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Spin Waves in the Spin-Flop Phase of an Antiferromagnet, and Metastability of the Spin-Flop Transition

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The spin-flop transition in a uniaxial antiferromagnet defines three critical fields; that of the true thermodynamic transition and those limiting the local stability of antiferromagnetic and spin-flop phases. The latter two are calculated by a spin-wave analysis. The results are in qualitative agreement with the hysteresis observed by Schelleng and Friedberg in the spin-flop transition in $MnBr_2 \cdot 4H_2O$. The spin-wave spectrum of the spin-flop phase is given, and the magnetization in the spin-flop phase is found to increase more rapidly than linearly with field because of quantum corrections absent in molecular field theory.

We consider a uniaxial antiferromagnet, at or very near zero temperature, with an applied field parallel to the unique easy axis. As the field is increased a transition occurs to a spin-flop phase, in which the spins are almost orthogonal to the field. Such transitions have been observed by many investigators, and in certain materials considerable hysteresis may be observed in the transition, with different critical fields as the transition is traversed upward and downward in field.[1,2] This is to be expected on the following basis. As the field is increased to a critical value H_c^u, a local instability occurs when one of the spin wave frequencies of the antiferromagnetic configuration becomes negative. As the field is decreased, a local instability in the spin-flop phase occurs at a lower field H_c^ℓ, when one of the spin wave frequencies of the spin-flop phase becomes negative. Between the two critical fields H_c^u and H_c^ℓ, there exists a third field H_c^o, at which the free energies of the two phases are equal. Whether the actual observed transitions occur at H_c^o, without hysteresis, or at H_c^u and H_c^ℓ, with hysteresis, depends upon the presence or absence of nucleating centers and local inhomogeneities. The problem is fully analogous to the super-heating and super-cooling metastability in a conventional gas-liquid first-order phase transition.

An alternative mechanism for the hysteresis has been suggested by Date and Nagata.[2] They ascribe the hysteresis to the existence of a fourth-order anisotropy, in addition to the dominant uniaxial anisotropy. This fourth-order anisotropy introduces

energy minima along both the longitudinal and transverse axes, with an intermediate energy maximum. The hysteresis is associated with the difficulty of overcoming this intermediate energy barrier. However, the hysteresis certainly occurs, and is a large effect, even in materials with very small fourth-order anisotropy, as in $MnBr_2.4H_2O$.(1)

For simplicity, we assume a model decomposable into two equivalent sublattices, with the nearest neighbors of a spin on one sublattice lying entirely on the other sublattice. The anisotropy is taken simply as $-K(S^z)^2$ for each ion, and $2S$ is the exchange interaction of nearest neighbor pairs. Labelling the spins on one sublattice by f and those on the other sublattice by g, the Hamiltonian is

$$\mathcal{H} = 2\sum_{(f,g)} J_{fg}\,\vec{S}_f\cdot\vec{S}_g - \mu H\left[\sum_f S_f^z + \sum_g S_g^z\right] - K\left[\sum_f (S_f^z)^2 + \sum_g (S_g^z)^2\right] \qquad (1)$$

Spin wave analyses of the antiferromagnetic phase have been given by P. W. Anderson(3) and by R. Kubo(4), to which we make one amendment. In application of the Holstein-Primakoff transformation the $K(S_f^z)^2$ operator is replaced by $K(S-a_f^+a_f)^2 = K[S^2-2Sa_f^+a_f + (a_f^+a_f)^2]$ where $a_f^+a_f$ is a boson number operator. The spin wave theory can be looked upon as an expansion in powers of the spin deviation, and $(a_f^+a_f)^2$ can then be neglected. Alternatively all operators can be replaced by simple operators which give the correct matrix elements

in the low-lying states (which alone are important in the spin wave regime) even though relatively large errors are introduced in the high-lying states; this is the procedure suggested by Van Kranendonk and Van Vleck.[5] Thus, for the lowest two levels (in which $a_f^+ a_f = 0$ and 1) we have $(a_f^+ a_f)^2 = a_f^+ a_f$, and in this procedure $K(S_f^z)^2 = K[S^2 - (2S-1)\, a_f^+ a_f]$. We note that for $S = 1/2$ both the right-hand and left-hand members then reduce to $K/4$, whereas the equation is inconsistent if $(a_f^+ a_f)^2$ is neglected. The alteration in the latter formalism is made by replacing $2SK$ by $(2S-1)K$, or K by $\xi^2 K$, where

$$\xi = \sqrt{1 - \frac{1}{2S}} \tag{2}$$

The familiar result of the analysis is that the spin wave spectrum[3,4,5] of the antiferromagnetic phase is composed of a doubly degenerate branch with an energy gap, concave upward at $k = 0$, and approaching linearity with increasing k. The applied field splits the degeneracy, driving one branch upward and one downward. At the critical field H_c^u the $k = 0$ mode of the lower branch is driven down to zero frequency, and this occurs at a field which, with the ξ^2 correction inserted, is

$$\mu H_c^u = 2S\sqrt{\xi^2 K (2zJ - \xi^2 K)} \tag{3}$$

where z is the number of nearest neighbors.

To calculate H_c^l we formulate a spin wave theory of the spin-flop phase. We choose coordinate systems x_1, y, z_1 and x_2, y, z_2 to characterize spins on the f and g sublattices respectively.

The z_1 and z_2 axes lie in the first and second quadrants of the x-z plane respectively, and each makes an angle θ with the z-axis. In choosing these coordinate systems it is anticipated that the spins, initially in the x-z plane, make only small oscillations in the vicinity of that plane. In particular, they do not precess around the z-axis, away from the x-z plane. To ensure that this is so we add an additional planar anisotropy to the Hamiltonian;

$$\mathcal{H}' = \mathcal{H} + K_1 \left[\sum_f (S_f^y)^2 + \sum_g (S_g^y)^2 \right] \tag{4}$$

At the end of the analysis we shall show that the planar anisotropy K_1 has no essential effect, that the spectrum and critical field are very weak functions of K_1, and that we can take $K_1 = 0$ without complication.

We make the Holstein-Primakoff transformation, followed by the replacement by operators appropriate to the low-lying states as discussed above.

$$S_f^z = S - a_f^\dagger a_f \tag{5}$$

$$S_f^+ \equiv S_f^{x_1} + i S_f^y = \sqrt{2S}\left(1 - \frac{a_f^\dagger a_f}{2S}\right)^{1/2} a_f \rightarrow \sqrt{2S}\left[a_f - (1-\tfrac{1}{2}) a_f^\dagger a_f a_f\right] \tag{6}$$

$$S_f^- \equiv S_f^{x_1} - i S_f^y = \sqrt{2S}\, a_f^\dagger \left(1 - \frac{a_f^\dagger a_f}{2S}\right)^{1/2} \rightarrow \sqrt{2S}\left[a_f^\dagger - (1-\tfrac{1}{2}) a_f^\dagger a_f^\dagger a_f\right] \tag{7}$$

and similarly for $S_g^{z\,2}$, S_g^+, S_g^-. These operators have correct matrix elements among the three lowest-lying states of each spin. Substituting in the Hamiltonian H', we neglect terms whose matrix

elements would be quadratic in the amplitude of the second excited state, such as $a_f^+ a_f^+ a_f a_f$, or those whose matrix elements would be proportional to the product of the amplitudes of the first and second excited states, such as $a_f^+ a_f a_f$. A term such as $a_f^+ a_f a_f a_f^+ a_f^+ a_f$ is replaced by $2a_f^+ a_f$. We thereby obtain a Hamiltonian involving zero, first, and second order terms in the boson operators. The condition that the first order terms vanishes determines θ:

$$\cos\theta = \frac{\mu H}{2S(2zJ - \xi^2 K)} \tag{8}$$

The resultant Hamiltonian is most conveniently written in terms of spin wave operators, defined by

$$a_k = \sqrt{\frac{2}{N}} \sum_f a_f e^{-i \vec{k}\cdot\vec{r}_f} \tag{9}$$

and

$$b_k = \sqrt{\frac{2}{N}} \sum_g a_g e^{-i \vec{k}\cdot\vec{r}_g} \tag{10}$$

whence

$$\begin{aligned} \mathcal{H}' = E_0 &+ A\sum_k (a_k^+ a_k + b_k^+ b_k) + \\ &+ B\sum_k (a_k a_{-k} + a_k^+ a_{-k}^+ + b_k b_{-k} + b_k^+ b_{-k}^+) + \\ &+ \sum_k d_k (a_k b_{-k} + a_k^+ b_{-k}^+) + \sum_k e_k (a_k b_k^+ + a_k^+ b_k) \end{aligned} \tag{11}$$

where

$$A = 2zJS - S\xi^2 K \sin^2\theta + \xi^2 K_1 S \tag{12}$$

$$B = -\tfrac{1}{2} S\xi K \sin^2\theta - \tfrac{1}{2} S\xi K_1 \tag{13}$$

$$d_k = -2zJS \sin^2\theta \; \gamma_k \tag{14}$$

$$e_k = 2zJS \cos^2\theta \; \gamma_k \tag{15}$$

and $z\gamma_k$ is defined, as usual, by the summation of $\exp(i\vec{k}.\vec{\delta}_i)$ over the z nearest neighbors at positions $\vec{\delta}_i$. The Hamiltonian is diagonalized by the transformations

$$\alpha_k = 2^{-3/2}(\lambda_k + \lambda_k^{-1})(a_k - b_k) - 2^{-3/2}(\lambda_k - \lambda_k^{-1})(a_{-k}^{+} - b_{-k}^{+})$$

$$\beta_k = 2^{-3/2}(\mu_k + \mu_k^{-1})(a_{-k} + b_{-k}) - 2^{-3/2}(\mu_k - \mu_k^{-1})(a_k^{+} + b_k^{+}) \tag{16}$$

where (17)

$$\lambda_k = \left(\frac{A - 2B + d_k - e_k}{A + 2B - d_k - e_k}\right)^{1/4} \tag{18}$$

$$\mu_k = \left(\frac{A - 2B - d_k + e_k}{A + 2B + d_k + e_k}\right)^{1/4} \tag{19}$$

giving

$$\mathcal{H}' = E_0 + \tfrac{1}{2}NA + \sum_k \hbar\omega_1(k)\left(\alpha_k^{+}\alpha_k + \tfrac{1}{2}\right) + \sum_k \hbar\omega_2(k)\left(\beta_k^{+}\beta_k + \tfrac{1}{2}\right) \tag{20}$$

with the spin wave energies

$$\hbar\omega_1(k) = 2zJS\left[1-\gamma_k+\xi(1-\xi)\tilde{K}\sin^2\theta+\xi(1+\xi)\tilde{K}_1\right]^{1/2}\left[1-\gamma_k\cos 2\theta-\xi(1+\xi)\tilde{K}\sin^2\theta+\xi(1-\xi)\tilde{K}_1\right]^{1/2} \quad (21)$$

$$\hbar\omega_2(k) = 2zJS\left[1+\gamma_k+\xi(1-\xi)\tilde{K}\sin^2\theta+\xi(1+\xi)\tilde{K}_1\right]^{1/2}\left[1+\gamma_k\cos 2\theta-\xi(1+\xi)\tilde{K}\sin^2\theta+\xi(1-\xi)\tilde{K}_1\right]^{1/2} \quad (22)$$

and with $\tilde{K}$ and $\tilde{K}_1$ denoting the "reduced" anisotropy constants

$$\tilde{K} = K/(zJ) \quad , \quad \tilde{K}_1 = K_1/(zJ) \quad (23)$$

It will also be recalled that $\xi = \sqrt{1-(2S)^{-1}}$ and $\cos\theta = \mu H[2S(2zJ - \xi^2 K)]^{-1}$, in terms of which the spectrum of the spin-flop phase is completely defined.

For small anisotropy the $\omega_1(k)$ branch is almost linear in k, because of the first square root, whereas the $\omega_2(k)$ branch has a large k = 0 intercept. Consequently we refer to the $\omega_1(k)$ branch as the acoustical branch and the $\omega_2(k)$ branch as the optical branch. The optical branch has vanishing initial slope, a negative initial curvature for large applied fields ($\cos^2\theta \gg \frac{1+\xi\tilde{K}}{3+\xi(2-\xi)\tilde{K}}$, if $K_1 = 0$) and a positive initial curvature for small applied fields, as indicated in Fig. 1. The change in initial curvature occurs because the values of $\omega_2(k)$ for small k decrease rapidly with increasing H, whereas the decrease is less rapid for large k. In contrast the applied field increases the frequency of modes in the acoustical branch.

As the field is decreased to the critical value H_c^{ℓ} the frequency of the k = 0 optical mode vanishes (see Fig. 1). This critical field is found by taking $\gamma_k = 1$ and setting the second

radical in equation (21) equal to zero, giving

$$\cos^2\phi = \frac{\xi(1+\xi)\tilde{K} - \xi(1-\xi)\tilde{K}_1}{2+\xi(1+\xi)\tilde{K}} \tag{24}$$

or

$$\mu H_c^{\ell} = 2S(2zJ - \xi^2 K)\sqrt{\frac{\xi(1+\xi)K - \xi(1-\xi)K_1}{4zJ + \xi(1+\xi)K}} \tag{25}$$

We now note that $\xi \to 1$ for large spin, and in the classical limit ($S \to \infty$) the critical field becomes independent of K_1. For even small spin the fictitious anisotropy has little effect; in the most extreme case ($S=1$) the coefficient of K_1 is only .21, whereas the coefficient of K is 1.20. The effect of the anisotropy K_1 for small spin values is traceable to the quantum fluctuations of S^y, which enables these spins to sense the energy out of the x-z plane. In accordance with the reality of the physical situation we henceforth take $K_1 = 0$.

For MnF_2 the ratio $\tilde{K} = K/(2zJ)$ is $\sim .01$, so that the two fields H_c^u and H_c^{ℓ} differ by only about 2%. But for $MnBr_2 \cdot 4H_2O$ the field $2S(2zJ)/\mu$ is approximately 25 kilo-oersteds, whereas $2SK/\mu$ is approximately 3 k-oe. Hence H_c^u and H_c^{ℓ} differ by about 2 k-oe., with a mean of about 8 k-oe. This in general agreement with the scale of the hysteresis observed by Schelleng and Friedberg[1] in the spin-flop transition.

It should perhaps be mentioned that the field H_c^u can be found alternatively by extrapolating to zero frequency the field $H(\omega)$ required for antiferromagnetic resonance at frequency ω. Thus the

separation of the critical fields H_c^u and H_c^o can be observed in principle even in materials in which impurities destroy the metastability of the "superheating" or "supercooling" states.

The net matnetization $\langle S_f^z \rangle$ and the sublattice magnetization $\langle S_f^{z1} \rangle$ are of interest. These quantities are related by

$$\langle S_f^z \rangle = \langle S_f^{z1} \rangle \cos\theta = \frac{\mu H}{2S(zJ - \xi^2 K)} \langle S_f^{z1} \rangle \tag{26}$$

and the sublattice magnetization is

$$\langle S_f^{z1} \rangle = S + \tfrac{1}{2} - \frac{1}{N} \sum_k \left\{ \frac{zJS(1-\gamma_k \cos^2\theta) - \xi^2 KS \sin^2\theta}{\hbar\omega_1(k)} \left[n_1(k) + \tfrac{1}{2} \right] + \right. \tag{27}$$

$$\left. + \frac{zJS(1+\gamma_k \cos^2\theta) - \xi^2 KS \sin^2\theta}{\hbar\omega_2(k)} \left[n_2(k) + \tfrac{1}{2} \right] \right\}$$

Here $n_1(k)$ is the average occupation of the acoustical mode of wave vector k; $n_1(k) = \left\{ \exp\left[\beta\hbar\omega_1(k)\right] - 1 \right\}^{-1}$, and similarly for $n_2(k)$.

Several limiting cases of interest can be identified immediately. Let $T = 0$ (or $\beta = \infty$), $H = 0$, and $K = 0$. We then are discussing the ground state of the simple antiferromagnet, and equation (27) reduces directly to

$$\langle S_f^{z1} \rangle = S - \frac{1}{N} \sum_k \left[\frac{1}{\sqrt{1-\gamma_k^2}} - 1 \right] \tag{28}$$

which is the familiar result of Anderson.[3] By numerical calculation of the summation in equation (28) Anderson has found a reduction of approximately .08 in the effective spin from its "ideal" value of S.

In the opposite limit we again take T = 0 and we note that when H takes the critical value

$$\mu H_c = 2S(zJ - \xi^2 K) \tag{29}$$

then $\theta = 0$ and $\langle S_f^z \rangle = S$. Thus the spin-flop phase undergoes a second order phase transition to a fully-aligned phase, with fully saturated spin components. This second-order transition has been discussed by Falk[6] for the special case of zero anisotropy by a variational method, and by Anderson and Callen[7] by a Green function method which extends the theory to higher temperatures. The latter authors have also analyzed the critical field H_c^u in the intermediate temperature region, and the thermodynamics of the antiferromagnetic and paramagnetic phases.

As the field is increased at constant temperature, through the spin-flop range, $\langle S_f^z \rangle$ increases through two contributions. Firstly, cos θ increases linearly with H, and secondly the sub-lattice magnetization $\langle S_f^z \rangle$ increases (becoming equal to S only at H_c). Consequently $\langle S^z \rangle$ increases faster than linearly with H, as contrasted with the strictly linear variation predicted by molecular field theory.[8]

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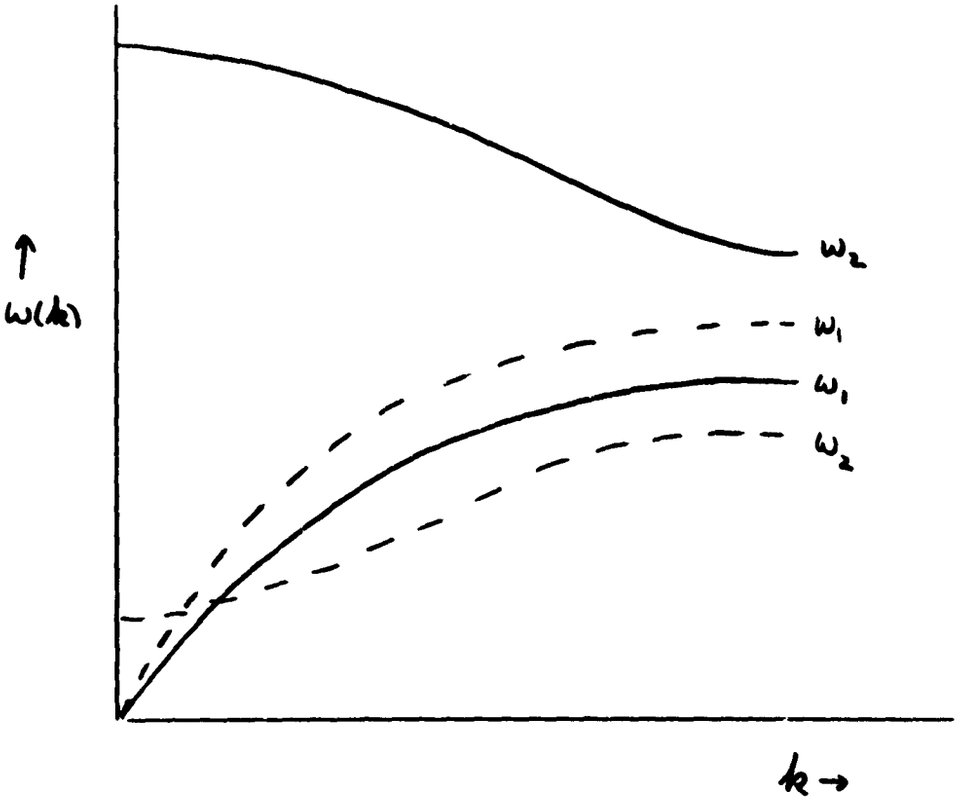

Fig. 1. Schematic Spin-Wave Spectrum of the Spin-Flop Phase
Solid curves correspond to high applied fields and
dotted curves correspond to low applied fields.