of crystalline electric fields and direct overlap interionic interactions are relatively more important. It is not proposed to discuss them here, but to restrict our attention to the heavier elements.

It is the purpose of this paper to briefly review the information at present available and to outline a phenomenological theory which appears to describe qualitatively the observed effects in terms of a few parameters. The nature and magnitude of the interactions involved in the model do not appear unreasonable. The essential requirements of the model have already been put forward by a number of other authors, and these basic ideas are only synthesized and extended here.

II. EXPERIMENTAL RESULTS

There are four types of measurement which have been performed on some of these metals and which display the effects of magnetic order:

- (a) Specific heat showing anomalies at the ordering transitions.

- (b) Neutron diffraction showing the actual ordering of the magnetic moments.
 (c) Bulk magnetic moment and susceptibility measurements, showing critical fields which induce a change in the type of magnetic ordering.
 (d) Electrical resistivity showing scattering of conduction electrons off the spin disorder.

In general there are at least two temperature regions of magnetic order. At a Néel point T_N , the paramagnetism changes to an ordering which shows a single sinusoidal variation along the c axis of the moments which are ordered within the a - b planes. At a lower temperature T_C , this changes to a more normal ferromagnetic ordering. In some cases there is an intermediate temperature below which the variation of the order along the c axis remains periodic but which is no longer purely sinusoidal. The variation in this region is often complicated but probably approximates in some cases to a square wave antiphase domain arrangement with several layers pointing moments one way, followed by the same number pointing the opposite way.

The details of the magnetic structures already known³⁻¹⁹ are summarized in Table I. The most

³ L. D. Jennings, R. M. Stanton, and F. H. Spedding, *J. Chem. Phys.* **27**, 909 (1957).

⁴ R. M. Stanton, L. D. Jennings, and F. H. Spedding, *J. Chem. Phys.* **32**, 630 (1960).

⁵ W. C. Koehler, E. O. Wollan, M. K. Wilkinson, and J. Cable, Rare-Earth Research Developments Conference, Lake Arrowhead, California, October, 1960 (unpublished), Paper III-5.

⁶ S. Arajs and R. V. Colvin, *J. Appl. Phys.* **32**, 336S (1961).

⁷ F. H. Spedding, S. Legvold, J. Doane, and L. D. Jennings, *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 368.

⁸ M. Griffel, R. E. Skochdopole, and F. H. Spedding, *J. Chem. Phys.* **25**, 75 (1956).

⁹ M. K. Wilkinson, W. C. Koehler, E. O. Wollan, and J. Cable, *J. Appl. Phys.* **32**, 48S (1961).

¹⁰ D. R. Behrendt, S. Legvold, and F. H. Spedding, *Phys. Rev.* **109**, 1544 (1958).

¹¹ P. M. Hall, S. Legvold, and F. H. Spedding, *Phys. Rev.* **117**, 971 (1960).

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¹ M. K. Wilkinson, H. R. Child, C. J. McHargue, W. C. Koehler, and E. O. Wollan, *Phys. Rev.* **122**, 1409 (1961).

² W. C. Koehler, E. O. Wollan, H. R. Child, and M. K. Wilkinson, Oak Ridge National Laboratory Report ORNL-2501, 41, 1958 (unpublished).

TABLE I. Magnetic ordering in the heavy rare-earth metals. I—paramagnetic phase; θ is the Curie-Weiss constant. IIA and IIB—intermediated phases with sinusoidal moment variations; the angles \angle are those between the moment components in the plane $\perp c$ in adjacent layers. III—low temperature phase, usually ferromagnetic; μ_0 is the saturation moment. Transition temperatures are given as determined by experiments of type (a), (b), (c) of Sec. II.

	I (c) para	T_N	IIA	T'	IIB	T_C	III	μ_0
Tb ^a	$\theta = 236$	227.7(a,c)			spiral $\mu \perp c$	220(a)	ferro $\mu \perp c$ transition at 2.4°K(a)	9.1(b) 9 Th
Dy ^b	$\theta = 154$ $\theta_{11} = 121$ $\theta_{\perp} = 169$	174(a) 179(b,c)	spiral $\mu \perp c$ $\angle 43^\circ \rightarrow 35^\circ$	140(b)	spiral $\mu \perp c$ plus second harmonic $\angle 35^\circ \rightarrow 26^\circ$? small $\mu \parallel c$?	83.5(a) 87(b)	ferro $\mu \perp c$	9.5(b) 10.2(c) 10 Th
Ho ^c	$\theta = 85$ $\theta_{\perp} = 88$	131.6(a) 125(b)	spiral $\mu \perp c$ $\angle 50^\circ \rightarrow 36^\circ$	35(b)	nonsinusoidal arrangement $\mu \perp c$ $\angle \sim 36^\circ$ spacing 10 layers small $\mu \parallel c$ ferro	19.4(a) 40(b,c)	ferro $\mu \perp c$ only induced by field (b)	spiral 9.5(b) ferro 5.1(c) 10 Th
Er ^d	$\theta = 42$ $\theta_{11} = 61.7$ $\theta_{\perp} = 32.5$	84(a,c) 80(b)	sin $\mu \parallel c$	53.5(a) 52(b)	sin $\mu \parallel c$ + harmonics spiral $\mu \perp c$, $\angle 51^\circ \rightarrow 43^\circ$	19.9(a) 20(b)	ferro $\mu \parallel c$ spiral $\mu \perp c$, $\angle = 41^\circ$	8.0(b) \parallel 4.1(b) \perp 9 Th
Tm ^e	$\theta = 20$	53(b) 50(c)			sinusoid $\mu \parallel c$?	20(c)	ferro?	6.8(c) 7 Th

^a See references 3-7.

^b See references 8-11.

^c See references 5, 12, 13.

^d See references 13-16.

^e See references 5, 17-19.

striking fact is that there is a very considerable anisotropy between the directions of the c axis and the basal plane, while there is a relatively much smaller hexagonal anisotropy in the plane. The elements Tb, Dy, and Ho have most of their ordered moment in the plane while Er and Tm have most of theirs along the c axis. The exchange effects which try to impose a harmonic variation in the spin order are thus able to produce a true spiral for moments in the plane which have two degrees of freedom, but only a sinusoidal variation of magnitude of the moment along the axis. Because of this difference in dimensionality it is necessary to treat these two cases separately.

In every case the maximum observed moment on an atom site approaches the value λJ , where λ is the Landé factor and J the total orbital momentum of the lowest multiplet in the trivalent rare-earth ion.

III. INTERACTIONS IN THE CRYSTALS

The high-temperature susceptibilities of the metals agree well with the value $\chi = N\beta^2\lambda^2J(J+1)/3kT$ appropriate to an assembly of tripositive rare-earth ions. Thus it would seem to be a good first approximation

¹² B. C. Gerstein, M. Griffel, L. Jennings, R. Miller, R. Skochdopole, and F. H. Spedding, J. Chem. Phys. **27**, 394 (1957).

¹³ S. Legvold, Rare-Earth Research Developments Conference, Lake Arrowhead, California, October, 1960 (unpublished), Paper III-4.

¹⁴ R. E. Skochdopole, M. Griffel, and F. H. Spedding, J. Chem. Phys. **23**, 2258 (1955).

¹⁵ J. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, J. Appl. Phys. **32**, 49S (1961).

¹⁶ J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **100**, 1595 (1955). See also reference 13.

¹⁷ B. L. Rhodes, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1547 (1958).

¹⁸ D. D. Davis and R. M. Bozorth, Phys. Rev. **118**, 1543 (1960).

¹⁹ W. E. Henry, J. Appl. Phys. **31**, 3235 (1960).

to consider them as such an assembly bathed in a sea of conduction electrons. The ion cores are subjected to various interactions with the crystal lattice, the conduction electrons and among themselves which are responsible for their magnetic properties. The main interactions are:

(1) Exchange interactions between the conduction electrons c and the localized ionic electrons f . While the conduction electron is on a particular atom the coupling is like an intra-atomic exchange, being summed over all the f electrons.

$$\sum_f K s_c \cdot s_f = K s_c \cdot S = K (s_c \cdot J) \nu, \quad (1)$$

ν is obtained by projecting the total spin S of the ion on to the total angular momentum J which is a good quantum number.²⁰

$$\nu = \lambda - 1 = 1/(8 - 2S) \text{ in this region.} \quad (2)$$

This interaction causes the magnetic disorder resistivity. In second order perturbation theory²¹ it also causes an effective interaction between ionic moments, which under the assumption of a spherical Fermi surface has the form

$$(9/2)\pi K^2 \nu^2 (\mathbf{J}_i \cdot \mathbf{J}_j) F(2k_0 R_{ij}) / E_0, \quad (3)$$

where E_0 is the Fermi energy, k_0 the electron wave vector there and $F(x) = (x \cos x - \sin x)/x^4$. The value of K , coming from the overlap between conduction and ionic electrons, probably does not vary very much along the series in spite of the contraction of the $4f$

²⁰ R. Brout and H. Suhl, Phys. Rev. Letters **2**, 387 (1959). G. S. Anderson and S. Legvold, Phys. Rev. Letters **1**, 322 (1958). P.-G. de Gennes, Compt. rend. **247**, 1836 (1958).

²¹ M. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954). K. Yosida, *ibid.* **106**, 893 (1957).

shell. The properties of the conduction electrons are probably also fairly constant, making the main variation along the series proportional to $(\lambda-1)^2 J^2$ which falls rapidly in general agreement with the observed trend. The most important property of this form of exchange interaction is its long-range and oscillatory variation. Such oscillations lead naturally to the oscillatory variations observed in the ordered structures.²² In particular if the Fourier transform

$$g(\mathbf{q}) = \int g(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \quad (4)$$

has a minimum at a nonzero value of \mathbf{q} , the molecular field treatment gives a spin order with this wave variation.

(2) Crystalline electric fields caused by the conduction electrons and ion cores. These tend to align the charge clouds and hence the magnetic moments of the f electrons relative to the crystal axis. From calculations on ions in ionic crystals²³ it is known that for a hexagonal crystal the potential takes the form

$$V = V_2^0 \alpha Y_2^0(\mathbf{J}) + V_4^0 \beta Y_4^0(\mathbf{J}) + V_6^0 \gamma Y_6^0(\mathbf{J}) + V_6^6 \gamma Y_6^6(\mathbf{J}). \quad (5)$$

The $Y_l^m(\mathbf{J})$ are operator equivalents of spherical harmonics and they and the numerical constants α, β, γ are defined in reference 23. The V_l^m are constants which depend on the structure. Assuming that the effect of all except the nearest neighbor ions is screened out by the conduction electrons and putting $+3e$ charges at these positions, one finds²⁴

$$\begin{aligned} V_2^0 &= -300\langle r^2 \rangle, & V_6^0 &= +15\langle r^6 \rangle, \\ V_4^0 &= -60\langle r^4 \rangle, & V_6^6 &= -90\langle r^6 \rangle, \end{aligned}$$

in cm^{-1} with $\langle r^n \rangle$ in Å^n . (V_2^0 would be zero for a perfect hcp lattice. (The author is particularly indebted to Dr. G. Trammell for pointing out this and other properties of the crystal field.) This model is certainly very crude and only gives an indication of the size and sign of the effect.

(3) Direct interactions between f electrons on nearby ions which depend on the charge cloud and spin orientation. If the ions are not regarded as spherically symmetric as in the above calculation and the deviations are expanded in spherical harmonics, the most important effect is quadrupole-quadrupole interaction.²⁵

²² A. Yosimori, J. Phys. Soc. (Japan) **14**, 807 (1959). A. Herpin, P. Mériel, and J. Villain, Compt. rend. **249**, 1334 (1959). A. Herpin and P. Mériel, Compt. rend. **251**, 1450 (1960). J. Villain, J. Phys. Chem. Solids **11**, 303 (1959). T. A. Kaplan, Phys. Rev. **116**, 888 (1959).

²³ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **218**, 553 (1953).

²⁴ R. J. Elliott, thesis, Oxford University, 1952 (unpublished).

²⁵ B. Bleaney, Proc. Phys. Soc. (London) **17**, 113 (1961).

For ions with charge clouds oriented generally, this has a very complicated angular dependence.

$$\sum_{m,n,p,q}^{j_i} \frac{e^2 \langle (r^2)_{\text{av}} \rangle^2}{R_{ij}^5} J_i^m J_i^n J_j^p J_j^q C_{ij}(mn, pq), \quad (7)$$

where i, j represent ions whose distance apart is R_{ij} and m, n, p, q represent components x, y, z . A reasonable magnitude of this effect would be 10°K .

The Coulomb interaction between f electrons on different ions also gives a direct exchange interaction if there is overlap. However, because of the correlation between the direction of the spins and the highly anisotropic charge clouds the coupling can no longer be considered to have the simple cosine form $(\mathbf{J}_i \cdot \mathbf{J}_j)$ but has terms containing higher powers of J including some similar to (7).

IV. CRYSTAL FIELD ANISOTROPY

Close to the ordering temperatures the susceptibilities of these substances still have the free-ion values, and at low temperatures the ordered moments approach the maximum λJ . This indicates that the exchange interactions must dominate over the crystal fields, while the oscillatory behavior of the order indicates that these exchange interactions are long range and probably of type 1. The crystal field effects show up predominantly as an anisotropy which is dominantly axial. The sign of α shows²³ how the quadrupole of the f electrons is related to the direction of \mathbf{J} :

$$\sum (3z_f^2 - r_f^2) = \alpha [3J_z^2 - J(J+1)]. \quad (8)$$

For Tb, Dy, and Ho, α is negative, while for Er and Tm it is positive. The fact that the moments of the first three are predominantly $\perp c$ while the last two are $\parallel c$ indicates that in all cases the charge clouds wish to lie largely in the plane. (The author is indebted to Dr. E. O. Wollan for pointing out this and other consequences of anisotropy.) If V_2^0 is the dominant effect a negative value would produce this effect, although the higher order V 's and some of the interactions of type 3 will also contribute. Negative values of $V_4^0 \beta$ and $V_6^0 \gamma$ would tend to make the direction of \mathbf{J} along the c axis while positive values tend to make the direction at some angle to that axis but not in the basal plane. This may account for the fact that some of the moments do point in intermediate directions.

The tendencies produced by fields of the sign evaluated on the model in Sec. III are given in Table II. The general trend of the experimental results is reproduced if the V_2^0 term dominates. Only in Tm do all the effects combine to predict a definite $\mu \parallel c$. In the three elements with μ predominantly in the plane, the tendency towards having some moment $\parallel c$ increases in the sequence Dy-Ho-Tb.

Magnetic fields as great as 20 kgauss seem to have no effect in any attempt to pull the ordered moments out

TABLE II. Properties of rare-earth ions Tb-Tm. J , λ , etc., relate to relative magnetic moments and exchange. $V_{2\alpha}$, etc., show tendencies of crystal field anisotropies. $2\alpha J^2$, etc., give relative magnitudes of these anisotropies.

	Tb	Dy	Ho	Er	Tm
J	6	15/2	8	15/2	6
λ	3/2	4/3	5/4	6/5	7/6
$(\lambda-1)^2 J(J+1)$	10.5	7.1	4.5	2.55	1.16
$S(S+1)$	12	8.75	6	3.75	2
$V_{2\alpha}$	\perp	\perp	\perp	\parallel	\parallel
$V_{4\beta}$	\parallel	\angle	\angle	\parallel	\parallel
$V_{6\gamma}$	\parallel	\angle	\parallel	\angle	\parallel
$V_{6\gamma}$	30	0	30	0	30
$2\alpha J^2$	0.73	0.71	0.28	0.29	0.73
$8\beta J^4$	1.27	4.48	2.16	3.36	1.71
$16\gamma J^6$	0.84	2.9	4.7	5.9	4.2

of the preferred directions relative to the c axis. This indicates that while the crystal field effects must be small with respect to the exchange they must nevertheless be of the order of tens of $^\circ\text{K}$ as predicted by the crude calculation in Sec. III.

The hexagonal anisotropy induced by the V_6^6 term tries to align the moment components in the plane relative to the hexagonal axes. For the sign predicted in the model these easy directions are given in Table II in terms of the angles to the hexagonal axes. The two known results, on Dy⁸ and Ho,¹² are predicted correctly.

The relative magnitudes of the anisotropies are also given in Table II when the maximum total moment is involved. This must be reduced in the case of the planar hexagonal anisotropy if the moment does not point wholly in the plane as in the case in Er. There the planar component 4.1 is less than half $\lambda J=9$ and the number should be reduced by $(4.1/9)^6$ to give 0.07, i.e., an anisotropy some 50 times smaller than that in Dy. No anisotropy in the plane has been detected in Er.

The temperature dependence of the hexagonal planar anisotropy is also of some interest since it will be shown that it sometimes controls the ferrospectral transition for moments $\perp c$. For spherical harmonics of order n the axial anisotropy energy in the theory of Zener,²⁶ Van Vleck,²⁷ and Keffer²⁸ varies like $M^{\frac{1}{2}n(n+1)}$, where M is the relative magnetization. Relative to the plane, however, the term

$$\sin^6\theta \cos 6\phi, \quad (9)$$

varies like M^6 on the classical theory since M is proportional to the average value of $\sin\theta$.

V. A SIMPLIFIED HAMILTONIAN

The interactions cited in Sec. III are complicated, but it can be seen that all the ingredients necessary to

account for the observed data are present. In this section we will write down a simplified Hamiltonian which includes all these complications and yet can be solved in the molecular field approximation.

If the crystal fields were the dominant effects they would determine the ionic ground states as in salts. For example in a strong axial field the lowest doublet might be $J_z = \pm J$. This doublet could be considered to have a fictitious spin σ of one-half. On projecting an interaction $\mathbf{J}_i \cdot \mathbf{J}_j$ like (3) on to this manifold it will become anisotropic in the form $\sigma_i^z \sigma_j^z$. In this problem although the crystal fields are not dominant they will tend to produce such an anisotropy in the effective exchange interactions. Thus we write

$$\sum_{ij} A_{ij} J_i^z J_j^z + B_{ij} (J_i^x J_j^x + J_i^y J_j^y). \quad (10)$$

Because of the sign of the anisotropy, A will be larger in Er and Tm, B in Tb, Dy, and Ho.

In all the elements discussed it is found that the planar layers $\perp c$ are always ferromagnetic. We may simplify the problem further by summing in layers and looking at the effective interactions between layers. If μ_x etc. are the maximum moments in the coordinate directions and M_x is the relative saturation of that component the effective interaction can be written

$$\sum_i \sum_n A_n' \mu_z^2 M_x^i M_x^{i+n} + B_n' \mu_x^2 (M_x^i M_x^{i+n} + M_y^i M_y^{i+n}). \quad (11)$$

It can be seen from the work of Yoshimori and others²² that in order to reproduce spiral effects, the smallest number of parameters that may be used in (11) is three. Accordingly we arbitrarily restrict interactions to those within a plane and between nearest, and next nearest neighbor planes, i.e., $n=0, 1, 2$, and for convenience we assimilate the μ^2 into the effective exchange parameters, i.e., $A_n' \mu_x^2 = A_n$, etc.

Since the effects of the crystal fields are more strongly felt at low temperatures, it is possible that the relative size of the A 's and B 's should be allowed some variation with temperature. Since the amount of anisotropy in the charge clouds will depend on the orientation of \mathbf{J} it seems reasonable to include this variation by letting the parameters vary with M . Certainly the direct exchange and quadrupole-quadrupole effects [like those in (7)] which are biquadratic in the \mathbf{J} , will introduce energies into (11) biquadratic in M . Thus the simplest way to introduce these effects would be to let

$$B_n = B_n - C_n M^2.$$

This has essentially the same kind of effect as the so-called magnetocrystalline energy which Kittel²⁹ shows to make possible the exchange inversion transitions. It will be shown in the next section only one further parameter of this form is necessary to obtain qualitatively correct results.

²⁶ C. Zener, Phys. Rev. **96**, 1335 (1954).

²⁷ J. H. Van Vleck, J. phys. radium **20**, 124 (1959).

²⁸ F. Keffer and T. Oguchi, Phys. Rev. **117**, 718 (1960).

²⁹ C. Kittel, Phys. Rev. **120**, 335 (1960).

VI. MOMENTS IN PLANE

Following the discussion of the last section we now consider the case when the moments are confined in the planes perpendicular to the c axis. Since the moments have, apart from the hexagonal anisotropy, freedom of rotation in the plane, we assume that the moments in each layer are aligned at angles which vary from layer to layer to give a spiral along the c axis. The exchange energy per atom, if the moment

$$\mu_n^x = \mu M \cos n\alpha, \quad \mu_n^y = \mu M \sin n\alpha, \quad (12)$$

is $M^2(B_0 + 2B_1 \cos\alpha + 2B_2 \cos 2\alpha)$. The higher order terms in M^2 , if they arise from quadrupole-quadrupole interaction or from magneto-crystalline anisotropy, must have symmetry for rotation by π , and hence their simplest term will be $\cos 2\alpha$, though this might arise from nearest-neighbor planes. The simplest phenomenological energy which will reproduce the observed affects is

$$M^2[B_0 + 2B_1 \cos\alpha + 2(B_2 - CM^2) \cos 2\alpha]. \quad (13)$$

For an investigation of the thermodynamic properties of the system it is necessary to know the free energy and hence the entropy. For a relative ordered moment M the entropy for N spins can be written

$$\begin{aligned} S &= \ln[N! / \frac{1}{2}N(1+M) \frac{1}{2}N(1-M)!] \\ &= N[\ln 2 - \frac{1}{2}(1+M) \ln(1+M) \\ &\quad - \frac{1}{2}(1-M) \ln(1-M)]. \end{aligned} \quad (14)$$

If the thermal energy is proportional to M^2 , minimization of the free energy with respect to M ,

$$F = -JM^2 - kTS, \quad (15)$$

gives

$$\ln\left(\frac{1+M}{1-M}\right) = \frac{4JM}{kT}, \quad \text{or} \quad M = \tanh(2JM/kT). \quad (16)$$

This is the result of the molecular field approximation which is usually obtained by a self-consistency argument instead of an explicit calculation of S .

Since quartic terms appear in (13), the actual solution for M is somewhat different—however, it will be found that the $CM^4 \cos 2\alpha$ term is relatively small and, as a first approximation in making numerical estimates, we shall use the usual form for M given in (16). The approximation, therefore, reduces to that of Enz³⁰ and is similar, apart from the spiral solution superimposed, to the model analyzed by Liu *et al.*³¹ However, we introduce the temperature variation of the parameters through the term in CM^4 , which appears to be physically reasonable. Other attempts to derive the temperature dependence from first principles without such terms have not been successful.³²

³⁰ U. Enz, *Physica* **26**, 698 (1960).

³¹ S. H. Liu, D. R. Behrendt, S. Legvold, and R. H. Good, *Phys. Rev.* **116**, 1464 (1959).

³² K. Yosida and H. Miwa, *J. Appl. Phys.* **32**, 8S (1961).

Furthermore, by minimizing F with respect to α ,

$$\cos\alpha = -B_1/[4(B_2 - CM^2)], \quad (17)$$

so that α now depends on T through M . This is borne out by the observations of turn angle in Er which show a striking resemblance to the variation of the component of \mathbf{u} in the plane,¹⁵ and further by the fact that hysteresis effects in \mathbf{u} produce a corresponding hysteresis in α (private communication by E. O. Wollan).

The transition to ferromagnetism will take place if the free energy of the ferromagnetic state ($\alpha=0$) becomes lower than that of the spiral. Within the molecular field approximation, the entropy is the same for the same relative ordered moment M of a spin, so that the free energy curves for different values of effective J in (15) cannot cross without the addition of extra terms. Large terms in CM^4 might cause such a transition as shown by Kittel²⁹ and Néel³³ but not terms of the size we are considering. The hexagonal anisotropy, however, provides a mechanism for the transition. This anisotropy cannot distinguish between the ferromagnetic arrangement $\alpha=0$ and spirals with turn angles $\alpha=n\pi/3$, which also allow all the spins to point in the easy directions. Thus for ferromagnetism it is also essential for $E(\alpha=0) < E(n\pi/3)$. Within the three-layer interactions described above, this is true, provided the turn angle α at the transition is $\leq 41.4^\circ$, so that it is consistent in Dy. In Ho, however, it appears that the lowest energy state has all the moments in the easy directions, at the expense of making a true spiral—the pattern repeats after 10 atomic layers and has higher harmonics. The energy is now a combination of several Fourier components of the exchange and will depend critically on its range and spatial variation, so that it is unlikely that this simple two-layer interaction model will form an adequate description.

As stated, to discuss the transition, the free energies should be compared and, in general, M will change discontinuously there. However, since in Dy at any rate the transition takes place when M is nearly saturated, we will follow Enz³⁰ in comparing only the energies and assume that M is unchanged. A more general problem concerns the effect of a magnetic field H in inducing the ferromagnetic transition. The energy of the ferromagnetic state is

$$-[B_0 + 2B_1 + 2(B_2 - CM^2)]M^2 - KM^6 - \mu HM, \quad (18)$$

and the energy of the spiral state is

$$-[B_0 + 2B_1 \cos\alpha + 2(B_2 - CM^2) \cos 2\alpha]M^2, \quad (19)$$

since the anisotropy also averages to zero. The transition takes place when

$$\begin{aligned} \mu H_c M + KM^6 &= -2M^2[B_1(1 - \cos\alpha) \\ &\quad + (B_2 - CM^2)(1 - \cos 2\alpha)]. \end{aligned} \quad (20)$$

Again assuming that H does not in first order change

³³ L. Néel, *Compt. rend.* **242**, 1549, 1824 (1956).

the angle of the spiral, we can use (17) for α and find

$$\mu H_c/M + KM^4 = B_1(1 - \cos\alpha)^2 / \cos\alpha. \quad (21)$$

For Dy, H_c has been determined from magnetic measurements⁹ and does have the form predicted above, rising from zero at T_c and falling to zero again like M as $T \rightarrow T_N$. In Fig. 1, H_c/M is plotted and compared with a plot of $(1 - \cos\alpha)^2 / \cos\alpha$, using the neutron diffraction data for α . Normalization of the curve at T_N gives B_1 , and hence B_2 and C ,³⁴ as

$$B_1/k = 170^\circ, \quad B_2/k = -57^\circ, \quad C/k = -11^\circ.$$

Using the Curie-Weiss θ of 170° , this gives also³⁴

$$B_0/k = -55^\circ.$$

The error in these numbers is probably about 10%. The deviations between the curves which represent the anisotropy field are shown in Fig. 2 and are in reasonable agreement with M^4 in temperature dependence and a K of order $1 \text{ cm}^{-1}/\text{atom}$.

It is rather difficult to estimate K from the observations of saturation magnetization in the plane. By minimizing the energy,

$$KM^6 \cos 6\varphi - \mu HM \cos \varphi, \quad (22)$$

with respect to φ , one can plot φ as a function of $\mu H/KM^5$ and compare with the saturation at 90° and 100°K . This seems to indicate a value of K , three or four times smaller than the value obtained above. Assuming $K = V_6^6 \gamma J^6$, a value of $V_6^6 = 5 \text{ cm}^{-1}$ gives $K = 1 \text{ cm}^{-1}$. This requires $\langle r^6 \rangle \sim 0.05 \text{ \AA}^6$ in (6) which is rather smaller than is usually assumed in rare-earth salts.²³ A value of $\langle r^2 \rangle \sim 0.3 \text{ \AA}^2$ would give an axial anisotropy of reasonable order of magnitude.

On the whole, however, the model proposed seems to give a satisfactory over-all fit with the data in Dy. It is unfortunately not possible to derive actual values of parameters in the other metals without measurements of H_c when T is sufficiently close to T_N for anisotropy effects to be negligible.

VII. MOMENTS ALONG AXIS

In the metals where the axial anisotropy produces moments parallel to the c axis, we use as a starting point the model where only the terms in A are kept in (11). In Er it is found experimentally that at high temperatures the stable ordered phase has

$$S_n^z = \mu M \sin(n\alpha + \delta). \quad (23)$$

The energy of such a phase is

$$M^2 \left\{ A_0 \sum_n \sin^2(n\alpha + \delta) + 2A_1 \sum_n \sin(n\alpha + \delta) \sin[(n+1)\alpha + \delta] + 2A_2 \sum_n \sin(n\alpha + \delta) \sin[(n+2)\alpha + \delta] \right\}, \quad (24)$$

³⁴ See Note added in proof at end of paper.

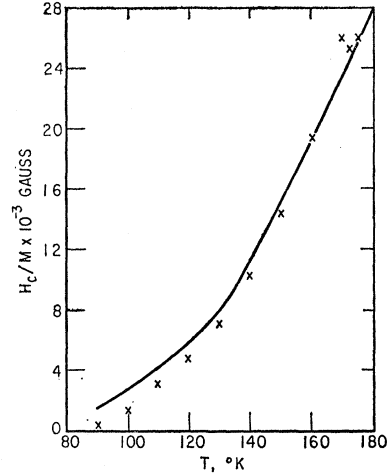


FIG. 1. Critical field H_c in Dy. Points are experimental values of H_c/M from reference 9. Curve is plot of $B_1(1 - \cos\alpha)^2 / \mu \cos\alpha$ using α values of reference 8, normalized to fit at T_N ; cf. Eq. (21).

since the terms in M^4 , etc., will not be present in this one-dimensional case. Using the multiple-angle formulas,

$$\begin{aligned} \sum \sin(n\alpha + \delta) \sin[(n+1)\alpha + \delta] \\ = \sum \frac{1}{2} \{ \cos\alpha - \cos[(2n+1)\alpha + 2\delta] \}, \quad \text{etc.}, \end{aligned}$$

the latter term averages to zero, and the energy has the form

$$E = \frac{1}{2} M^2 [A_0 + 2A_1 \cos\alpha + 2A_2 \cos 2\alpha] = -\frac{1}{2} A M^2. \quad (25)$$

Just as in the last section, it is possible for this to have a minimum for some α given by

$$\cos\alpha = -A_1/4A_2. \quad (26)$$

However, the factor $\frac{1}{2}$ which appears in (25) for all cases except $\alpha=0$ tends to make the energy of the ferromagnetic arrangement lower. This is particularly true if A_0 is large, since the sinusoidal arrangement loses the intraplanar interaction for some of the planes. But in considering stable arrangements, it is necessary to compare *free energies*, and it is clear that the sinusoidal arrangement has considerably more entropy than the ferromagnetic one.

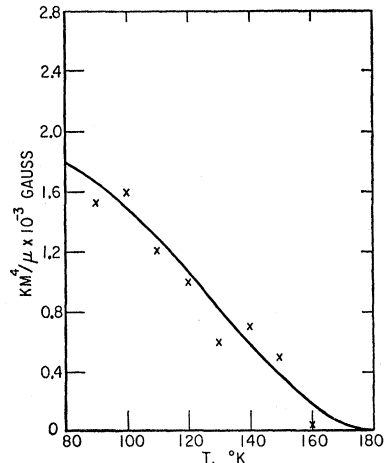


FIG. 2. Anisotropy field in Dy. Points represent deviations of experimental points from curve in Fig. 1, i.e., of $KM^4 / \mu M^2$. Curve is a plot of M^4 with best normalization near T_c .

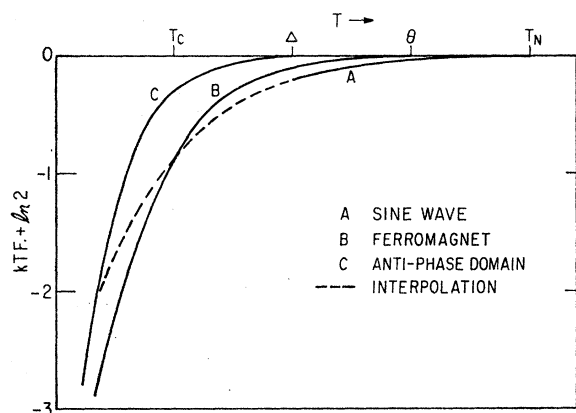


FIG. 3. Free energy F when spins confined along c axis. Plots of $kTF + \ln 2$ for (A) sine wave, (B) ferromagnet, (C) anti-phase domain spin arrangements in the Bragg-Williams approximation. Characteristic temperatures T_n , θ , Δ are arbitrarily chosen. Arrangement (A) exists only $T_n > T > \frac{1}{2}T_n$, below which the arrangement squares up and tends towards (C). The dashed curve is an extrapolation for this regime. T_c occurs where this curve crosses (B).

Using (14) for the entropy with $M \rightarrow |M \sin \theta|$ and averaging over θ ,

$$S = Nk \left[\ln 2 - \frac{1}{2\pi} \int_0^\pi (1 + M \sin x) \ln(1 + M \sin x) + (1 - M \sin x) \ln(1 - M \sin x) dx \right] \\ = -Nk [\ln 2(1 + p^2) - (2p^2/1 + p^2)], \quad (27)$$

where

$$M = 2p/(1 + p^2), \quad p = [1 - (1 - M^2)^{1/2}]/M, \quad (28)$$

provided M and $p \leq 1$. Differentiating $F = E - TS$ with respect to M gives

$$2A = kT(p^2 + 1),$$

i.e.,

$$M = 2 \left[\left(1 - \frac{kT}{2A} \right) \frac{kT}{2A} \right]^{1/2}. \quad (29)$$

Thus

$$T_N = 2A = A_0 + 2A_1 \cos \alpha + 2A_2 \cos 2\alpha, \quad (30)$$

and the factor of $\frac{1}{2}$ in the energy has been exactly compensated by the greater entropy. This will be a higher temperature than that at which it would have gone ferromagnetic,

$$\theta = A_0 + 2A_1 + 2A_2, \quad (31)$$

if A_1 and A_2 have the same type of relative magnitudes as the B 's in Dy.

The ordered moment M reaches its maximum value of unity at

$$T' = A = \frac{1}{2}T_N, \quad (32)$$

and below this temperature the above expressions are not valid. If, by the time this temperature has been reached, the system has not gone ferromagnetic, the spin modulation will begin to take on a square profile, gaining in energy because of the increased value of $\langle S_z^2 \rangle$ at the expense of some entropy. Unfortunately we have not been able to find an approximate expression for this squaring process which allows us to do the integrals analytically; and we have therefore not yet explored the theory in this region. It is interesting, however, that so simple a model predicts a transition from sine wave to a squarer arrangement which would show higher harmonics in the neutron scattering. If this arrangement persisted down to low temperatures, it would become an antiphase domain structure, with several layers of up spin followed by several layers of down, and so on. Since here the mean spin moment is the same in each layer, the entropy and hence the free energy have the same functional form as for a ferromagnetic arrangement. Thus for the system to be ferromagnetic at 0°K, the effective exchange energy of the ferromagnetic state $-\theta M^2$ must be more negative than that for the antiphase state, say $-\Delta M^2$.

The transition to ferromagnetism will take place when the free energy of that state becomes lowest. In Fig. 3, curves of F are plotted for the sine, ferromagnetic, and antiphase structures. The first is given by (25) and (27) and the last two by (15) and (14), where T_N , θ , and Δ have been chosen relative to one another for display purposes, although the values have some similarity to the possible situation in Er. The dashed curve extrapolating A to C represents the general trend of F for a squared-up arrangement.

If $\theta > 0.87T_N$, there would be a direct sine-ferro transition. For smaller θ the squaring takes place, and it is not possible to find T_c without numerical calculation.

In the sinusoidal arrangement it is also possible to calculate the susceptibility if it is assumed that in the presence of a field H ,

$$S_n^z = (\chi H/\mu) + \mu M \sin(n\alpha + \delta). \quad (33)$$

Assuming further that M is unchanged in a small H , this simply adds terms to the free energy. It is necessary to keep only those as far as H^2 , which are

$$-\theta(\chi H/\mu)^2 + \frac{1}{2}kT(\chi H/\mu)^2/(1 - M^2)^{1/2}, \quad (34)$$

and since $(\partial F/\partial H) = \chi H$ for small H , the differential of (34) gives, after some manipulation,

$$\chi = N\mu^2(2T - T_N)/k[T(T_N - 2\theta) + T_N\theta].$$

This joins smoothly on to the paramagnetic susceptibility $N\mu^2/k(T - \theta)$ at $T = T_N$, and then has a sharp maximum falling rapidly to zero at $T = \frac{1}{2}T_N$. At this temperature some spins are saturated so that it is to be expected that with this model $\chi = 0$. In practice, however, some variation in the form of S_z must be

allowed, and it is to be expected that the above form of χ will not be correct as $T \rightarrow \frac{1}{2}T_N$.

The experimental results on Er can be partially interpreted on the above model. From the high-temperature phase with a knowledge of α , θ , and T_N , it is possible to find³⁴

$$A_0/k = -40^\circ, \quad A_1/k = 80^\circ, \quad A_2/k = -30^\circ.$$

Again it can be seen that the simple two-layer interaction model evaluated in the spirit of the molecular field approximation leads to a satisfactory overall description of the phenomena. For a more complete description it will be necessary to calculate a model which includes all three components as in (11) and allows for more complex variation of S^z intermediate between a simple wave and an antiphase domain structure. For Er has a transition at 50°K below which S^z is not a simple wave and where the moments in the plane have a spiral ordering.

The relative values of the A_i found in Er are very similar to the B_i in Dy, which is consistent with a dominant interaction of type (3). However, there must

be some variation of the ratio $-B_1/4B_2$ along the series, in particular to account for the very narrow spiral region in Tb and its absence in Gd. There does not appear to be any reason associated with anisotropy why this ratio should be larger in those two elements.

After this was completed, the work of Kaplan³⁵ was brought to my attention which gives a rather similar theory of these effects, although he starts from a rather different simplified Hamiltonian, and he evaluates the properties in a different approximation.

ACKNOWLEDGMENTS

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Note added in proof. The author is indebted to Dr. A. Arrott for pointing out an error in sign in the original calculations. The negative sign of B_0 and A_0 is surprising in view of the ferromagnetic ordering within planes.

³⁵ T. A. Kaplan, Phys. Rev. **123**, 329 (1961).