Prediction of a Possible New Intermediate Spin Ordering in Holmium

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Holmium exists in low-temperature conical and intermediate-temberature spiral magnetic phases, implying a temperature-dependent variation of effective anisotropy. We show that if this anisotropy is varied from the spiral to the conical region there will first be a second-order transition to an intermediate phase whose order is essentially a tilted spiral and then a first-order transition to the cone. The intermediate phase might be found at around 20 K.

The magnetic properties of the heavy rare-earth metals may be described in terms of a Heisenberg exchange due to indirect Ruderman-Kittel-Kasuya-Yosida interaction through the conduction electrons. As a consequence of the long-ranged oscillatory character of this interaction, many rare-earth metals order in helical spin arrangements in which all the spins in any basal plane of the hcp lattice are ordered ferromagnetically but with the direction of magnetization rotating in the c direction with wave vector $\vec{Q}$, where $\vec{Q}$ is that wave vector for which the Fourier transform of the exchange function is maximum.[1] There are two such helical orderings known to date: the spiral, where the ferromagnetic spin direction is in the basal plane; and the cone, where there is a constant ferromagnetic component in the c direction as well as a spiraling basal-plane component. As examples of the spiral arrangement, we may cite intermediate-temperature phases of Tb, Dy, and Ho, and as examples of the conical order the low-temperature phases of Ho and Er. The relative stability of these two phases depends on the axial anisotropy.

It was assumed in the past that if one imagined that the axial anisotropy could be varied, then there would be a certain critical anisotropy separating the spiral and conical phases, the cone angle growing continuously as the anisotropy is varied past the critical value in the appropriate direction.[2] The normal analysis of the relative stability of the two phases ensures stability against long-wavelength excitations. It has however recently been pointed out by Woods *et al.*[3] that the physical requirement of stability against all excitations implies that there is a region of anisotropy around the above-mentioned critical value for which neither the spiral nor the cone is stable. In this paper we show that for anisotropy values within this "forbidden region," and for some values outside it, the true ordered phase is approximately a tilted spiral obtained by tilting the spiral ferromagnetic planes of spins of the "normal phase" about an axis in the crystal basal plane. The various spin orders are illustrated in Fig. 1; Fig. 1(c) shows a structure more stable than 1(d) in a certain region but less stable than 1(b).

A good candidate for experimental investigation may be holmium which exists in both spiral and conical ordered phases and exhibits a tendency for $\vec{Q}$-magnon mode softening near to the transition between these phases.[3] Experimentally, the axial anisotropy is effectively temperature dependent through renormalization effects,[4] and the very existence of the two phases implies that it sweeps through or across the "forbidden" region. It is not known whether the effective anisotropy changes continuously or discontinuously, the discontinuity possibly being stabilized by changes in lattice parameters, exchange, etc. It does, however, seem unlikely that any discontinuous change would completely avoid the intermediate anisotropy region, and it is consequently relevant to examine the nature of the intermediate phase.

The model we use is a system of localized

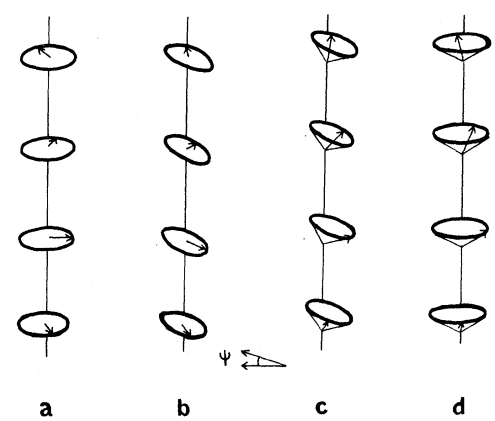

FIG. 1. Possible helically ordered phases. (a) Flat spiral, (b) tilted spiral, (c) tilted cone, (d) normal cone.

spins S_i situated on lattice sites R_i on an hcp lattice described by the Hamiltonian

$$H = -\sum_{i\neq j} J(\vec{R}_i - \vec{R}_j)\vec{S}_i\cdot\vec{S}_j + \sum_i [K_2(S_{i\zeta})^2 + K_4(S_{i\zeta})^4], \tag{1}$$

where the first term is the exchange and K_2 and K_4 are axial anisotropy coefficients. The coordinate system (ξ, η, ζ) is chosen with ζ in the crystal c direction. Defining the Fourier transform of $J(\vec{R}_i - \vec{R}_j)$ by $J(\vec{k})$, we denote by $\vec{Q}$ the $\vec{k}$ value for which $J(\vec{k})$ is maximum. The spins then order in a helical fashion with wave vector $\vec{Q}$. Since $\vec{Q}$ is in general incommensurate with the lattice, we may ignore basal-plane anisotropy. We also ignore the sixfold axial anisotropy as giving no important changes.

For definiteness we consider K_4 to be positive as it is in Ho, and examine the behavior of the system described by (1) as K_2 is varied. The standard conditions for the relative stability of the spiral and conical phases, as found by minimizing the energy with respect to the cone angle, are[2]

$$\begin{aligned} &K_2 > J(\vec{0}) - J(\vec{Q}), \text{ flat spiral;} \\ &K_2 < J(\vec{0}) - J(\vec{Q}), \text{ conical spiral.} \end{aligned} \tag{2}$$

In the conical phase the cone angle is given by

$$2K_4S^2\cos^2\theta = J(\vec{0}) - J(\vec{Q}) - K_2. \tag{3}$$

The elementary excitation spectrum of the normal phases is given by

$$\omega(\vec{k}) = S[J(\vec{Q}+\vec{k}) - J(\vec{Q}-\vec{k})]\cos\theta + S(F_1F_2)^{1/2}, \tag{4}$$

where

$$F_1(\vec{k}) = 2J(\vec{Q}) - J(\vec{Q}+\vec{k}) - J(\vec{Q}-\vec{k}), \tag{5a}$$

$$F_2(\vec{k}) = F_1(\vec{k})\cos^2\theta + 2[J(\vec{Q}) - J(\vec{k}) + K_2 + 6K_4S^2\cos^2\theta]\sin^2\theta. \tag{5b}$$

For a stable state the $\omega(\vec{k})$ must be everywhere real and positive. This requirement imposes restrictions more stringent than (2). The possibility of $\omega(\vec{k})$ becoming nonreal first occurs for $\vec{k} = \pm\vec{Q}$, F_2 becoming negative. Reality requires

$$K_2 > 0, \text{ flat spiral;} \tag{6a}$$

$$K_2 < \tfrac{2}{3}[J(\vec{0}) - J(\vec{Q})] + \tfrac{1}{4}[2J(\vec{Q}) - J(2\vec{Q}) - J(\vec{0})]\cot^2\theta, \text{ cone.} \tag{6b}$$

In the conical phase some $\omega(\vec{k})$ can become negative, indicating instability, before the anisotropy reaches the critical value given by (6b). However, within the approximation of taking $\cot\theta = 0$ in the inequalities, we find in either case

$$K_2 < \tfrac{2}{3}[J(\vec{0}) - J(\vec{Q})], \text{ cone.} \tag{6c}$$

The prediction of a soft mode of wave vector of order $\pm\vec{Q}$ implies that we expect the true stable phase to be essentially describable by the creation of a coherent-phase condensate of magnons of this wave vector.[5] Consideration of the symmetry of the soft mode suggests that the new order is obtained by rotating the plane of the normal spiral or cone base about an axis in the crystal plane.[6]

To analyze this prediction we transform the spin operators in the Hamiltonian (1) to local coordinate systems $(x, y, z)_m$ defined such that the z axes lie on a tilted conical spiral of apex angle θ, tilt angle ψ, and wave vector $\vec{Q}$. We take the y axis to lie in the (ξ, η) plane. In this basis we express H in terms of deviations from classical ordering along the z directions as

$$\begin{aligned} H = E(\theta,\psi) &+ \sum_{N=0}^{4}\sum_m [S_{mx}\lambda_{Nx}(\theta,\psi) + S_{my}\lambda_{Ny}(\theta,\psi)]\exp(iN\vec{Q}\cdot\vec{R}_m) \\ &+ \sum_{N=-4}^{4}\sum_{\vec{k}}\{A_N(\vec{k})a^\dagger(\vec{k})a(\vec{k}+N\vec{Q}) + \tfrac{1}{2}[B_N(\vec{k})a^\dagger(\vec{k})a^\dagger(-\vec{k}-N\vec{Q}) + \text{H.c.}]\} \\ &+ \text{terms of higher order in } a \text{ and } a^\dagger. \end{aligned} \tag{7}$$

In the third term we have expressed the spin deviations of bilinear order in S_x and S_y, including those from $(S_z - S)$,[7] in terms of Holstein-Primakoff boson operators, a and $a^\dagger$, defined by

$$S_{m+} \equiv S_{mx} + iS_{my} = (2S)^{1/2}(1 - a_m{}^\dagger a_m/2S)^{1/2} a_m, \tag{8a}$$

$$S_{m-} \equiv S_{mx} - iS_{my} = (2S)^{1/2} a_m{}^\dagger (1 - a_m{}^\dagger a_m/2S)^{1/2}, \tag{8b}$$

$$a(\vec{k}) = N^{-1/2} \sum_m a_m \exp(i\vec{k}\cdot\vec{R}_m), \tag{9}$$

and have retained terms explicitly up to second order in a and $a^\dagger$. The coefficients λ, A, and B are not necessarily nonzero in all cases; for example, in the normal phase with $\psi = 0$, only $A_0(\vec{k})$ and $B_0(\vec{k})$ are nonzero.

The normal semiclassical approach is to consider only the $E(\theta, \psi)$ term of (7) and minimize with respect to θ and ψ to obtain a model ground state Φ. The presence of terms linear in S_x and S_y in (7) for $\psi \neq 0$ indicates, however, that Φ cannot in this case have the symmetry of the true ground state.[8] Rather, if H is written completely in terms of the Holstein-Primakoff operators to bilinear order, it is recognized as the Hamiltonian of a set of harmonic oscillators some of whose centers are displaced from the origin; the displacement terms are proportional to the λ's. Consequently H may be brought to an acceptable (even) form by a canonical transformation

$$\tilde{H} = UHU^\dagger, \tag{10}$$

where U has the form

$$U = \exp\Big[\sum_{N=-4}^{4} w(N\vec{Q}) a^\dagger(N\vec{Q}) - \text{H.c.}\Big] \tag{11a}$$

$$= \prod_m \exp\Big\{\sum_{N=0}^{4} [S_{my}\mu_{Nx}(\theta,\psi) + S_{mx}\mu_{Ny}(\theta,\psi)] \exp(iN\vec{Q}\cdot\vec{R}_m)\Big\}, \tag{11b}$$

using the linearized version of (8) in the second line. In (11b) the μ are linearly proportional to the λ of corresponding label. The terms of (11b) of the form $\mu_{1x}(\theta,\psi)S_{my}\exp(i\vec{Q}\cdot R_m)$ correspond to altering the angle of tilt of the ground state with respect to the semiclassical model Φ. Similarly terms of the form $\mu_{0x}(\theta,\psi)S_{my}$ correspond to altering the cone apex angle. It is obviously most sensible to include any such effects at the earliest stage possible in the calculation and thus ψ and θ are found more appropriately by requiring that λ_{0x} and λ_{1x} vanish, coupled with the requirement that we take the solution with the lowest $E(\theta,\psi)$ in each case. We call the resulting ground state $\tilde{\Phi}$. The other linear terms of (7) are removed by canonical transformation as above (with different μ from before), and the true ground state Ψ is given by

$$\Psi = U\tilde{\Phi}. \tag{12}$$

We may readily demonstrate that the μ now entering U are small, and consequently Ψ differs from $\tilde{\Phi}$ only in having small higher-harmonic perturbations of pitch and of out-of-plane oscillation superimposed on a basic tilted spiral or cone. These minor modifications will not be discussed further here.

For K_2 positive, $\tilde{\Phi}$ is the normal flat spiral but at $K_2 = 0$ there is a second-order transition to a tilted spiral for $K_2 < 0$. This is precisely the K_2 value at which we found a soft-mode instability in the normal flat spiral; see Eq. (6a). Similarly we find that the normal cone becomes unstable against tilting its base plane as K_2 is increased through $\frac{3}{2}[J(\vec{0}) - J(\vec{Q})](1 - \frac{1}{3}\cot^2\theta)$, ψ and θ varying continuously. This critical K_2 value is that corresponding to soft-mode instability of the normal cone in either the approximation of taking $\cos\theta \ll 1$ or $J(\vec{0}) = J(2\vec{Q})$; see Eqs. (6b) and (6c). The tilted-cone phase will however not occur in practice since energetic considerations indicate that there will be a first-order change from a normal cone to a tilted spiral at

$$K_2 = (1 - 1/\sqrt{2})^{-1}[J(\vec{0}) - J(\vec{Q})]; \tag{13}$$

that is before the soft-mode instability to the tilted conical phase would occur. In the spiral phase

$$\sin^2\psi = -K_2/3K_4S^2. \tag{14}$$

Since the basis for our discussion has been the instability of the normal spiral and cone against $\vec{k} = \pm\vec{Q}$ magnon softening we must ensure that any new phase has stable excitations. To examine the elementary excitation spectra, we consider the bilinear terms of (7). If we retain only the diagonal ($N = 0$) bilinear terms, we predict that in the tilted-spiral phase the magnon energies are as given in the flat spiral phase but with

$$K_2 \to -\tfrac{1}{4}K_2 \sin^2\psi = (K_2)^2/12K_4S^2. \qquad (15)$$

This corresponds to real positive magnon energies. The off-diagonal ($N\neq 0$) bilinear terms lead to superzone band gaps when

$$\tilde{\omega}(\vec{k}) = \tilde{\omega}(\vec{k} \pm N\vec{Q}), \qquad (16)$$

where $\tilde{\omega}$ is the dispersion given by the $N=0$ terms. We must ensure that these gaps do not lead to softening of the modes. In this connection only the $N=1, 2$ terms are of any significance, since only at $\vec{k} \simeq \vec{0}, \pm\vec{Q}$ are the $\tilde{\omega}(\vec{k})$ small. Because of condition (14),

$$A_1(\vec{k}) = B_1(\vec{k}) = 0 \qquad (17)$$

and the leading terms (in $\sin^2\psi$) of A_2 and B_2 are, using (14),

$$A_2(\vec{k}) = B_2(\vec{k}) = \tfrac{1}{2}K_2S. \qquad (18)$$

The split modes at $\vec{k} = \vec{Q}$, which corresponds to the lowest-energy state in the $\vec{k} \sim \vec{Q}$ region, have energies ω given by

$$\omega^2 = \tilde{\omega}^2 + \tfrac{1}{2}(K_2S)^2 \pm K_2S[\tilde{\omega}^2 + \tfrac{1}{4}(K_2S)^2]^{1/2}. \qquad (19)$$

These two solutions are evidently real and positive, and the tilted spiral is consequently stable with respect to $\vec{k} \sim \vec{Q}$ magnon excitation.

We conclude therefore that if the axial anisotropy of a helically ordered array of spins is varied from a value for which a flat spiral is stable to one in which a conical order is stable, then the system will first exhibit a second-order phase transition to a phase which is essentially a tilted spiral with wave vector equal to that of the normal phases but with small harmonic perturbations both of pitch and of out-of-plane oscillation. This phase will then transform by a first-order transition to a normal conical order. It is suggested that this effect may occur in holmium at around 20 K.

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[1]For reviews of the magnetic properties of rare-earth metals see B. R. Cooper, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 21, p. 393; "Magnetic Properties of Rare Earth Metals," edited by R. J. Elliot (to be published).

[2]B. R. Cooper, R. J. Elliott, S. J. Nettel, and H. Suhl, Phys. Rev. 127, 57 (1962).

[3]A. D. B. Woods, T. M. Holden, B. M. Powell, and M. W. Stringfellow, Phys. Rev. Lett. 23, 81 (1969); M. W. Stringfellow, T. M. Holden, B. M. Powell, and A. D. B. Woods, Metal Phys. No. 2, S189 (1970).

[4]H. B. Callen and E. Callen, J. Phys. Chem. Solids 27, 1271 (1966).

[5]W. Kohn and D. Sherrington, Rev. Mod. Phys. 42, 1 (1970).

[6]R. J. Elliott (unpublished) has also come to this conclusion, although his analysis has not been as complete as ours.

[7]$S_z - S$ may be expressed as a (finite) power series in S_+S_-; M. Wortis, Ph.D. thesis, Harvard University, 1963 (unpublished); D. A. Goodings and B. W. Southern, Can. J. Phys. 49, 1137 (1971).

[8]As we have seen bilinear terms can also indicate instability. They may also change the effective $E(\theta,\psi)$ by zero-point effects. We shall ensure there is no instability but shall not consider zero-point modifications, which are of detail, not essence.