

Some Effects of Anisotropy on Spiral Spin-Configurations with Application to Rare-Earth Metals*

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This is a theoretical study of effects of anisotropy on spiral spin-configurations, emphasizing the problem of the magnetic ordering in rare-earth metals. The principal results are as follows: It is shown that the ferromagnetic spiral observed at low temperatures by Wilkinson, Koehler, Wollan, and Cable in erbium can be the classical ground state of a spin Hamiltonian containing exchange and anisotropy terms, provided the latter includes terms of at least the fourth power in the spin variables. Furthermore, the observed cone angles (which imply large deviations from configurations possible with exchange forces alone) can be obtained with anisotropy forces much smaller than the exchange forces. The spin-wave spectrum and susceptibility for ferromagnetic spirals were also considered. The former has the interesting properties that $\omega(\mathbf{k})$ is linear in \mathbf{k} for small \mathbf{k} (even though the net moment is not zero), and there are two distinct branches, as contrasted with the

case of simple antiferromagnetic spirals. For high temperatures, calculations are made on the basis of the molecular field approximation. It is shown that a small easy-axis anisotropy implies that at the highest transition temperature, T_c , the ordered spin configuration is a *static longitudinal spin wave*; the average spins are collinear, their lengths varying sinusoidally through the crystal. As T decreases below T_c , the amplitude of the wave grows in order $(T_c - T)^{1/2}$, other Fourier components entering in higher order. The perpendicular components remain zero until a second transition temperature is reached, below which they begin to order. Since this complex type of behavior, which has been observed in erbium, can also occur with the same exchange and anisotropy constants needed to give the observed ground state, the possibility exists of describing erbium through the whole temperature range by this type of theory.

I. INTRODUCTION

SINCE spirals were discovered theoretically,¹ they and related configurations have been found experimentally in a number of materials. Some of the most interesting examples of spiral-like states have been obtained in rare earth metals by Wilkinson *et al.*² using neutron diffraction. Important qualitative aspects of their results on dysprosium and erbium are summarized in Fig. 1, where the types of ordering and their respective temperature regions are shown. (Holmium, which is intermediate between Dy and Er, will be discussed in Sec. IV.) There are many interesting details which are not shown such as thermal variation of wavelength and the actual values of transition temperatures, magnetic moments, etc. In the figure, the vertical corresponds to the c axis of the hcp structure—the direction of propagation is always found to be parallel to this axis. Successive spins along this direction correspond to successive c planes of metal atoms.

A striking aspect of these results is the large deviation, in some cases, from what would be allowed by exchange interactions alone. (The reason that this is striking is that although one expects anisotropy forces to be much larger than in the iron group, they are still only of the order of 10% of the exchange forces in the case of dysprosium.³) It is shown in the Appendix that if the only forces are exchange type, then the ground state for the hcp lattice must be a simple spiral (SS), that is, a

spiral of the type discussed previously,¹ in which all the spins must be parallel to one plane, fixed in space. It is seen that this is not satisfied in the low-temperature configuration of erbium, in which the spins all lie on the surface of a cone; the transverse, ξ - η components forming a simple spiral, the longitudinal, ζ components being constant. We have called this configuration a ferromagnetic spiral (FS).⁴ Furthermore, the cone half-angle is ~ 30 degrees,² showing a large deviation from coplanarity. In the high-temperature phase of erbium, which we call a longitudinal spin wave (LSW), the average spins are collinear, their lengths varying sinus-

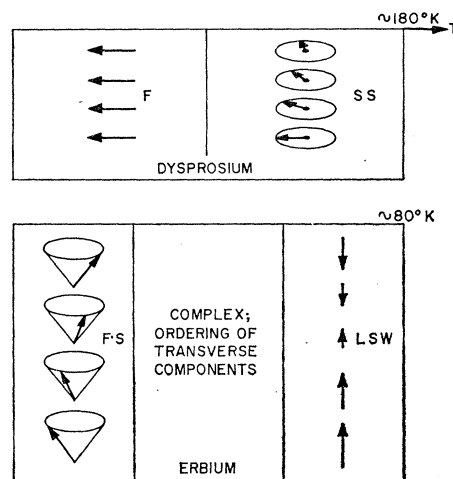


FIG. 1. Magnetic ordering found by neutron diffraction (Wilkinson, *et al.*), showing the approximate temperature ranges in which the various types of ordering occur. Symbols: F=simple ferromagnet, SS=simple spiral, FS=ferromagnetic spiral, LSW=longitudinal spin wave.

* Partial results of this paper were presented previously, Bull. Am. Phys. Soc. 6, 1127 (1961).

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¹ A. Yoshimori, J. Phys. Soc. Japan 14, 807 (1959); J. Villain, J. Phys. Chem. Solids 11, 303 (1959); T. A. Kaplan, Phys. Rev. 116, 888 (1959).

² M. K. Wilkinson, W. C. Koehler, E. O. Wollan, and J. W. Cable, J. Appl. Phys. 32, 48S and 49S (1961); W. C. Koehler, Suppl. J. Appl. Phys. 32, 20S (1961).

³ S. H. Liu, D. R. Behrendt, S. Legvold, R. H. Good, Jr., Phys. Rev. 116, 1464 (1959).

⁴ T. A. Kaplan, K. Dwight, N. Menyuk, Bull. Am. Phys. Soc. 5, 460 (1960). T. A. Kaplan, K. Dwight, D. Lyons, N. Menyuk, J. Appl. Phys. 32, 13S (1961). Similar configurations have been shown in these papers to be theoretically possible in spinels with exchange forces only.

oidally as one moves along the c axis—the transverse components are completely disordered to within the accuracy of experiment. This configuration is, of course, quite unlike anything discussed previously.

Because of these features of erbium—large deviation in the ground state from what is possible by exchange forces only, and apparent intuitive opaqueness as to the reason for the high-temperature state—we shall concentrate on this type of behavior. We shall find in fact that the first feature is entirely reasonable on the basis of small anisotropy, and, assuming appropriate exchange and anisotropy parameters consistent with the ground state, we shall see that the molecular field theory implies LSW ordering at the highest transition temperature. Other details, such as ordering of transverse components, variation of wavelength with temperature, and the appearance of higher harmonics will also be discussed.

II. LOW TEMPERATURES

The theoretical foundation for the exchange coupling of the localized rare-earth magnetic moments via the conduction electrons has been considered by many writers.⁵ For our purposes we may simply take the exchange energy as $E_{\text{ex}} = -\sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, where the J_{ij} are exchange parameters of fairly long range, and the “spin” operators \mathbf{S}_i actually correspond to the total angular momentum \mathbf{J} of the metal ion (the dimensionality of the space of eigenvectors of \mathbf{S}_i is $2J+1$; for purposes of notation we put $J=S$). Since the S values of interest are large (~ 5 to 10), the \mathbf{S}_i can reasonably be treated semi-classically, at least insofar as the type of spin-correlation is concerned. Furthermore, the energy difference between the lowest multiplet and the next is $\approx 10kT_c$, so that we assume S is a constant.

It is shown in the Appendix that the minimum exchange energy in the hcp structure is always attained by a simple spiral. Comparison with experiment on erbium, for example, therefore forces the conclusion that anisotropy forces must play an important role in determining the magnetic ordering in the ground state.⁶ The origin of these anisotropy forces will be an interplay between spin-orbit forces and electrostatic interaction between the localized magnetic electrons and the rest of the crystal, just as in Van Vleck's theory.⁷ However, because of the different relative magnitudes between spin-orbit and crystal forces, we expect that the coefficients of the various types of terms (self-energy, dipole-dipole, quadrupole-quadrupole, etc.) will be different from those occurring in the small spin-orbit approximation. As far as we know investigations of these questions have not appeared. We hope to make such a study but for the

present we will content ourselves with a strictly phenomenological treatment.

Our first object is to write down the simplest spin Hamiltonian having the proper symmetry that will give a ferromagnetic spiral as the ground state. Assuming that in the ground state, all spins in any one basal plane are parallel (in accordance with the experimental results),² the most general quadratic function of the spins consistent with the hexagonal symmetry is $E_2 = E_{\text{ex}} - \sum K_{ij} S_i^z S_j^z$, where the self-energy terms $K_{ii} (= K_{jj})$ are not necessarily zero, and S_i^z is the component of \mathbf{S}_i along the c axis. (The terms for $i \neq j$ arise from dipolar coupling.) Now it is easy to see that a ferromagnetic spiral cannot minimize E_2 , since E_2 for any FS will contain one term proportional to $(S^z)^2$ (where S^z is the constant ξ component) and another term independent of S^z ; the only possible cone angles are 0 or $\pi/2$.⁸ Hence we must consider higher order terms; we will take these to be of the simplest type, namely $\sum (S_i^z)^4$. We then have the energy function

$$E = -\sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum K_{ij} S_i^z S_j^z + \frac{1}{2} K' \sum (S_i^z)^4, \quad (1)$$

which we will assume for the rest of the paper. For the actual hexagonal close-packed structure, assuming all spins within one c plane to be parallel, i and j refer to the various such planes, J_{ij} and K_{ij} being sums of interatomic coupling constants. In this case (1) reduces to a linear chain problem. In our calculations, however, i and j can formally be considered to refer to atomic sites in any Bravais lattice.

The ferromagnetic spiral can be written as

$$\mathbf{S}_i = S [\sin \theta (\xi \sin \mathbf{k} \cdot \mathbf{R}_i + \boldsymbol{\eta} \cos \mathbf{k} \cdot \mathbf{R}_i) + \cos \theta \boldsymbol{\zeta}], \quad (2)$$

where θ is the cone half-angle, \mathbf{R}_i is the position of the i th site, and ξ , $\boldsymbol{\eta}$, and $\boldsymbol{\zeta}$ are orthonormal (with $\boldsymbol{\zeta}$ along the c axis for our examples of chief interest). The corresponding energy per particle is

$$E_0 = -\mathcal{J}(\mathbf{k}) S^2 + \cos^2 \theta [\mathcal{J}(\mathbf{k}) - \mathcal{J}(0) - \mathcal{K}(0)] S^2 + \frac{1}{2} K' S^4 \cos^4 \theta, \quad (3)$$

where

$$\begin{aligned} \mathcal{J}(\mathbf{k}) &= \sum_j J_{ij} \cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j), \\ \mathcal{K}(\mathbf{k}) &= \sum_j K_{ij} \cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j); \end{aligned} \quad (4)$$

the latter two are independent of i because of the translational symmetry of J_{ij} and K_{ij} . The minimum energy over this class of configurations is obtained by choosing $\mathbf{k} = \mathbf{k}_0$, where $\mathcal{J}(\mathbf{k}_0)$ is the maximum over \mathbf{k} of $\mathcal{J}(\mathbf{k})$, and $\theta = \theta_0$ where

$$\cos^2 \theta_0 = \frac{\mathcal{K} S^2 - [\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(0)] S^2}{K' S^4}, \quad (5)$$

provided $0 < \cos^2 \theta_0 < 1$ and

$$K' > 0. \quad (6)$$

⁵ See for example, P. G. deGennes, *Compt. rend.* **247**, 1836 (1958); S. H. Liu, *Phys. Rev.* **121**, 451 (1961), and references contained therein.

⁶ This conclusion was reached by deGennes (reference 5) through a different argument.

⁷ J. H. Van Vleck, *Phys. Rev.* **52**, 1178 (1937).

⁸ This type of result was pointed out to the author by K. Dwight, in connection with the “umbrella” spin configuration found in CrSe₂ by L. Corliss and J. Hastings (private communication).

[We have put $\mathcal{K} = \mathcal{K}(0)$.] It follows that we must have

$$\mathcal{K} > \mathcal{J}(\mathbf{k}_0) - \mathcal{J}(0); \quad (7)$$

hence the second-order terms must provide an easy axis and the fourth-order terms must give an easy plane in order to obtain a FS. Note that the wave vector \mathbf{k}_0 is determined in this case entirely by the exchange forces (this will not be true in general if, for example, two-body forces are included in the fourth power terms).

The interesting feature of (5) and (7) is that the anisotropy needn't compete with the full exchange energy $\mathcal{J}(\mathbf{k}_0)$ but only with the difference $\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(0)$. Thus, for example, if the wavelength is long, the requirement that $0 < \cos^2\theta_0 < 1$ can be satisfied with small values of \mathcal{K} and K' . To get an idea of orders of magnitude, we have assumed first and second neighbor J_{ij} only (for the linear chain model). Then, using the wavelength of roughly 8 layers found in erbium,² we find that $[\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(0)]/|\mathcal{J}(\mathbf{k}_0)| \sim 10\%$, which is of the order of magnitude of the c -axis anisotropy found in dysprosium.³

Before proceeding to questions of local stability and spin waves, we point out that the susceptibility parallel to ζ is a simple but useful quantity. Adding a term $-H \sum S_i^z$ to Eq. (1), we find that at equilibrium

$$\delta^3 + 3C_0\delta^2 + 2C_0^2\delta - HS/2K'S^4 = 0, \quad (8)$$

where $\cos\theta = C_0 + \delta$ and $C_0 = \cos\theta_0$. Hence the zero-field susceptibility is essentially

$$\chi_0 = \left[\frac{\partial(S\delta)}{\partial H} \right]_{H=0} = \frac{1}{4C_0^2K'S^2}, \quad C_0 \neq 0. \quad (9)$$

Thus a measurement of χ_0 , together with the neutron diffraction results (which yield C_0), gives a direct measurement of K' and therefore of the numerator in (5). (This assumes a knowledge of the g factor that must enter.) We might also add that, neglecting domain effects, complete saturation will be reached ($\theta = 0$) when $HS = 2K'S^4 \sin^2\theta$.

If our ferromagnetic spiral is to actually minimize the energy (1), it clearly must be stable with respect to small but otherwise arbitrary rotations of all the spins. To investigate this question of local stability, we calculate the energy for small deviations from their equilibrium positions in the FS. This is most conveniently done by expressing the \mathbf{S}_n in terms of their components in coordinate systems that vary with n , as follows⁴:

$$\mathbf{S}_n = \hat{x}_n S_n^x + \hat{y}_n S_n^y + \hat{z}_n S_n^z,$$

where

$$\hat{x}_n = (\xi \cos \mathbf{k}_0 \cdot \mathbf{R}_n + \eta \sin \mathbf{k}_0 \cdot \mathbf{R}_n) \cos \theta_0 - \zeta \sin \theta_0,$$

$$\hat{y}_n = -\xi \sin \mathbf{k}_0 \cdot \mathbf{R}_n + \eta \cos \mathbf{k}_0 \cdot \mathbf{R}_n,$$

$$\hat{z}_n = (\xi \cos \mathbf{k}_0 \cdot \mathbf{R}_n + \eta \sin \mathbf{k}_0 \cdot \mathbf{R}_n) \sin \theta_0 + \zeta \cos \theta_0.$$

That is, \hat{z}_n is in the direction of \mathbf{S}_n^0 , the unperturbed spin at site n , \hat{x}_n is in the $\zeta - \hat{z}_n$ plane, with \hat{y}_n chosen to form a right-handed system. Taking $S_n^z = 1$ and keeping

only up to second-order terms in the deviations S_n^x and S_n^y , we obtain

$$E = NE_0 + \sum_{\mathbf{k}} \sum_{u,v} M_{uv}(\mathbf{k}) Q_{\mathbf{k}}^{u*} Q_{\mathbf{k}}^v, \quad (10)$$

where u, v each run over x and y ,

$$\begin{aligned} S_n^u &= N^{-\frac{1}{2}} \sum_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_n) Q_{\mathbf{k}}^u, \\ M_{xx}(\mathbf{k}) &= C_0^2 \{ \mathcal{J}(\mathbf{k}_0) - \frac{1}{2} [\mathcal{J}(\mathbf{k}_0 + \mathbf{k}) + \mathcal{J}(\mathbf{k}_0 - \mathbf{k})] \} \\ &\quad + S_0^2 [\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(\mathbf{k}) - \mathcal{K}(\mathbf{k}) + 3C_0^2 K'], \quad (11) \\ M_{xy}(\mathbf{k}) &= (i/2) C_0 [\mathcal{J}(\mathbf{k}_0 - \mathbf{k}) - \mathcal{J}(\mathbf{k}_0 + \mathbf{k})] = M_{yx}(\mathbf{k})^*, \end{aligned}$$

and

$$M_{yy}(\mathbf{k}) = \mathcal{J}(\mathbf{k}_0) - \frac{1}{2} [\mathcal{J}(\mathbf{k}_0 + \mathbf{k}) + \mathcal{J}(\mathbf{k}_0 - \mathbf{k})].$$

(We have put $S_0 = \sin\theta_0$.)

For local stability of the ferromagnetic spiral, the eigenvalues of the matrices $M_{uv}(\mathbf{k})$ must be non-negative for all \mathbf{k} . Hence the diagonal elements each must be ≥ 0 . The condition that \mathbf{k}_0 maximize $\mathcal{J}(\mathbf{k})$ ensures that

$$M_{yy}(\mathbf{k}) \geq 0. \quad (12)$$

Hence for $M_{xx}(\mathbf{k}) \geq 0$, it is sufficient to have

$$\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(\mathbf{k}) - \mathcal{K}(\mathbf{k}) + 3C_0^2 K' \geq 0. \quad (13)$$

This is, of course, stronger than is necessary, but it is clear that it is possible to choose the parameters such that (13) is satisfied without violating previous requirements. A sensitive point is the value of $M_{xx}(0)$, since the coefficient of C_0^2 vanishes; however, using (5), we have

$$\begin{aligned} M_{xx}(0) &= S_0^2 [3C_0^2 K' + \mathcal{J}(\mathbf{k}_0) - \mathcal{J}(0) - \mathcal{K}(0)] \\ &= 2S_0^2 C_0^2 K', \quad (14) \end{aligned}$$

which is positive. Incidentally, (14) provides us an easy check on our arithmetic, since it should be true that $M_{xx}(0) = (1/2) \partial^2 E_0 / \partial \theta^2$ evaluated at $\theta = \theta_0$. Given (13), local stability will be guaranteed if only the determinant D of M is ≥ 0 . But

$$\begin{aligned} D &= C_0^2 [\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(\mathbf{k}_0 + \mathbf{k})] [\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(\mathbf{k}_0 - \mathbf{k})] \\ &\quad + S_0^2 M_{yy}(\mathbf{k}) [\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(\mathbf{k}) - \mathcal{K}(\mathbf{k}) + 3C_0^2 K'], \end{aligned}$$

which is certainly ≥ 0 if (13) is true.

It is interesting to note that our FS can be metastable—to consider an extreme example, FS will not be the ground state if the exchange forces alone should give a simple antiferromagnet (collinear spins, alternating in direction from layer to layer) and $\mathcal{K}(\mathbf{k}) = \mathcal{K}(0)$ for all \mathbf{k} , and yet the FS can be locally stable. This might be of interest in connection with the Yosida-Miwa⁹ explanation of the transition from ferro- to antiferromagnetism in dysprosium. It also points up the importance of being able to determine rigorously the ground state of a function like Eq. (1). This is a difficult question, particularly

⁹ K. Yosida and H. Miwa, J. Appl. Phys. **32**, 8S (1961).

since the Luttinger-Tisza trick¹⁰ works only for a quadratic function of the spins. However, another method, based on a cluster analysis,¹¹ shows considerable promise—this is under investigation.

The spin-wave frequencies (which are different from the eigenvalues of M_{uv}) may be determined easily from (10) and (11). Putting $Q_k^x = Q_k$ and $Q_k^y = P_{-k}$, it follows from the commutation relations for the S_n^u that (Q_k, P_k) are canonically conjugate coordinate-momentum pairs, in the usual spin-wave approximation. The canonical transformation that diagonalizes (10) can be obtained from solutions of the equations of motion

$$\begin{aligned}\dot{Q}_k &= 2M_{yy}P_{-k} + 2M_{xy}^*Q_k, \\ \dot{P}_{-k} &= -2M_{xx}Q_k + 2M_{xy}P_{-k},\end{aligned}$$

or, assuming $e^{i\omega t}$ time dependence,

$$\begin{aligned}(2M_{xy}^* - i\omega)Q_k + 2M_{yy}P_{-k} &= 0, \\ -2M_{xx}Q_k + (2M_{xy} - i\omega)P_{-k} &= 0.\end{aligned}\quad (15)$$

Hence the spin-wave spectrum is given by

$$\omega_{\pm}(\mathbf{k}) = C_0[g(\mathbf{k}_0 + \mathbf{k}) - g(\mathbf{k}_0 - \mathbf{k})] \pm 2[M_{xx}(\mathbf{k})M_{yy}(\mathbf{k})]^{1/2}. \quad (16)$$

Equation (16) is to be used in (15) to determine the normal coordinates; however, the physically significant frequencies are $|\omega_{\pm}(\mathbf{k})|$ as long as the configuration is locally stable.¹² Putting $C_0 = 0$, $K' = 0$, and $\mathcal{K}(\mathbf{k}) = \mathcal{K}(0)$, (16) reduces properly to the expression found by Yosida and Miwa.⁹

Clearly

$$\omega_{\pm}(0) = 0; \quad (17)$$

the two modes correspond to the two uniform rotations (in opposite senses) in which the spins remain on the surface of the equilibrium cone. For sufficiently small k the two frequency branches remain degenerate. For a linear chain,

$$|\omega_{\pm}(\mathbf{k})| \cong 2[-C_0^2 S_0^2 K' g''(\mathbf{k}_0)]^{1/2} k, \quad (18)$$

where $g''(\mathbf{k}_0) = (\partial^2 g / \partial k^2)_{\mathbf{k}_0}$ (which is < 0). Hence we have the interesting result that a basically ferromagnetic configuration (the net moment is not zero) gives a linear dispersion law, which has usually been associated with antiferromagnets.¹³

Another interesting feature of this spectrum is the existence of two distinct branches (as contrasted with the spectrum for a simple spiral, for which $C_0 = 0$). The splitting for small k is approximately $(1/3)C_0 g'''(\mathbf{k}_0)k^3$, giving an indication of the type of detailed information that can be obtained from an experimental determination of the spectrum.

We might mention that the inclusion of anisotropy in

the basal plane will remove the zero of $\omega(\mathbf{k})$ at $\mathbf{k} = 0$, just as the zero¹⁴ at $\mathbf{k} = \mathbf{k}_0$ has been removed by the anisotropy terms considered here.

A more detailed investigation of this spectrum and its various consequences (on the magnetization, specific heat, inelastic neutron scattering cross section, etc.) is not of interest here because of the idealized nature of Eq. (1); in the rare-earth metals the spins are not all parallel within a plane (except at $T = 0$), the lattice is not Bravais, etc. However, since it is our feeling that the most powerful way of experimentally determining the fundamental properties of these materials is by low-temperature measurements [due to the present lack of any reliable theory for treating the high-temperature properties of energies like Eq. (1)], we intend to carry out similar calculations using a more realistic energy function. It should be pointed out that we do not expect Eq. (18) to be drastically modified, since the anisotropy in the basal plane is much smaller than that out of the plane, at least in dysprosium.³

III. HIGH TEMPERATURES

We shall investigate the predictions of the molecular field approximation to the statistical mechanical properties of Eq. (1). Classically, the molecular field theory is easily derived as follows.¹⁵ The true probability distribution is $\rho(\mathbf{S}_1, \dots, \mathbf{S}_n) = C \exp[-\beta E(\mathbf{S}_1, \dots, \mathbf{S}_n)]$, where $\beta = 1/kT$, and k = Boltzmann's constant. We want to find an approximate distribution $\rho_a(\dots, \mathbf{S}_n, \dots)$ of the form $\prod_i \rho_i(\mathbf{S}_i)$. It is easy to show, classically, that the free-energy functional of ρ_a ,

$$A = \int d\Omega \rho_a E + kT \int d\Omega \rho_a \ln \rho_a, \quad (19)$$

is minimized when $\rho_a = \rho$. Here $d\Omega = d\omega_1 d\omega_2 \dots$, $d\omega_i$ being the element of solid angle corresponding to the i th spin. Hence, one criterion for the "best" ρ_a , subject to the restriction that it be a product $\prod_i \rho_i(\mathbf{S}_i)$, is to choose the $\rho_i(\mathbf{S}_i)$ to minimize (19) (subject, of course, to normalization). Using Eq. (1), stationarity of (19) gives

$$\rho_i(\mathbf{S}_i) = Z_i^{-1} \exp[-\beta E_i(\mathbf{S}_i)], \quad (20)$$

where

$$E_i(\mathbf{S}) = -\mathbf{H}_i \cdot \mathbf{S} - K(S^x)^2 + \frac{1}{2}K'(S^x)^4, \quad (21)$$

with the u th component of \mathbf{H}_i given by

$$\begin{aligned}H_{iu} &= 2 \sum_{j \neq i} L_{ij}^u \langle S_j^u \rangle, \quad u = \xi, \eta, \zeta, \\ L_{ij}^u &= J_{ij}, \quad u = \xi, \eta, \\ L_{ij}^{\zeta} &= J_{ij} + K_{ij}, \\ K &= K_{ii},\end{aligned}\quad (22)$$

¹⁰ See D. Lyons and T. A. Kaplan, Phys. Rev. **120**, 1580 (1960).

¹¹ T. A. Kaplan and D. Lyons (to be published).

¹² T. A. Kaplan, Phys. Rev. **109**, 782 (1958).

¹³ A somewhat similar result has been reported in connection with Yafet-Kittel configurations (Kaplan, reference 1).

¹⁴ Yoshimori (reference 1).

¹⁵ See for example, R. H. Fowler and E. A. Guggenheim, *Statistical Mechanics*, (Oxford University Press, New York, 1939). [A more recent derivation including anisotropy effects has been given by M. Freiser, Phys. Rev. (to be published).]

and

$$\langle S_i^u \rangle = \int d\omega S^u \rho_i(\mathbf{S}), \quad (23)$$

where $d\omega$ is the element of solid angle. Z_i^{-1} is the normalization for ρ_i . In other words, the stationarity of the free energy leads directly to just what one would write down intuitively. Inclusion of other types of terms in E , such as $\sum_{i \neq j} K_{ij}' (S_i^x)^2 (S_j^x)^2$, would of course lead to similar additional terms in E : [for the example, we would get $2(S^x)^2 \sum_j K_{ij}' \langle (S_j^x)^2 \rangle$]. The problem now is to determine the solution, $\langle \mathbf{S}_1 \rangle, \dots, \langle \mathbf{S}_n \rangle$, of (23), that minimizes (19), using (20) through (22). Quantum-mechanically, the customary procedure is to simply replace $\int d\omega$ by trace (considering the \mathbf{S}_i to be angular momentum operators), although there are difficulties in giving the same type of basic derivation. This need not concern us here, as we are interested mainly in the qualitative predictions of this type of theory (which will not be significantly altered for the large spins of interest in the rare earths).

1. The Highest Transition Temperature, T_c

It is expected that a solution of (23) that has nonzero values of

$$\sigma_i \equiv \langle \mathbf{S}_i \rangle \quad (24)$$

gives lower free energy than the solution $\sigma_i = 0$, all i [the latter satisfies (23) for all T]. Accordingly, we shall first find the highest temperature T_c for which such a nonzero solution exists and later show that the corresponding solution does minimize the free energy (Sec. III-2). Since $\sigma_i = 0$ at $T = T_c$, we expand the exponential in powers of H_i^u :

$$Z_i = \int d\omega f \left\{ 1 + \frac{1}{2} \beta^2 [\langle S_x^2 \rangle_f H_{ix}^2 + \langle S_y^2 \rangle_f H_{iy}^2 + \langle S_z^2 \rangle_f H_{iz}^2] + \dots \right\}, \quad (25)$$

where for convenience we have replaced S_i^x, S_i^y, S_i^z by S_x, S_y, S_z ,

$$f = \exp \beta (K S_z^2 - \frac{1}{2} K' S_z^4) \equiv \exp \beta F, \quad (26)$$

and

$$\langle Q \rangle_f = \int d\omega Q f / \int d\omega f. \quad (27)$$

Clearly

$$\begin{aligned} \sigma_i^u &= \frac{1}{Z_i} \frac{\partial Z_i}{\partial (\beta H_{iu})} \\ &= \beta \langle S_u^2 \rangle_f H_{iu}, \end{aligned} \quad (28)$$

to lowest order. Since

$$\langle S_x^2 \rangle_f = \langle S_y^2 \rangle_f = \frac{1}{2} (S^2 - \langle S_z^2 \rangle_f), \quad (29)$$

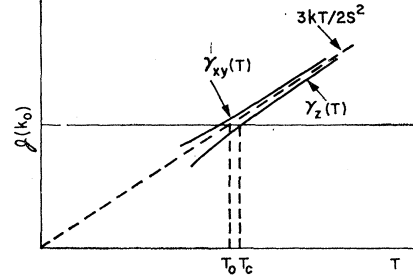


FIG. 2. Qualitative behavior of the functions $\gamma(T)$; illustration of the determination of the highest transition temperature T_c , when $K_{ij} = K\delta_{ij}$, and the easy axis dominates the easy plane.

(28) becomes

$$\begin{aligned} \sum_{j \neq i} (J_{ij} + K_{ij}) \sigma_j^z &= \frac{kT}{2 \langle S_z^2 \rangle_f} \sigma_i^z, \\ \sum_{j \neq i} J_{ij} \sigma_j^u &= \frac{kT}{S^2 - \langle S_z^2 \rangle_f} \sigma_i^u, \quad u = x, y. \end{aligned} \quad (30)$$

The transition temperature T_c is now determined by the maximum T for which nonzero values of σ_i^u (for any u) satisfy these linear homogeneous equations.

To get a feeling for these equations, let us first consider the case of no anisotropy. Then $\langle S_z^2 \rangle_f = S^2/3$, independent of T , and (30) becomes $\sum J_{ij} \sigma_j^u = (3kT/2S^2) \sigma_i^u$. Hence $3kT_c/2S^2 = g(\mathbf{k}_0)$, the maximum eigenvalue of J_{ij} , in agreement with Villain's result.¹ [S^2 is simply replaced here by $S(S+1)$ for the quantum-mechanical case.] Next suppose that $K_{ij} = K\delta_{ij}$. Then (30) becomes

$$\begin{aligned} \sum J_{ij} \sigma_j^z &= \gamma_z(T) \sigma_i^z, \\ \sum J_{ij} \sigma_j^u &= \gamma_{xy}(T) \sigma_i^u, \quad u = x, y, \end{aligned} \quad (31)$$

where

$$\begin{aligned} \gamma_z(T) &= kT/2 \langle S_z^2 \rangle_f, \\ \gamma_{xy}(T) &= kT/(S^2 - \langle S_z^2 \rangle_f). \end{aligned} \quad (32)$$

Assuming KS^2/kT_c and $K'S^4/kT_c$ to be small ($\lesssim 0.1$), we have

$$\begin{aligned} \langle S_z^2 \rangle_f &\cong \frac{S^2}{3} \left[1 + \frac{4KS^2}{15kT} \left(1 - \frac{3K'S^2}{7K} \right) \right] \\ &\cong \frac{1}{3} S^2 (1 + a/kT), \end{aligned} \quad (33)$$

so that

$$\begin{aligned} \gamma_z(T) &\cong \frac{kT}{\frac{2}{3} S^2 (1 + a/kT)}, \\ \gamma_{xy}(T) &\cong \frac{kT}{\frac{2}{3} S^2 (1 - a/2kT)}. \end{aligned} \quad (34)$$

Hence if $3K'S^4/7KS^2 < 1$, and $K > 0$ (that is, the easy axis dominates), then a is positive and $\gamma_z(T)$ and $\gamma_{xy}(T)$, respectively, lie below and above the line $3kT/2S^2$, as shown in Fig. 2. The Curie temperature is then de-

terminated by $\gamma_z(T_c) = g(\mathbf{k}_0)$. At $T = T_c$, it is clear that the only possible value of σ_i^x, σ_i^y satisfying (31) is zero, i.e., these components are disordered. Furthermore, the solution of (31) when $T = T_c$, is $\sigma_i^z = \sigma \cos \mathbf{k}_0 \cdot \mathbf{R}_i$, so that we have a static *longitudinal spin wave* (LSW) as a consequence of molecular field theory in conjunction with the energy function (1) with appropriate parameters. In this case ($K_{ij} = 0$ for $i \neq j$), we see that the wavelength at T_c is the same as that at $T = 0$.

An intuitive reason for the occurrence just below T_c of this longitudinal wave for any finite positive K , no matter how small, is as follows. For no anisotropy there are many configurations that are degenerate, in the sense that they all correspond to the same ordering temperature. Examples of these degenerate configurations [all of which are given by the solutions of (31) with $\gamma_z = \gamma_{xy}$] are simple spirals, elliptically polarized waves, and linearly polarized waves, the LSW being a special case of the latter. Although the free energies for these various states are not equal at finite intervals below T_c (Villain¹ essentially showed the simple spirals to be lowest), they become equal at infinitesimal intervals since the amplitudes all tend to zero. The introduction of anisotropy removes this degeneracy: If the easy plane dominates, the simple spiral lying in the easy plane is lowest; if the easy axis dominates, the linearly polarized wave with polarization along the easy axis gives the lowest free energy.

Returning now to the more general Eqs. (30), we again make the (nonessential) assumption of small anisotropy so that (34) holds for $T \gtrsim T_c$ and therefore $\gamma_z(T)$ and $\gamma_{xy}(T)$ clearly monotonically decrease as T decreases in the region of interest. Then T_c is determined by the larger of the solutions of

$$\gamma_z(T) = g(\mathbf{k}_0') + \mathcal{K}_0(\mathbf{k}_0') \equiv L_z(\mathbf{k}_0'), \quad (35)$$

$$\gamma_{xy}(T) = g(\mathbf{k}_0), \quad (36)$$

where \mathbf{k}_0' maximizes $g(\mathbf{k}) + \mathcal{K}_0(\mathbf{k})$,¹⁶ and

$$\mathcal{K}_0(\mathbf{k}) = \sum_{j \neq i} K_{ij} \cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j) = \mathcal{K}(\mathbf{k}) - K. \quad (37)$$

There are two possibilities which we define using (34):

(a). $L_z(\mathbf{k}_0') - g(\mathbf{k}_0) + 9a/4S^2 > 0$. Then T_c is determined by (35) and the spins first order in a LSW. This gives the possibility of the wavelength at T_c being different from that ($2\pi/\mathbf{k}_0$) at $T = 0$, provided K_{ij}/J_{ij} is not independent of i and j .¹⁷ In this case, to the same order as (33),

$$kT_c = \frac{2}{3}S^2L_z(\mathbf{k}_0') + a, \quad (38)$$

¹⁶ Note that J_{ij} and K_{ij} commute since $\exp i\mathbf{k} \cdot \mathbf{R}_i$ diagonalizes both; thus the eigenvalues of $J_{ij} + K_{ij}$ are simply the sum $g(\mathbf{k}) + \mathcal{K}(\mathbf{k})$, of their respective eigenvalues. $\mathcal{K}_0(\mathbf{k})$ appears in (35) because the sum in (30) excludes $j = i$.

¹⁷ A similar variation of wavelength with temperature has been discussed by Freiser (reference 15). In his case, the cause of the variation is a nonequivalence of spins rather than the dipolar anisotropy in the present work.

or

$$T_c \cong T_{c0} \left[1 + \frac{\mathcal{K}_0(\mathbf{k}_0')}{g(\mathbf{k}_0')} + \frac{a}{kT_{c0}} \right], \quad (39)$$

where

$$kT_{c0} = \frac{2}{3}S^2g(\mathbf{k}_0), \quad (40)$$

the transition temperature in the absence of anisotropy. The wavelength shift for the linear chain, in this order, is easily seen to be given by

$$k_0' - k_0 = -\mathcal{K}_0'(k_0')/g''(k_0), \quad (40')$$

where the primes on \mathcal{K}_0 and g indicate differentiation, or the appropriate directional derivatives in other than a linear chain.

(b). $L_z(\mathbf{k}_0') - g(\mathbf{k}_0) + 9a/4S^2 < 0$. Then T_c is determined by (36) and the spins first order in a simple spiral, the spins being perpendicular to the z direction. In this case the wavelength must be the same as that in the ground state. The expression for T_c is obtained by an obvious modification of (39).

Note that the condition (a) is consistent with the requirements of Sec. II for a ferromagnetic spiral ground state. Hence with our simple energy function (1), in which the parameters (J_{ij} , etc.) are taken to be independent of temperature, we can match both the low- and the high-temperature configurations in erbium, including such details as the proper cone angle at $T = 0$ and the difference in wavelength at $T = 0$ and at $T = T_c$ (as well as further details discussed in the following sections). On the other hand, dysprosium cannot be handled by the present molecular field approximation (MFA) to the thermal properties of (1), since at low temperatures the parallel spins are found experimentally to lie in the basal plane.^{2,3} This of course is not a serious objection to the MFA since it is known³ that there is considerable anisotropy in the basal plane; furthermore the addition of such anisotropy to (1) would favor the Dy ordering, even in the MFA.

However, there is a recent example⁹ in which the MFA is qualitatively misleading, contrary to general expectations. Suppose we put $K' = 0$ in (1) and take $K_{ij} = K\delta_{ij}$, with $K < 0$. Then (1) is identical to the energy considered by Yosida and Miwa,⁹ who showed by spin-wave theory that it is possible to have a simple ferromagnetic ground state ($\mathbf{k}_0 = 0$), and have a transition at some finite temperature to a simple spiral, with the spins always lying the basal plane. However in this case, the MFA insists that the high- T ordering be simple ferromagnetic [by (31) and (36)]. Since the spin-wave theory is almost certainly correct, we must conclude that the molecular field approximation is almost certainly incorrect, barring the unlikely possibility that the exact statistical mechanics would give transitions from a ferromagnet to a simple spiral back to a ferromagnet.

In other words, in this example, the MFA probably gives *qualitatively* incorrect results.¹⁸

Hence a fitting of the experimental results for Dy by using the MFA in connection with an energy function more general than Eq. (1) is questionable. Logically the same skepticism is valid in connection with Er as well. However, the MFA could be qualitatively or even semiquantitatively correct for energy functions of the type that characterize Er, even though it is not for the Dy type of function. Moreover, we feel that our investigation of the predictions of the MFA is justified because we have shown that the unusual magnetic behavior observed in Er at high temperatures corresponds (for appropriate parameter values) to the lowest free energy over the class of independent-particle distributions, this class forming much of the basis for present intuitive understanding in magnetism.

2. $T \lesssim T_c$

In this section we investigate the behavior of the spin system as T decreases below T_c , assuming LSW ordering at T_c . We first point out that it is highly unlikely that the simple expression $\sigma_i^z = \sigma \cos \mathbf{k}_0' \cdot \mathbf{R}_i$, $\sigma_i^x = \sigma_i^y = 0$ is an exact solution to (23). For, if we assume such an expression, it follows that $H_{iz} = 2L_z(\mathbf{k}_0')\sigma_i^z$ so that (23) becomes

$$\sigma_i^z = SG[2\beta L_z(\mathbf{k}_0')\sigma_i^z],$$

where

$$G(x) = \int_{-1}^1 d\mu \mu \exp(\mu x + \beta K \mu^2 - \frac{1}{2}\beta K' \mu^4) / \int_{-1}^1 d\mu \exp(\mu x + \beta K \mu^2 - \frac{1}{2}\beta K' \mu^4),$$

with $\sigma_i^x = \sigma_i^y = 0$.

If we are to have such a solution, then there must be more than one solution to $Cx = G(x)$, (C is a constant), and in fact the various solutions x_i must be proportional to $\cos \mathbf{k}_0' \cdot \mathbf{R}_i$; in general, therefore, there must be an infinite number of such x_i . Now $G(x)$ never decreases with increasing x , $G(0) = 0$, $G(\pm \infty) = \pm 1$, and $G(x)$ is single-valued, so that the oscillations that $G(x)$ must exhibit, in order that it cross the line Cx in many places, cannot be large. In the familiar limiting cases, $K = K' = 0$ (G = Langevin function) and $K \rightarrow \infty$ (Ising model), there is no such oscillatory behavior, so that any oscillations (for $x > 0$) are unlikely in the general case, let alone the particular complex type of oscillations needed.

However, we have seen that $\sigma_i^z = \sigma \cos \mathbf{k}_0' \cdot \mathbf{R}_i$ is a

¹⁸ The essential reason for this, as pointed out by Yosida and Miwa, is that at $T=0$ there are two locally stable states of nearly the same energy, but the curvature of the energy function is different for the two states. The state corresponding to higher energy at $T=0$ can be of lower free energy at finite T if its corresponding curvature is smaller. The molecular field theory does not handle this effect of curvature adequately.

solution of (23) (giving minimum free energy) provided only the lowest order term in $G(x)$ (for x small) is retained. In the following we obtain the corresponding solution that is valid to higher orders.

Writing

$$\sigma_i^u = \sum_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_i) Q_u(\mathbf{k})$$

and carrying the expansion (25), (28) to higher terms we get

$$\begin{aligned} Q_u(\mathbf{k})^* &= 2\beta \langle u^2 \rangle_f Q_u(\mathbf{k})^* + \frac{8\beta^3}{3!} [\langle u^4 \rangle_f - 3(\langle u^2 \rangle_f)^2] \\ &\times \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \delta(\mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, \mathbf{K}) L_u(\mathbf{k}_1) L_u(\mathbf{k}_2) \\ &\times L_u(\mathbf{k}_3) Q_u(\mathbf{k}_1) Q_u(\mathbf{k}_2) Q_u(\mathbf{k}_3) \\ &+ 4\beta^3 \sum \delta(\mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, \mathbf{K}) [a_{uv} L_u(\mathbf{k}_1) L_v(\mathbf{k}_2) \\ &\times L_v(\mathbf{k}_3) Q_u(\mathbf{k}_1) Q_v(\mathbf{k}_2) Q_v(\mathbf{k}_3) \\ &+ a_{uw} L_u(\mathbf{k}_1) L_w(\mathbf{k}_2) L_w(\mathbf{k}_3) Q_u(\mathbf{k}_1) Q_w(\mathbf{k}_2) Q_w(\mathbf{k}_3)] \\ &+ \dots, \end{aligned} \quad (41)$$

where

$$\begin{aligned} \langle u^n \rangle_f &= \langle S_u^n \rangle_f, \\ a_{uv} &= \langle u^2 v^2 \rangle_f - \langle u^2 \rangle_f \langle v^2 \rangle_f, \\ L_u(\mathbf{k}) &= \sum_j L_{ij}^u \cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j), \end{aligned}$$

and no pair of u, v, w are equal. Also \mathbf{K} are vectors of the rationalized reciprocal lattice. We now follow a procedure identical to that used in a perturbation theory¹⁹ developed in another connection. We write

$$\beta = \beta_c (1 + \eta), \quad (42)$$

$$\beta_c = 1/kT_c = 1/[2\langle z^2 \rangle_0 L_z(\mathbf{k}_0')], \quad (43)$$

with $\langle z^2 \rangle_0 = \langle z^2 \rangle_f$ evaluated at $T = T_c$, and obtain a solution of (41) in the form

$$Q_u(\mathbf{k}) = \eta^\alpha \sum_{n=0}^{\infty} q_{un}(\mathbf{k}) \eta^n, \quad 0 < \alpha \leq 1. \quad (44)$$

In lowest order, we get

$$q_{u0}(\mathbf{k}) = 2\beta_c \langle u^2 \rangle_0 L_u(\mathbf{k}) q_{u0}(\mathbf{k}), \quad (45)$$

so that $q_{z0}(\mathbf{k}_0')$ and $q_{z0}(\mathbf{k}_0')^*$ are arbitrary in this order, with all other $q_{u0}(\mathbf{k}) = 0$. [We assume that $L_z(\mathbf{k}) = L_z(\mathbf{k}_0')$ only for $\mathbf{k} = \pm \mathbf{k}_0'$.] This is just the LSW solution obtained in the previous section.

Considering the next order leads to

$$\alpha = \frac{1}{2}, \quad (46)$$

which gives the temperature dependence $(T_c - T)^{\frac{1}{2}}$ (which is characteristic of the usual Langevin and Brillouin function dependence—the coefficient, however,

¹⁹ T. A. Kaplan, Phys. Rev. 119, 1460 (1960).

is different). Neglecting terms like ηa (small anisotropy) and assuming \mathbf{k}_0 small (so that the only term in $\sum \delta(\mathbf{k}_0' + \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, \mathbf{K})$ is that for $\mathbf{K} = 0$, as is true for the wavelength found² in Er) we find

$$|q_{z0}(\mathbf{k}_0')|^2 = \frac{2\langle z^2 \rangle_0^3}{3\langle z^2 \rangle_0^2 - \langle z^4 \rangle_0}. \quad (47)$$

Furthermore,

$$q_{u1}(\mathbf{k}) = 0, \quad u = x, y, \quad (48)$$

that is, the transverse components are zero to order $\eta^{\frac{1}{2}}$ —we expect this to be true to all orders. This is not to say that the transverse components remain zero for all T (below we find the contrary). It is expected that the present series, at least for the x, y components, is asymptotic, so that zero values for these components down to some temperature T_c' , below which they are non-zero is consistent with this description.

For the next term in the longitudinal components, we have for $\mathbf{k} \neq \pm \mathbf{k}_0'$,

$$q_{z1}(\mathbf{k})^* \left[1 - \frac{L_z(\mathbf{k})}{L_z(\mathbf{k}_0')} \right] = \frac{1}{3!} \frac{\langle z^4 \rangle_f - 3\langle z^2 \rangle_f^2}{\langle z^2 \rangle_f^3} \sum_{r,s,t=\pm 1} \sum_{\mathbf{K}} \delta[\mathbf{k} + \mathbf{k}_0'(r+s+t), \mathbf{K}] \times q_{z0}(r\mathbf{k}_0') q_{z0}(s\mathbf{k}_0') q_{z0}(t\mathbf{k}_0'). \quad (49)$$

Thus higher harmonics at $\mathbf{k} = 3\mathbf{k}_0'$, etc., enter in order $\eta^{\frac{1}{2}}$. For those at $3\mathbf{k}_0'$, we get

$$q_{z1}(3\mathbf{k}_0') = -\frac{1}{3} \frac{L_z(\mathbf{k}_0')}{L_z(\mathbf{k}_0') - L_z(3\mathbf{k}_0')} q_{z0}(\mathbf{k}_0'), \quad (50)$$

where we have taken $q_{z0}(\mathbf{k}_0')$ real and have used Eq. (47). Such higher harmonics were not observed in the high-temperature phase of erbium²; however, it is possible that these terms (which go as $\eta^{\frac{1}{2}}$ in the cross section) actually remain quite small for a fair temperature range.

We can now show that, for appropriate parameter values, the longitudinal spin wave solution actually gives the minimum free energy over all product-distribution functions for $T_c - T$ sufficiently small and positive. Noting that the only other solution in this temperature region of the equilibrium equations (23) is the disordered state, we need only show that

$$A - A_d = \frac{1}{2} \sum \sigma_i \cdot \mathbf{H}_i - kT \sum \ln(Z_i/Z_f) \quad (51)$$

is negative, A and A_d being the free energies for the LSW and the disordered state, respectively. [Z_f is the denominator of Eq. (27).] Writing $\sigma_i = \sigma_i^{(0)} + \sigma_i^{(1)} + \dots$, where $\sigma_i^{(n)}$ corresponds to the n th term of (44), and similarly for \mathbf{H}_i we see from (45), (22), and (30), that $\sigma_{iz}^{(0)} = (1/kT_c) \langle z^2 \rangle_0 H_{iz}^{(0)}$, the other components being zero. Then, using (25) and the small anisotropy approximation used in the series development, (51) be-

comes to lowest order

$$A - A_d = \frac{\langle z^2 \rangle_0}{2kT_c} \frac{T - T_c}{T} \sum_i H_{iz} H_{iz}^{(0)2}, \quad (52)$$

which is negative for $T < T_c$. A similar result holds for the other type of solution (dominant easy plane).²⁰

3. The Second Transition Temperature for the LSW Case—Ordering of the Transverse Components

The considerations of the previous section suggest that the minimum free energy solution of (23), for appropriate values of the force constants, behaves as follows. As T decreases from high values, the σ_i are zero until $T = T_c$, below which σ_i^x and σ_i^y first remain identically zero, but $\sigma_i^z \neq 0$. For $T_c - T$ very small (and positive), $\sigma_i^z \cong \sigma \cos \mathbf{k}_0' \cdot \mathbf{R}_i$, where $\sigma \sim (T_c - T)^{\frac{1}{2}}$, \mathbf{k}_0' is constant; as $T_c - T$ increases, corrections [of order $(T_c - T)^{\frac{1}{2}}$] appear in σ_i^z . We now wish to investigate the possibility of the existence of a second transition temperature, $T_c' (< T_c)$, at which the x and y components begin to order. Our problem is to solve (23), which we write out:

$$\sigma_i^u = \int d\omega S_u \exp \beta [H_{ix} S_x + H_{iy} S_y + H_{iz} S_z + F(S_z)] / \int d\omega \exp \beta [\mathbf{H}_i \cdot \mathbf{S} + F(\mathbf{S})]. \quad (23')$$

F is the anisotropy function defined in (26). If the picture suggested by the series solution is to be true, then it must be that for $T_c' < T < T_c$, the only possible solution of (23') written to lowest order in the σ_i^x and σ_i^y and with $\sigma_i^z \neq 0$, is to have $\sigma_i^x = \sigma_i^y = 0$. To this order, (23') is

$$\sigma_i^u = 2\beta \langle S_u^2 \rangle_i \sum J_{ij} \sigma_j^u, \quad u = x, y \quad (53)$$

where

$$\langle S_u^2 \rangle_i = \int d\omega S_u^2 \exp \beta [H_{iz} S_z + F(S_z)] / \int d\omega \exp \beta [H_{iz} S_z + F(S_z)]; \quad (54)$$

we have used $L_{ij}^x = L_{ij}^y = J_{ij}$. As we have seen, at $T = T_c$, $\langle S_u^2 \rangle_i$ is independent of i , and the only solution to (53) is $\sigma_i^u = 0$, $u = x, y$. For T sufficiently close to T_c , H_{iz} will be small, and we can write (54) as

$$\langle S_u^2 \rangle_i \cong \langle S_u^2 \rangle_f + \frac{1}{2} \beta^2 [\langle S_u^2 S_z^2 \rangle_f - \langle S_u^2 \rangle_f \langle S_z^2 \rangle_f] H_{iz}^2. \quad (55)$$

²⁰ Freiser (reference 15), without resorting to a series solution of (23), proved that $A - A_d < 0$, where A corresponds to any ordered solution, for the case of no single-particle terms in the energy. The generalization of his proof to include these terms does not appear to be simple.

For small anisotropy ($a/kT_c \ll 1$), we can simplify further and write (55) as

$$\langle S_u^2 \rangle_i \cong \frac{1}{3} S^2 (1 - \beta a / 2 - (\beta^2 S^2 / 15) H_{iz}^2) + O[(\beta a)^2, \beta a H_{iz}^2]. \quad (56)$$

Then (53) becomes approximately,

$$\sigma_i^u = \frac{2}{3} \beta S^2 (1 - \beta a / 2 - (\beta^2 S^2 / 15) H_{iz}^2) \sum J_{ij} \sigma_j^u, \quad (57)$$

Using the lowest order solution for σ_i^z obtained in the previous section,

$$\sigma_i^z = \sigma \cos \mathbf{k}_0' \cdot \mathbf{R}_i, \quad (58)$$

we have

$$H_{iz} = 2\sigma L_z(\mathbf{k}_0') \cos \mathbf{k}_0' \cdot \mathbf{R}_i$$

and (57) becomes

$$\sigma_i^u = (A + B \cos^2 \mathbf{k}_0' \cdot \mathbf{R}_i) \sum J_{ij} \sigma_j^u, \quad u = x, y, \quad (59)$$

where

$$\begin{aligned} A &= \frac{2}{3} \beta S^2 (1 - \frac{1}{2} \beta a) (> 0), \\ B &= -8\beta^3 S^4 \sigma^2 L_z(\mathbf{k}_0')^2 / 45, \end{aligned} \quad (60)$$

or, in terms of the Fourier transforms,

$$[1 - C \mathcal{J}(\mathbf{k})] Q_u(\mathbf{k}) - \frac{1}{4} B [\mathcal{J}(\mathbf{k} + 2\mathbf{k}_0') Q_u(\mathbf{k} + 2\mathbf{k}_0') + \mathcal{J}(\mathbf{k} - 2\mathbf{k}_0') Q_u(\mathbf{k} - 2\mathbf{k}_0')] = 0, \quad (61)$$

where

$$C = A + \frac{1}{2} B. \quad (62)$$

Equation (61) with $B=0$ is, of course, equivalent to (30) for the transverse components, using the approximation (33). Writing (61) as $\sum M(\mathbf{k}, \mathbf{k}') Q_u(\mathbf{k}') = 0$, we see that T_c' is the highest temperature (which enters through B, C) for which there is a zero eigenvalue of $M(\mathbf{k}, \mathbf{k}')$. So it is convenient to consider the equations

$$\sum M(\mathbf{k}, \mathbf{k}') Q_u(\mathbf{k}') = m(\mathbf{k}) Q_u(\mathbf{k}), \quad (63)$$

where

$$\begin{aligned} M(\mathbf{k}, \mathbf{k}') &= [1 - C \mathcal{J}(\mathbf{k})] \delta(\mathbf{k}, \mathbf{k}') \\ &\quad - \frac{1}{4} B [\mathcal{J}(\mathbf{k} + 2\mathbf{k}_0') \delta(\mathbf{k}', \mathbf{k} + 2\mathbf{k}_0') \\ &\quad + \mathcal{J}(\mathbf{k} - 2\mathbf{k}_0') \delta(\mathbf{k}', \mathbf{k} - 2\mathbf{k}_0')]; \end{aligned}$$

$\delta(\mathbf{k}, \mathbf{k}')$ is the Kronecker delta function. If $B=0$, the highest temperature would be determined by $1 - C \mathcal{J}(\mathbf{k}_0) \equiv m_0(\mathbf{k}_0) = 0$, where \mathbf{k}_0 maximizes $\mathcal{J}(\mathbf{k})$. Since we are interested in small B , we can use standard perturbation theory. The only degeneracy (which is assumed) is $m_0(\mathbf{k}) = m_0(-\mathbf{k})$; since the only such degenerate pair that is connected by the perturbing matrix is that for $\mathbf{k} = \mathbf{k}_0'$, $m(\mathbf{k}_0')$ is the only eigenvalue that will be changed in first order. This change is determined by a simple 2×2 secular equation whose off-diagonal elements are

$$M(\mathbf{k}_0', -\mathbf{k}_0') = -\frac{1}{4} B \mathcal{J}(\mathbf{k}_0') = M(-\mathbf{k}_0', \mathbf{k}_0'), \quad (64)$$

giving

$$\begin{aligned} m_{\pm}(\mathbf{k}_0') &= 1 - C \mathcal{J}(\mathbf{k}_0') \pm \frac{1}{4} B \mathcal{J}(\mathbf{k}_0') \\ &= 1 - \mathcal{J}(\mathbf{k}_0) [A - \frac{1}{2} |B| (1 \mp \frac{1}{2})], \end{aligned} \quad (65)$$

since by (40'), $\mathcal{J}(\mathbf{k}_0') - \mathcal{J}(\mathbf{k}_0)$ is of second order in the

ratio of anisotropy to exchange. All the other eigenvalues in this order are²¹

$$m(\mathbf{k}) = 1 - \mathcal{J}(\mathbf{k}) (A - \frac{1}{2} |B|), \quad \mathbf{k} \neq \mathbf{k}_0'. \quad (66)$$

Since the coefficients of $-\mathcal{J}(\mathbf{k}_0)$ and $-\mathcal{J}(\mathbf{k})$ in (65) and (66), respectively, decrease with increasing T for $T_c - T \gtrsim 0$, the only solution to (61) is $Q_k^u = 0$ ($u = x, y$) unless $T < T_c'$, where T_c' makes the minimum eigenvalue m_0 equal to zero (m_0 is the minimum for fixed A and B). Clearly the minimum of (65) and (66) is $m_+(\mathbf{k}_0')$ so that at T_c' we have

$$\mathcal{J}(\mathbf{k}_0) = 1 / (A - \frac{1}{4} |B|). \quad (65)$$

Using (40), (44), (47) and (60), this yields

$$\Delta \equiv \frac{T_{c0} - T_c'}{T_{c0}} \cong \frac{a}{2kT_{c0}} + \frac{T_c - T_{c0} + T_{c0}\Delta}{3T_{c0}}, \quad (66)$$

so that $\Delta > 0$, giving consistency with our conjecture that the x and y components vanish to every order in the series (44). The first term, $a/2kT_{c0}$, is just what one would have obtained using (34) and (36) as a first guess. The second term represents an added depression in T_c' due to the influence of the z components on the transverse components. The most interesting aspect of this latter effect actually comes through the coupling of \mathbf{k}_0' to $-\mathbf{k}_0'$ [in (59)]—this means that the phase of the transverse wave is coupled to that of the longitudinal wave, which is reasonable. It also gives the result that the wavelength of the transverse wave, when it first orders, is the same as that of the longitudinal wave, as observed in erbium.²

Combining (66) and (39), we finally obtain to lowest order in the anisotropy,

$$\frac{T_c - T_c'}{T_{c0}} = \frac{\mathcal{K}_0(\mathbf{k}_0) S^2}{kT_{c0}} + \frac{3KS^2}{5kT_{c0}} \left(1 - \frac{3K'S^2}{7K} \right). \quad (67)$$

Hence the difference of the transition temperatures is of the order of the anisotropy energy. If the latter is $\approx 10\%$ of kT_c , then (67) gives order of magnitude agreement for erbium² [where $(T_c - T_c')/T_c \cong 35\%$].

IV. SUMMARY AND DISCUSSION

We have shown that the simple energy function (1) and the molecular field approximation to it, imply a surprisingly detailed reproduction of the complex and

²¹ Of course, the high density of points, \mathbf{k} , means that the $m_{\mathbf{k}}$ for \mathbf{k} near \mathbf{k}_0' will be appreciably changed in higher orders, so that $m_{\mathbf{k}}$ will exhibit two branches near \mathbf{k}_0' instead of only at \mathbf{k}_0' . This should not affect our conclusions. What we are doing is analogous to a common elementary treatment of energy bands [F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940)] in which free electrons are perturbed by a periodic lattice—lowest order perturbation theory gives an energy spectrum that is double-valued only at a single point (in one dimension), the point defined by the Bragg condition.

unusual magnetic ordering observed in erbium by neutron diffraction.² In particular, making the reasonable assumption that the anisotropy coefficients are of the order of 10% of the exchange terms, we have obtained the following results. The ground state of (1) can be a ferromagnetic spiral (FS), as observed in Er at low temperatures. For constant values of the energy parameters consistent with such a ground state, the molecular field approximation must give, for appropriate parameter values, a static longitudinal-spin-wave (LSW) ordering at the highest transition temperature T_c as found in Er. The existence of this possibility, FS at $T=0$ and LSW at $T=T_c$, obtained with constant parameters, is our principal qualitative result. The ingredients required for the FS ground state are sufficiently long range, competing exchange forces and competition between an easy axis and an easy plane coming respectively from the second- and fourth-order terms in our simple spin Hamiltonian. To obtain the LSW at high temperatures one requires, in addition to the competing exchange forces, that the easy axis dominates the easy plane, in the explicit sense of Sec. III-1. We emphasize the fact that when these conditions are satisfied, the longitudinal spin wave gives the lowest free energy over all possible configurations in the molecular field theory (i.e., in the general independent-particle approximation).

Further details obtained in this theory are as follows. The wavelength of the LSW can differ from that at $T=0$ by the order of magnitude found in Er. The wavelength first remains constant as T decreases, as observed. The transverse spin-components remain disordered until a second transition occurs, at T'_c , below which these components order. The calculated value of $T_c - T'_c$ is in order-of-magnitude agreement with experiment. The wavelength of the principal Fourier component characterizing these transverse components near T'_c is the same as that for the longitudinal wave, in agreement with experiment. Further, the phase of the transverse components is coupled to that of the longitudinal wave as expected on intuitive grounds. Finally, higher harmonics of odd order appear in the expression for the longitudinal components in the high temperature phase and these were not observed experimentally. However, these occur in the diffraction cross section in order $(T_c - T)^3$ (as contrasted with the order $(T_c - T)$ characterizing the lowest harmonic), so that they should be small over most of the high-temperature phase, becoming appreciable as T decreases further. Since such higher harmonics were observed below T'_c , it appears that even this detail might well be in agreement with experiment. However, such a detailed comparison seems premature for a number of reasons, one of which is that higher terms in our approximate solution for $T < T_c$ might be important, as suggested by the fact that $T_c - T'_c$ is fairly large in erbium ($\sim 0.35T_c$).

We also calculated the spin-wave spectrum associated with a ferromagnetic spiral ground state. One interesting aspect of the result is that $\omega(\mathbf{k})$ is linear in \mathbf{k} for small \mathbf{k} ,

even though the net spin is not zero. The reason for this is that in this region, the normal modes correspond approximately to oscillations of the components perpendicular to the magnetization, these components themselves forming an antiferromagnetic structure.

To obtain qualitative agreement in the molecular field approximation with the observed ordering in Dy,² one would have to include the anisotropy in the basal plane (which was excluded in our energy expression). However, Yosida and Miwa⁹ showed, using spin-wave theory, that a special case of our Hamiltonian could give such agreement with the experiment on Dy. This points up a basic theoretical difficulty with the molecular field approximation, relating to questions of a qualitative nature.

Holmium, which lies between Er and Dy in the periodic table, is also intermediate in its magnetic ordering.² At low temperatures it is essentially a ferromagnetic spiral like Er, but with a much smaller ζ component. At high temperatures, there is a simple spiral, as in Dy. This type of behavior is possible with our energy function treated in the molecular field approximation. The smaller value of $\cos^2\theta_0$ can be obtained with smaller, but still positive, $\mathcal{K} - [\mathcal{J}(\mathbf{k}_0) - \mathcal{J}(0)]$ [see Eq. (5)], and then having \mathcal{K}/K' smaller can lead to the dominance of the easy plane, in the sense of Sec. III-1, giving a simple spiral at high temperatures. However, because of the above-mentioned fundamental difficulty with the molecular field approximation, it does not seem worthwhile pursuing this now in any greater detail.

Because of this difficulty, and despite the very detailed agreement of our results with experiment in Er, we suggest that the best way of obtaining information as to the basic energy parameters is by means of low-temperature measurements. One of the most powerful tools in this connection is the coherent inelastic scattering of neutrons,²² by means of which one can directly obtain the spin-wave spectrum. Such experiments should be feasible, because of the availability of single crystals of the rare earth metals and because of their large moments.

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NOTE ADDED

After this work was completed, I learned that R. J. Elliott had been considering the same problems. His work, which is different in approach from ours, appears in the *Physical Review*.²³

²² See B. N. Brockhouse, *Phys. Rev.* **106**, 859 (1957); **111**, 1273 (1958).

²³ R. J. Elliott, *Phys. Rev.* **124**, 346 (1961).

APPENDIX

We show here that a spiral minimizes the exchange energy associated with a hexagonal close-packed lattice, the proof being needed since this structure is not a Bravais lattice,¹⁰ there being two sites per primitive unit cell. In the notation of Lyons and Kaplan,¹⁰ the exchange energy is

$$E_{\text{ex}} = - \sum_{n\nu, m\mu} J_{n\nu, m\mu} \mathbf{S}_{n\nu} \cdot \mathbf{S}_{m\mu} \\ = \sum_k \sum_{\nu\mu} L_{\nu\mu}(\mathbf{k}) \mathbf{Q}_{k\nu} \cdot \mathbf{Q}_{k\mu}^*.$$

Here, ν and μ each run over two values, 1 and 2, referring, respectively, to the two different kinds of sites, A_1 and A_2 . Since the A_1 sublattice can be obtained by a translation of the A_2 sublattice, it is clear that $J_{n1, m1} = J_{n2, m2}$ so that $L_{11}(\mathbf{k}) = L_{22}(\mathbf{k})$. Hence the matrices

$\mathbf{L}(\mathbf{k})$ are all of the form

$$\begin{pmatrix} a & b \\ b^* & a \end{pmatrix},$$

the unnormalized eigenvectors of which are always of the form

$$\begin{pmatrix} \exp i\phi_1 \\ \exp i\phi_2 \end{pmatrix},$$

($\phi_2 - \phi_1 = -\gamma$ or $\pi - \gamma$, where γ is the phase of b). By Eq. (24) of reference 10, it immediately follows that the minimum energy over the weak constraints is given by a simple spiral, and therefore the minimum energy for the original problem is always given by such a spiral.