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Stability limit of the antiferromagnetic phase near the spin-flop boundary in MnF_2

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The spin-flop phase boundary in MnF_2 has been accurately measured by antiferromagnetic-resonance techniques. The new data, which show discrepancies with previous differential magnetization data, are in very good agreement with the results of calculations of the renormalized $k = 0$ magnon energy due to four-magnon scattering arising from exchange and magnetic dipolar interactions.

I. INTRODUCTION

It is well known that spin-wave theory can be used to describe the properties of antiferromagnets below their Néel temperature T_N. However, quantitative agreement with experiments, particularly at temperatures near T_N, can only be obtained if the renormalization of the magnon energies due to the appropriate interactions is taken into account. This has been recently demonstrated in investigations of the antiferromagnetic resonance linewidth.[1,2]

A quantity that is quite sensitive to the details of the interactions and at the same time is experimentally accessible is the critical field for the antiferromagnetic (AF)–spin-flop (SF) transition. This is a first-order transition[3] in which the thermodynamic phase boundary lies between the limits of stability of the AF and of the SF phases. With the anisotropy written in an effective single-ion form,[1,2] the separation between these boundaries at zero temperature is of the order of H_A^2/H_c, where H_A and H_c are respectively, the anisotropy and spin-flop critical fields, and tends to zero as the temperature approaches the bicritical point. Therefore, the various phase boundaries are nearly identical for small anisotropy and can be experimentally measured by several techniques, such as ultrasonic attenuation,[4] (differential) magnetization,[4-6] nuclear magnetic resonance[6,7] (NMR), optical absorption,[7] etc. Since the limit of stability of the AF phase is characterized by the field H_c at which one of the $k = 0$ magnon frequencies goes to zero, the phase boundary can also be determined by antiferromagnetic-resonance (AFMR) measurements.[8] The temperature dependence of H_c is clearly a direct result of the renormalization of the magnon energies due to the various magnon interactions.

The present investigation was motivated by the fact that in the nearly ideal uniaxial antiferromagnet MnF_2, there is a considerable discrepancy between the calculated spin-flop phase boundary and the experimental data in the temperature range in which spin-wave theory should be quite accurate. One of the difficulties of the measurements in MnF_2 arises from the large value of its spin-flop field ($H_{SF} \simeq 100$ kOe). Small misalignments of the easy axis with respect to the direction of the applied field results in sizeable transverse fields which not only shift the phase boundary but also alter the character of the transition. In this paper we present the results of AFMR measurements of the AF-SF phase boundary of MnF_2 up to $\frac{3}{4}T_N$. The technique consists of measuring at several frequencies the resonance field of the AFMR mode whose frequency decreases with increasing field. This can be done very accurately in large fields with a carefully aligned sample. Extrapolation of the frequency to zero gives the value of the critical field $H_c(T)$. On the theoretical side the main difficulty has been in the treatment of the anisotropy interaction which plays a key role in the spin-flop transition. Since the anisotropy associated with the S-state Mn^{2+} ions arises primarily from the magnetic dipole interaction,[9] the calculation should be done by treating this interaction explicitly rather than introducing a phenomenological anisotropy energy. The theory previously published by two of the present authors (J.P.T. and R.M.W.)[10] accounted for this fact. However, a random-phase approximation was employed without diagonalizing the quadratic part of the magnon Hamiltonian. This gave reasonable agreement with the existing experimental data at low temperatures ($T < \frac{1}{4}T_N$) but deviated at higher tem-

peratures. In the present paper the quadratic terms are diagonalized before the random-phase approximation is applied to the higher-order four-magnon terms. The calculated phase boundary is in excellent agreement with our experimental data obtained by AFMR.

II. EXPERIMENTS

Antiferromagnetic-resonance experiments were performed between 2 and 18 GHz in high dc magnetic fields generated by a superconducting coil on a polished sphere ($d \simeq 2.5$ mm) of MnF_2, which was shown by a ^{19}F NMR experiment[11] to consist of a single AF domain. The resonance was excited and detected by two crossed fine wires connected between the center conductors of two coaxial cables and 50-Ω chip resistors. This broad-band untuned arrangement had a poor standing wave ratio but the isolation between input and output cables outside the dewar was better than 20 dB over the whole band. At low temperatures the resonance signal was strong enough to permit direct observation on the oscilloscope with frequency sweep. Sample alignment with the c axis along the applied field H_0 was obtained by observing the resonance at fixed field close to the spin-flop field H_c, and tilting the sample until the frequency was at a minimum. One knows that the minimum frequency is limited by $\gamma(2H_\perp H_E)^{1/2}$, where γ is the gyromagnetic ratio, $H_\perp$ is the transverse field due to imperfect alignment, and H_E is the exchange field. Since we were able to observe the resonance as low as 2 GHz (the lower limit of the sweep oscillator), we can estimate that the alignment was better than 3×10^{-4} deg. The field measurements were made using a ^{27}Al NMR probe which allowed an accuracy of 1 Oe. Thus the precision of the measurements

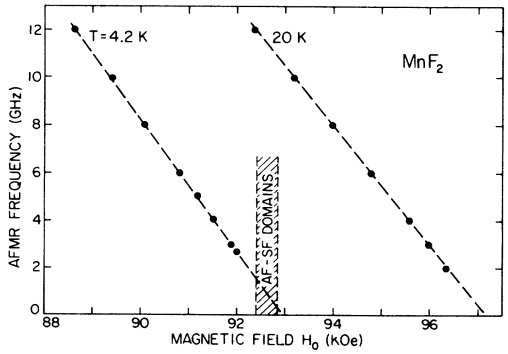

FIG. 1. Measurements of the antiferromagnetic-resonance frequency vs applied field at two temperature values. The linear extrapolation to zero frequency yields $H_c(T)$. The shaded region corresponds to the field range where AF-SF domains were observed at 4.2 K (Ref. 7).

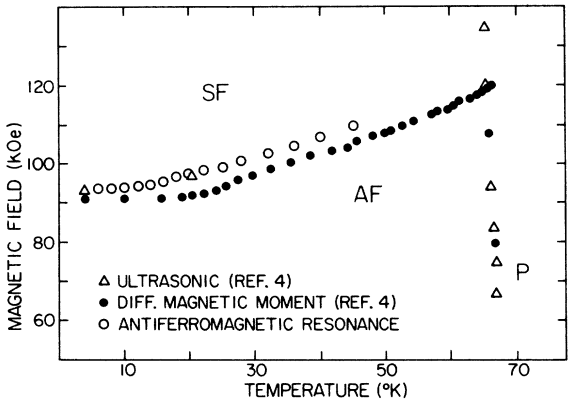

FIG. 2. Comparison between the present AFMR data for the AF-SF phase boundary and previous measurements. Also shown are measurements of the AF-paramagnetic (P) and SF-P phase boundaries (Ref. 4).

was limited by the linewidth ΔH of the AFMR. At low temperatures $\Delta H \simeq 15$ Oe and is probably caused by pit-imperfection scattering. At high temperatures, ΔH is dominated by magnon-magnon interactions and increases with T^4, making the measurements above 50 K difficult and inaccurate. The temperature was measured with a capacitance thermometer[12] and capacitance bridge, and stabilized with a standard temperature controller.

Figure 1 shows a typical plot of resonance frequency versus field for two different temperatures. The shaded region indicates the field range at 4.2 K in which AF-SF domains exist.[7] The transition field H_c is determined by extrapolating the value of H at which the resonance frequency ω_0 goes to zero. Note that the lowest AFMR frequency is more than two orders of magnitude smaller than the zero field gap, $\nu(H=0) \simeq 260$ GHz.

In Fig. 2 we compare the new AFMR data for the phase boundary with the previous data of Shapira *et al.*[4] Note that our measurements agree well with the scarce ultrasonic attenuation data. Both, however, differ substantially from the differential-magnetic-moment (DMM) measurements. The origin of the discrepancy, which is as large as 5 kOe at some temperatures, cannot be attributed to the fact that the critical field measured by the DMM technique is not necessarily H_c. This is so because that difference would not be larger than H_A^2/H_c (about 0.7 kOe in MnF_2) at low temperatures, and should become progressively less at higher temperatures. We believe that the DMM measurements are not as accurate as our AFMR data because of combined effects of several factors. First, in the experiments of Ref. 4 the sample is aligned outside the measuring apparatus. This may result in small misalignments which are sufficient to broad-

en the transition. Second, the fields used in the DMM measurements of Ref. 4 are pulsed. This makes the field measurement itself less accurate and introduces difficulties in the thermometry. Since the relatively short pulse duration almost certainly represents an adiabatic process, the increase of the parallel susceptibility with temperature leads to an increasing discrepancy between the actual spin temperature and the measured one until the lattice entropy becomes large enough to overcome the effect. This would result in effects in the direction of the discrepancies of the experiment of Ref. 4. We notice that the few measurements in Ref. 4 made with ultrasonic techniques and cw fields are in good agreement with our data.

Apart from the differences in magnitudes of the DMM and AFMR data, which might arise from several of the above-mentioned factors, we note a sizable difference in the *variation* of H_c with T, particularly in the region around 20 K. This is shown more dramatically in Fig. 3. Since it is this variation which is predicted by the magnon renormalization theory, we consider this discrepancy to be much more serious. Since the DMM data give a very poor fit to both the theory and the ultrasonic-attenuation data, and are subject to experimental difficulties to which the other experiments are not, we conclude that they are much less accurate than the present data.

We also note that plotting our data on a log-log graph paper shows two distinct temperature dependences for $H_c(T)$, which can be well fitted by the expressions

$$H_c(T)=\begin{cases}92.88+9.5\times10^{-4}T^{2.85}\ \text{kOe}, & 4<T<20\ \text{K},\\ 92.88+3.8\times10^{-2}T^{1.6}\ \text{kOe}, & 20<T<50\ \text{K}.\end{cases}$$

III. THEORY OF THE ENERGY RENORMALIZATION

We shall take for the Hamiltonian of the two-sublattice antiferromagnet MnF_2,

$$\mathcal{H}=g\mu_B H_0\Big(\sum_i S_i^z+\sum_j S_j^z\Big)+\sum_{ij}2J_{ij}\,\vec{S}_i\cdot\vec{S}_j$$
$$+\tfrac{1}{2}g^2\mu_B^2\sum_{ij}\left(\frac{\vec{S}_i\cdot\vec{S}_j}{r_{ij}^3}-3\frac{(\vec{S}_i\cdot\vec{r}_{ij})(\vec{S}_j\cdot\vec{r}_{ij})}{r_{ij}^5}\right), \tag{1}$$

where i and j refer to up and down spin sublattices, H_0 is the magnetic field applied along the easy axis, and J_{ij} is the exchange constant (only the next-nearest neighbor $J_2=1.76$ K will be kept). The dipolar interaction is responsible for essentially all the magnetic anisotropy in MnF_2 and will

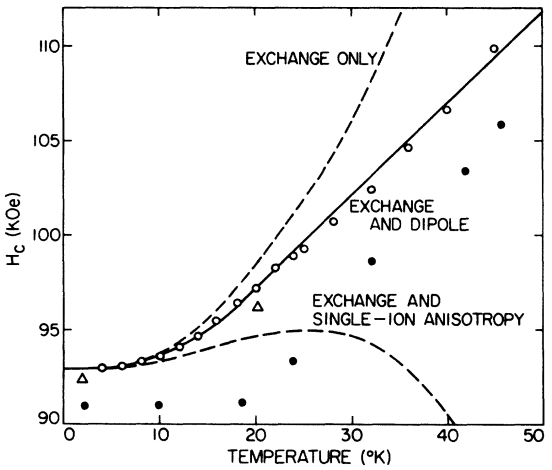

FIG. 3. Comparison of the experimental AFMR data (open circles) for the AF-SF phase boundary with the results of calculations based on the renormalization of the $k=0$ magnon energy due to four-magnon interactions. A few representative points from the DMM (solid circles) and ultrasonic attenuation (triangles) data of Ref. 4 are included for reference.

be treated as accurately as possible. The details of the application of spinwave theory to a Hamiltonian with a single-ion anisotropy may be found in many references.[1,2,13] In the case of Eq. (1) the development is essentially the same. With the Holstein-Primakoff transformations one obtains two sets of operators $a_{\vec{k}}$, $a_{\vec{k}}^\dagger$ and $b_{\vec{k}}$, $b_{\vec{k}}^\dagger$. The intersublattice coupling gives rise to quadratic terms of the form $a_{\vec{k}}^\dagger a_{\vec{k}}$, $b_{\vec{k}}^\dagger b_{\vec{k}}$, $a_{\vec{k}}b_{-\vec{k}}$, and $a_{\vec{k}}^\dagger b_{-\vec{k}}^\dagger$. The dipolar interaction contributes with the same types of terms, as does the single-ion anisotropy, but, in addition, it contains terms like $a_{\vec{k}}^\dagger a_{-\vec{k}}$ and $a_{\vec{k}}b_{-\vec{k}}^\dagger$. Since these complicate substantially the calculations[14] while contributing negligibly to the spin-wave frequencies, they can be neglected. The diagonalization of the quadratic Hamiltonian is then carried out as in the usual theory.[1,2,13] New normal-mode operators $\alpha_{\vec{k}}$, $\alpha_{\vec{k}}^\dagger$, $\beta_{\vec{k}}$, $\beta_{\vec{k}}^\dagger$ are obtained by a canonical transformation in which the transformation coefficients are now

$$u_k=[(A_k+\omega_k)/2\omega_k]^{1/2},\quad v_k=(u_k^2-1)^{1/2}, \tag{2}$$

with

$$\omega_k=(A_k^2-B_k^2)^{1/2}, \tag{3}$$

$$\hbar A_k=2z_2J_2S+\tfrac{1}{2}g^2\mu_B^2S\Big(2\sum_0-2\sum_s-\sum_s e^{i\vec{k}\cdot\vec{r}}\Big), \tag{4a}$$

$$\hbar B_k=2z_2J_2S\gamma_k-\tfrac{1}{2}g^2\mu_B^2S\sum_0 e^{i\vec{k}\cdot\vec{r}}, \tag{4b}$$

$$\gamma_k=\cos(\tfrac{1}{2}k_xa)\cos(\tfrac{1}{2}k_ya)\cos(\tfrac{1}{2}k_zc),$$

where z_2 denotes the number of second-nearest neighbors (eight for MnF_2), $\sum_0$ stands for the dipole sum $\sum_r (1-3z^2/r^2)/r^3$, where r runs over all the lattice sites on the *opposite* sublattice from the ion at the origin, and $\sum_s$ stands for the sum over all the sites on the *same* sublattice.

The unrenormalized normal mode frequencies are

$$\omega_{\alpha_k}(0)=\omega_k-\gamma H_0, \quad \omega_{\beta_k}(0)=\omega_k+\gamma H_0 , \tag{5}$$

where $\gamma=g\mu_B/\hbar$. In computing the frequencies, the dipolar sums in (4) are carried out explicitly. Since the sums converge rapidly, one needs only to consider terms out to next-next-nearest neighbors. The Lorentz and surface contributions are much smaller and are neglected.

Since the Holstein-Primakoff representation is nonlinear, the Hamiltonian (1) also contains higher-order products of boson operators. When these are expressed in terms of the normal modes one obtains terms which contain all types of combinations of α_k, $\alpha_k^\dagger$, β_k, and $\beta_k^\dagger$ operators. It can be easily shown that the three-magnon terms cannot contribute to the energy renormalization. The four-magnon term is thus the lowest order one of interest, and it has contributions from both exchange and dipolar interactions. To compute the temperature dependence of the spin-wave spectrum due to the four-magnon interaction we use the usual random phase approximation. This involves approximation of a sum by a few terms and a systematic replacement of pairs of operators by their averages. For example, a typical term

$$\sum_{k_1k_2k_3k_4} \alpha_{k_1}^\dagger \alpha_{k_2} \beta_{k_3}^\dagger \beta_{k_4} \Delta(k_1-k_2+k_3-k_4)$$

is replaced by

$$\sum_{kq} \alpha_k^\dagger \alpha_k \langle \beta_q^\dagger \beta_q \rangle + \langle \alpha_k^\dagger \alpha_k \rangle \beta_q^\dagger \beta_q ,$$

where

$$\langle \alpha_k^\dagger \alpha_k \rangle = \mathrm{Tr}(e^{-\beta \mathcal{H}} \alpha_k^\dagger \alpha_k)/\mathrm{Tr}(e^{-\beta\mathcal{H}}) . \tag{6}$$

The averages of other pairs of operators vanish. Applying this approximation to each four-magnon term, the Hamiltonian $\mathcal{H}^{(4)}$ reduces to a quadratic form and therefore renormalizes the normal-mode energies. Using the contributions to $\mathcal{H}^{(4)}$ from the exchange and dipolar interactions we obtain for the α_k spin-wave frequency

$$\omega_{\alpha_k}(T)=\omega_k-\gamma H_0+\Delta\omega_{\alpha_k}(T) , \tag{7}$$

where

$$\begin{aligned}\hbar\Delta\omega_{\alpha_k}(T) = {} & 2z_2J_2S[(u_k^2+v_k^2-2u_kv_k\gamma_k)C_q+(u_kv_k\gamma_k-v_k^2)E_q+(u_kv_k\gamma_k-u_k^2)F_q] \\ & +\tfrac{1}{2}g^2\mu_B^2S\left[3(u_k^2+v_k^2)D_q^s+\left(2+\sum_s e^{i\vec{k}\cdot\vec{r}}\right)u_k^2E_q+\left(2+\sum_s e^{i\vec{k}\cdot\vec{r}}\right)v_k^2F_q-(u_k^2+v_k^2-2u_kv_k)D_q^0\right. \\ & \left.-\left(2v_k^2+u_kv_k\sum_0 e^{i\vec{k}\cdot\vec{r}}\right)E_q-\left(2u_k^2+u_kv_k\sum_0 e^{i\vec{k}\cdot\vec{r}}\right)F_q\right] ,\end{aligned} \tag{8}$$

where the coefficients C_q, D_q, E_q, and F_q are summed over the thermal averages

$$\begin{aligned} C_q &= \frac{1}{2NS}\sum_q u_qv_q\gamma_q(2\bar{n}_{\alpha_q}+2\bar{n}_{\beta_q}+1), \\ D_q^{0(s)} &= \frac{1}{2NS}\sum_q u_qv_q\sum_{0(s)} e^{i\vec{q}\cdot\vec{r}}(2\bar{n}_{\alpha_q}+2\bar{n}_{\beta_q}+1), \\ E_q &= \frac{1}{NS}\sum_q u^2\bar{n}_{\alpha_q}+v_q^2\bar{n}_{\beta_q}, \\ F_q &= \frac{1}{NS}\sum_q v_q^2\bar{n}_{\alpha_q}+u_q^2\bar{n}_{\beta_q}. \end{aligned} \tag{9}$$

In Eqs. (9) N is the number of spins in each sublattice and the thermal occupation numbers are computed with the *renormalized* frequencies, as in (6). The correction for the frequency of the β_k mode is given by the same expression as (8) with E_q and F_q interchanged. Equations (7)–(9) must be solved self-consistently for each value of temperature and field. This was done numerically for MnF_2. The procedure consists of initially calculating the parameters C, D, E, and F, with the unrenormalized frequencies. Then at each point k in the Brillouin zone the magnon frequencies for both modes are calculated. With the new bose factors new coefficients are calculated and the process is repeated. The process converges more rapidly at low fields and low temperatures and does not converge at all at temperatures about $0.9T_N$. For most cases the criterion $|C_n-C_{n-1}|<10^{-6}$ was met in less than eight iterations. One iteration involving a sum over 8000 points in $\frac{1}{8}$ of the Brillouin zone takes a few seconds on the computer. The sums in the dipole part are done independently neglecting surface contributions. They are approximated by sums over 106 neighbors, which have been found to account for almost all the contribution.

Before discussing the numerical results we would

like to point out that the energy renormalization for antiferromagnetic magnons has been previously calculated by several authors.[15-17] However, they do not apply to the present problem because they have usually been carried out for $H_0 = 0$, neglecting the effects of the dipolar four-magnon interaction. Nevertheless it is worth noting that with $H_0 = 0$ and no dipolar terms the lengthy expressions (7)–(9) reduce to the previously obtained result[15-17]

$$\Delta\omega_k(T) = -\frac{1}{2NS}\,\omega_k(0)\sum_q (1-\gamma_k^2)^{1/2}(2\bar{n}_q+1). \qquad (10)$$

The measured temperature dependence of H_c can be qualitatively explained as well by simple analytical calculations. The temperature-dependent part of H_c is proportional to the change in frequency ω_{α_0}, which may be written approximately as $\Delta\omega_\alpha = \sum_k C_k \bar{n}_{\alpha_k}$ if we assume that the zero gap α-mode states are much more populated than the β ones. At small and intermediate temperatures we replace the sum over k by an integral with upper limit extended to infinity and assume a linear dispersion relation $\omega = vk$ for the zero-gap magnons.[2] A simple change of variables in the integral gives a T^3 dependence to $\Delta\omega_\alpha$, if C_k is assumed constant; this is very close to the measured $T^{2.85}$ dependence at $T < 20$ K. As the temperature increases the T dependence decreases mainly due to the effects of the finite extent of the Brillouin zone.

IV. SPIN-FLOP PHASE BOUNDARY

The spin-flop phase boundary for MnF_2 was obtained by determining the value of $H_0 = H_c(T)$ for which $\omega_{\alpha_0}(T)$ becomes zero. The solid line in Fig. 3 shows the result of the calculation based on exchange and dipolar four-magnon interactions as described in Sec. III. Since the anisotropy in MnF_2 is not entirely of dipolar origin, the zero-temperature value of H_c had to be adjusted to the experimental value. However, this correction is only 0.5 kOe and it introduces a negligible error into the calculation of the renormalization. The calculated phase boundary is seen to be in excellent agreement with the AFMR data of Sec. II. Of course, the critical field calculated here is the same quantity measured by the AFMR experiments but it is remarkable that a spin-wave calculation can describe the measurements at temperatures as high as $\frac{3}{4}T_N$ so well.

In order to demonstrate the role of the various four-magnon interactions we also show in Fig. 3 the results of two other calculations, one in which only the exchange part is considered and another in which we assume exchange and single-ion anisotropy $-K\sum_i (S_i^x)^2$ instead of the dipolar one. It is evident from Fig. 3 that when only the exchange interaction is considered the magnon renormalization is overestimated. This is a consequence of two facts. First, the anisotropy becomes relatively important because in the exchange part of the coefficients in Eq. (2) there are cancellations due to the negative sign of v_k. Second, there is a destructive interference in the scattering amplitudes of the exchange and anisotropy magnon interactions, an effect previously found in the relaxation of the $k = 0$ antiferromagnetic magnon.[1,2] This conclusion is relevant because in the usual treatments of the magnon renormalization the role of the anisotropy is overlooked.

We also note from Fig. 3 that in order to reproduce the experimental data for $H_c(T)$ in MnF_2 the correct dipolar anisotropy must be considered. A temperature- and wave-vector-independent single-ion anisotropy form interferes too strongly with the exchange interaction, resulting in a spin-flop field that tends to decrease at higher temperatures. This result demonstrates how sensitive the spin-flop phase boundary is to magnon interactions. We note that the importance of the role of the form of the anisotropy was not realized in previous investigations[1,2] of the AFMR relaxation rates in MnF_2. This was so because the agreement between the calculation using the four-magnon interaction due to the single-ion anisotropy and the experiments was sufficiently good at low temperatures. At higher temperatures, where the details of the form of the anisotropy would probably be more pronounced, the relaxation was dominated by higher order processes which did not depend on the anisotropy. However, presumably the agreement at low temperatures would be better if the correct dipolar anisotropy had been used in the calculations.

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