that absorption of energy by spin waves of a particular k-number can take place even though their thermal excitation is very small.

D. O. SMITH: One may ask whether the disappearance of neutron spin wave scattering for Ni-Fe alloys containing more than 85% Ni is related to the negative magnetostriction of these alloys.

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Surface Spin Pinning in Permalloy by an Oxide Layer

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Standing spin waves in thin magnetic films can be excited by uniform microwave fields if the surface spins are pinned. Observation of spin wave resonances by uniform microwave fields in thin permalloy (80% Ni-20% Fe) films in the oxidized and reduced state indicates that the major portion of the surface spin pinning is due to the oxide layer on the surface of the film. The oxidized films show strong resonances of odd numbered spin wave modes with even numbered spin wave modes almost totally absent. This indicates strong pinning at both surfaces. The reduced films show weak resonances of both odd and even spin waves. This is interpreted as indicating a strong pinning at the substrate surface of the film and a weak pinning at the free, reduced surface of the film.

We conclude that surface spin pinning in our permalloy films is due mainly to the effects of an oxide layer on the surface of the film, probably by the "exchange anisotropy" of Meiklejohn and Bean, rather than to the "surface anisotropy" proposed by Néel.

Introduction

Ferromagnetic resonance experiments in ferromagnetic films of certain thicknesses (generally in the range 3000 to 6000 Å) reveal a number of microwave power absorption peaks attributable to standing spin waves.[1,2] These are caused by pinning of the surface spins and excitation of the magnetization in simple sinusoidal modes analogous to the vibration of a string with fixed ends[3]. The propagation vector, k, must satisfy the relation $k=n\pi/L$ where n is an integer and L is the thickness of the film. In a uniform microwave field only the odd numbered spin wave modes are excited. However, as shown below, if the spin pinning is relaxed at one surface the even modes appear. This is the basis of the present experiment. We look for the amplitude of the even modes as a function of surface treatment in order to determine the mechanism of surface spin pinning.

The pinning of the surface spins has been attributed to a) an antiferromagnetic surface layer presumably an oxide of nickel or iron and b) a surface anisotropy due to the lower symmetry in which a surface spin is located as compared to an interior spin[3,4,5]. By ferromagnetic resonance experiments on oxidized and reduced permalloy films we have found

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that the pinning is due to an oxide layer on the surface of the film.

Experimental Results

Ferromagnetic resonances at 9300 mc/sec were observed in a permalloy (20 Fe, 80 Ni) film 2700Å thick. The static field, H_0, was applied perpendicular to the film and the microwave field, h, was applied parallel to the film. The film was deposited at a substrate temperature of 225°C in a vacuum of 2×10^{-5} mmHg. The substrate was fused quartz. A film simultaneously deposited on a glass substrate gave identical results but a film simultaneously deposited on a mica substrate showed poor resonances.

The resonance pattern observed in the film after deposition and with no further treatment is shown in Fig. 1. The even numbered modes are present but at a reduced intensity. The film was then broken into two pieces. One piece was oxidized at a temperature of 250°C for 6 hours in wet O_2 with some O_3 present. The other piece was reduced in dry hydrogen for 6 hours at

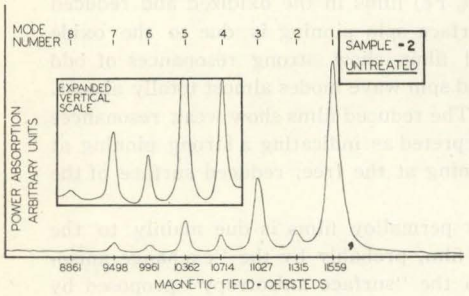

Fig. 1. Spin wave spectrum of a 2700 Å vacuum evaporated permalloy film. The static magnetic field was perpendicular to the film and the microwave field was parallel to the film.

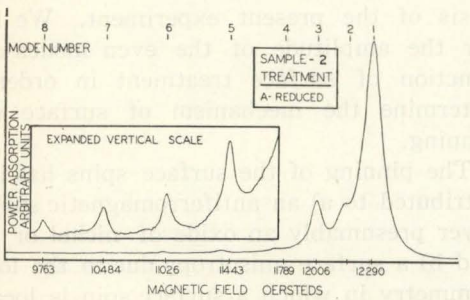

Fig. 2. Spin wave spectrum of one half of the film of Fig. 1 after the surface had been reduced.

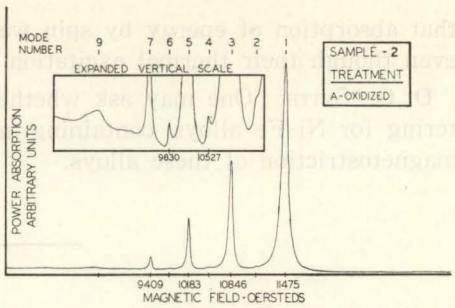

Fig. 3. Spin wave spectrum of the other half of the film of Fig. 1 after the surface had been oxidized.

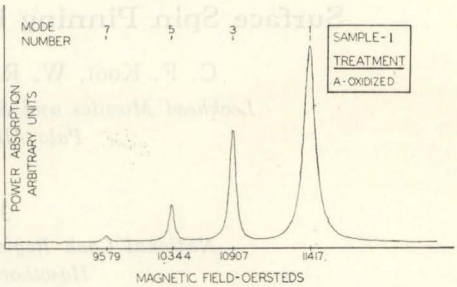

Fig. 4. Spin wave spectrum of a 2700 Å vacuum evaporated permalloy film after oxidation.

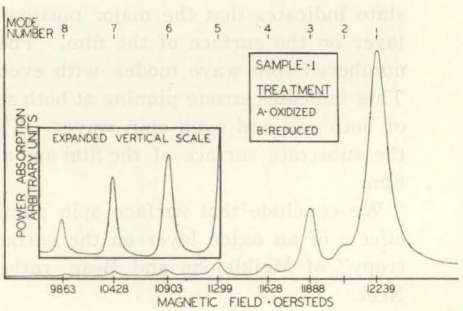

Fig. 5. Spin wave spectrum of the film of Fig 4 after a subsequent reduction in hydrogen.

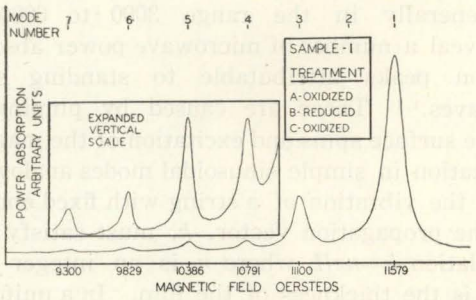

Fig. 6. Spin wave spectrum of the film of Fig. 5 after a subsequent oxidation. The film has become somewhat damaged.

250°C. The resulting resonance patterns are shown in Figs. 2 and 3. In the reduced film both the even and odd peaks are present with very little difference in intensity except for mode number 2 while in the oxidized film, the even peaks have almost completely disappeared. The saturation magnetic moment was lowered by the oxidation as indicated by the shift of the resonances to lower fields. A subsequent reducing treatment restored both the saturation moment and the even resonances. The results of this treatment are shown in Figs. 4, 5 and 6 where the sample was oxidized (Fig. 4), then reduced (Fig. 5) and finally oxidized again (Fig. 6). The original "oxidized" resonance pattern was not obtained after the final treatment but this can perhaps be ascribed to the mechanical condition of the film after the final treatment.

Discussion of Experimental Results

For perfect surface spin pinning one expects only odd modes to appear as shown in Figs. 3 and 4. In the case of the reduced film we assume perfect pinning at the substrate side of the film and a degree of non-pinning at the other film surface. Placing the substrate side of the film at the origin of the z-axis and the other surface at $z=L$ we can write

$$\left.\begin{aligned} M_{xy}&=0 \qquad \text{at} \quad z=0 \\ M_{xy}&=b\frac{\partial M_{xy}}{\partial z} \qquad \text{at} \quad z=L \end{aligned}\right\} \tag{1}$$

where b is a constant representing the degree of non-pinning and M_{xy} is the component of magnetization in the xy plane.[6]

The non-pinning condition, represented by the second of conditions (1), gives the amount of cosine character associated with the usual sine character of the spin wave which one would have at $z=L$ if the pinning were complete. Letting $M_{xy}=\sin kz$ the resonance value for the propagation vector of the spin wave, k, is

$$\tan kL=bk \tag{2}$$

The graphical solution of Eq. 2 shows that all the resonances are shifted to higher k values as b increases. For $b>L$ a new solution appears. It is a long wavelength mode which reduces to $k=\pi/2L$ at $b=\infty$ (no pinning at $z=L$). We did not observe this mode probably because of eddy current damping.

The power absorbed by each mode from a uniform microwave field is proportional to

$$\left[\int_0^L \sin kz dz\right]^2=\left[\frac{1-\cos kL}{k}\right]^2 \tag{3}$$

where k is given by Eq. 2. From this it is seen that the even modes absorb more power as the pinning at $z=L$ is reduced. If the pinning is reduced equally at $z=0$ the even modes are not excited. In order to excite even modes, it is necessary to have a lack of mirror symmetry at the center plane of the film such as what produced by assymetrical pinning,[3,7]

Absorption peaks calculated from (2) and

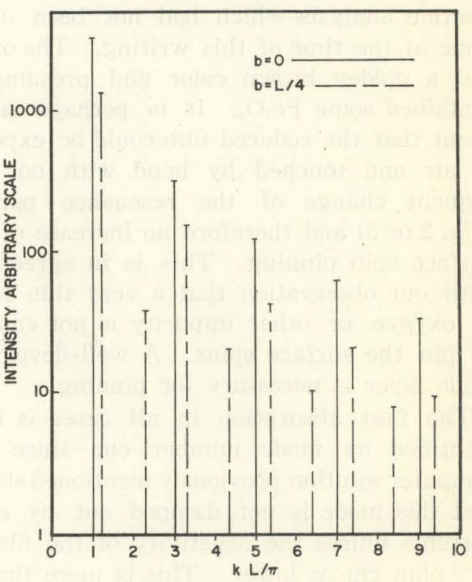

Fig. 7. Power absorption calculated from equations 2 and 3 for the case of complete pinning on both sides ($b=0$) as given by the solid lines and for incomplete pinning on one side ($b=L/4$) as given by the broken lines.

Table I. Values of A and J in Ni films.
(At room temperature, $f=9300$ Mc/sec, $a=3.52_4$Å, $g=2.18$, $M=490$ and $2S=0.53_2$.)

L(Å)	p	$A(\times 10^{-6}$ erg/cm)	$J(\times 10^{-14}$ erg)
2000	3 6	0.66	8.3
2500	3 5	0.83	10.4
1570	2 4	0.74	9.3
1570	2 4	0.72	9.0
1570	2 4	0.80	10.0
		mean ⟨0.75⟩	mean ⟨9.4⟩

(3) with the non-pinning condition $b=0$ and $L/4$ are shown in Fig. 7. Note that for the case of non-pinning at one surface ($b=L/4$) the even modes appear while the odd modes become less intense. Since both the phenomenological line width and eddy current effects have been neglected in this treatment, it is not possible to make more than a qualitative comparison to experiment. It is significant that for even a modest relaxation of the pinning at one surface the even modes come in strongly. We therefore conclude that the spin pinning at the free surface of our permalloy films is due mainly to the presence of oxides. Preliminary results from a computer solution of the surface impedance expression including eddy current effects and a Bloch type damping term confirm the foregoing conclusions[8,9].

The substrate side of the film seems to be strongly pinned at all times. This may be due to adsorbed layers of oxygen present on the substrate before deposition of the film or to the release of oxygen by the SiO_2 of the substrate to the metal to form metal oxides at the quartz-film interface.

The oxide formed on the surface of the oxidized films was not identified because of difficulties encountered during electron diffraction analysis which had not been overcome at the time of this writing. The oxide had a golden brown color and presumably contained some Fe_2O_3. It is perhaps significant that the reduced film could be exposed to air and touched by hand with no consequent change of the resonance pattern (Fig. 2 or 5) and therefore no increase of the surface spin pinning. This is in agreement with our observation that a very thin layer of oxygen or other impurity is not enough to pin the surface spins. A well developed oxide layer is necessary for pinning.

The first absorption in all cases is here identified as mode number one since the computer solution previously mentioned shows that this mode is not damped out by eddy currents unless the resistivity of the film is 10^{-6} ohm cm or lower. This is more than a factor of ten lower than the resistivity of our permalloy films. The rule $H_n \propto n^2$ (H_n is the resonant field for the nth mode) is not followed[5]. Instead we have $H_n \propto n^s$ where $1.4<s<2.3$. Only part of this variation can be ascribed to non-pinning at the free surface of the film. We have no explanation for the remaining variation.

The surface anisotropy energy, K_s, can be deduced from the ratio of the intensity of an even mode to the intensity of an odd mode. From the resonances of Figs. 2 and 3 we derive approximate values of $K_s=3$ ergs/cm^2 for an oxidized surface and $K_s=0.1$ ergs/cm^2 for a reduced surface. Meiklejohn and Bean[4] find a value of 2 ergs/cm^2 for a Co-CoO interface. Soohoo[7] calculates, from Néel's[5] formula for surface anisotropy, values of -0.05 ergs/cm^2 for nickel and 0.2 ergs/cm^2 for iron. Similarly, Rado and Weertman[6] calculate from Néel's formulae, a value of 0.03 ergs/cm^2 for a 66% Ni permalloy. Since we assume our film to be randomly oriented polycrystalline and several possibilities for error exist, such as non-uniform film composition, non-uniform microwave fields and incomplete pinning at the substrate surface of the film, it is not profitable to make more exact comparisons of theory and experiment at the present time.

Resonance measurements on a permalloy film recently obtained from Dr. John Blades[10] confirm that the oxide layer is responsible for the major part of the surface anisotropy.

Summary

For an oxidized permalloy film on quartz or glass only odd modes are present in the spin wave spectrum indicating strong pinning at both the substrate surface of the film and at the free surface of the film. For a reduced film, free of an oxide layer on the surface, both even and odd modes are present, indicating weak pinning at the free surface of the film and strong pinning at the substrate surface of the film. We conclude that the pinning at the free surface of the film is due to the presence of oxides, probably by the "exchange anisotropy" mechanism of Meiklejohn and Bean[3], rather than to the "surface anisotropy" of Néel.[4]

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DISCUSSION

G. T. Rado: What fraction of the observed line width of the first mode (and of the higher order modes) do you attribute to the phenomenological damping?

C. F. Kooi: Depending on the particular film and its state of oxidation, we can say that roughly one half of the linewidth of the first mode is due to the phenomenological damping, while the other half is due to eddy current damping. For modes three and higher the linewidth remains constant and we attribute it entirely to the phenomenological term. We have obtained higher order mode linewidths as narrow as 60 Oe.

G. W. Rathenau: Did you make sure that the Néel temperature of the oxide on your film is higher than the temperature of measurements? We made experiments on a Co-film oxidized at both sides and investigated the spin wave resonance above and below the Néel temperature of CoO. The results (M. Aress) are not yet quite certain.

C. F. Kooi: No, since we have not yet identified the oxides present on the surface. We did look at the resonance pattern of an oxidized film as the temperature was raised from room temperature to about 350°C and saw no increased even mode intensities indicating that NiO (Néel temperature about 250°C) was not responsible for the pinning. Fe_2O_3 which has a higher Néel temperature may be responsible.

R. S. Prosen: We have been dissolving permalloy films with dilute acid and find that a thin layer remains which does not dissolve in this solvent. This layer does dissolve in aqua regia and is believed to be an oxide layer. We are in the process of determining its actual composition. We have determined by interferometic means that its thickness is less than 100Å.

C. F. Kooi: We are happy to hear this since we had been worried about the pinning mechanism at the substrate surface and the oxide you observe may be the answer.

S. Chikazumi: You did assume that spins at the bottom of film are always pinned.

C. F. Kooi: Right.

S. Chikazumi: Can you guess how strong the surface anisotropy at the substrate surface will be?

C. F. Kooi: I am not sure but I guess that it will be the same order of magnitude as that of the top surface, i. e., about 3 erg/cm^2.

C. D. Smith: Did you use several substrates?

C. F. Kooi: Glass and fused quartz.