PHYSICAL REVIEW VOLUME 131, NUMBER 2 15 JULY 1963

General Exchange Boundary Condition and Surface Anisotropy Energy of a Ferromagnet

R. F. Soohoo
California Institute of Technology, Pasadena, California

(Received 14 December 1962)

The general exchange boundary condition applicable to a line of spins placed in a static field of arbitrary orientation and whose end spins are subjected to different environments are first formulated. The result is then applied to the problem of spin wave resonance in thin magnetic films. Both the line and absorption spectra are calculated assuming different types of surface anisotropy. By comparing our theoretical results with various experiments, it is concluded that the shape of the energy surface of the surface anisotropy energy are uniaxial with the easy axis of magnetization in the direction of the surface normal and the hard plane of magnetization parallel to the film plane. The possible origin of this anisotropy, including the question of dynamic pinning, is discussed in some detail. Aside from the usual volume spin-wave resonance modes, we found also some surface spin wave modes whose presence may have an important bearing upon the magnetization reversal process in thin Permalloy films. An apparent departure from the k^2 dispersion low for spin waves and its relevance upon the determination of the exchange constant is also discussed.

INTRODUCTION

SINCE the observation of spin wave resonance in thin films,[1] there has been considerable interest in the origin and nature of the surface anisotropy which gives rise to pinning of the surface spins. Two sources of surface energy[2,3] have been proposed, one having to do with the lower order symmetry of the surface spin environment calculated by Néel[4] and the other having to do with the possible existence of an antiferromagnetic surface layer. However, our earlier calculation and experiment[5] have shown that the Néel surface energy (~0.05 erg/cm^2) is at least an order of magnitude too small to account for the intensity of the observed spin-wave resonance modes. Subsequently, by a combined theoretical-experimental approach,[6] utilizing results of surface oxidation experiments,[7] we were able to identify the shape of surface-energy surface as uniaxial with the easy axis of magnetization parallel to the film normal. This result is consistent with the recent experimental observations of Wigen *et al.*[8] However, they proposed a dynamic pinning mechanism having its origin in the presence of a slightly different magnetization surface layer instead of the surface pinning condition due to surface anisotropy. A critical examination of the origin of the surface anisotropy is, therefore, of interest.

In this paper, we shall carry out a rather extensive calculation of the spin-wave absorption spectrum in a thin film for various surface conditions for both an insulator and a conductor. From the results of this calculation and by comparison with experiment, the nature and shape of the energy surface are then identified. Furthermore, the equivalence of the microscopic and macroscopic exchange boundary condition is demonstrated and generalized to include the case of unequal spin pinning at the two surfaces of the film. In addition to the ordinary volume spin wave modes, we found also some surface spin wave modes which may have some influence upon the flux reversal process in Permalloy films.

By examining the spin-wave absorption spectrum for an arbitrary orientation of the static magnetic field with respect to the film normal, we found that the spin system becomes unpinned when the magnetization makes an angle of very close to $\pi/4$ with the film normal, consistent with experiment.

FORMULATION OF PROBLEM

Consider a system of spins in a magnetic field. The Hamiltonian of the system is given by

$$\mathcal{H} = -2J \sum_j{}' \mathbf{S}_i\cdot\mathbf{S}_j - g\mu_b \sum_i \mathbf{S}_i\cdot\mathbf{H}_i, \qquad (1)$$

where $\mathbf{S}_i$ is the spin operator in units of $\hbar$ and each atom has $2S_0$ resultant spins. J is the exchange integral and $\mathbf{H}_i$ is the total field at spin $\mathbf{S}_i$ due to external field, static demagnetization field, anisotropy field, or dipolar fields due to dynamic interaction between spins themselves. The quantum-mechanical equation of motion of $\mathbf{S}_m$ can be easily shown to be

$$i\hbar\dot{\mathbf{S}}_m = [\mathbf{S}_m, \mathcal{H}] = i2J\mathbf{S}_m \times \sum_j \mathbf{S}_j + i\hbar\gamma\mathbf{S}_m\times\mathbf{H}_m. \qquad (2)$$

If we consider a finite chain of N spins and nearest neighbor exchange interaction only, we find the equations of motion for the end spins $\mathbf{S}_1$ and $\mathbf{S}_N$ as

$$\frac{\partial\mathbf{S}_1}{\partial t} = \frac{2J}{\hbar}\mathbf{S}_1\times\mathbf{S}_2 + \gamma\mathbf{S}_1\times\mathbf{H}_1 \qquad (3)$$

$$\frac{\partial\mathbf{S}_N}{\partial t} = \frac{2J}{\hbar}\mathbf{S}_N\times\mathbf{S}_{N-1} + \gamma\mathbf{S}_N\times\mathbf{H}_N, \qquad (4)$$

---

[1] M. H. Seavey, Jr., and P. E. Tannenwald, Phys. Rev. Letters **1**, 168 (1958).
[2] C. Kittel, Phys. Rev. **110**, 1295 (1958).
[3] P. Pincus, Phys. Rev. **118**, 658 (1960).
[4] L. Néel, J. Phys. Radium **15**, 225 (1954).
[5] R. F. Soohoo, Suppl. J. Appl. Phys. **32**, 148 (1961).
[6] R. F. Soohoo, MIT Lincoln Lab Rept 53-G-0062 (1961).
[7] C. F. Kooi, W. R. Holmquist, and J. T. Doherty, J. Phys. Soc. Japan (to be published).
[8] P. E. Wigen, C. F. Kooi, M. R. Shanabarger, and T. D. Rossing, Phys. Rev. Letters **9**, 206 (1962).

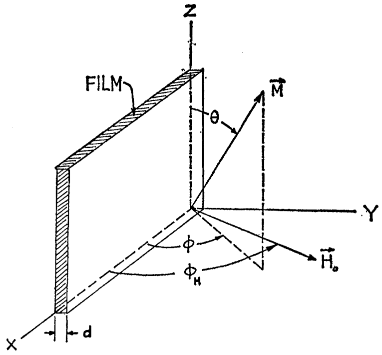

FIG. 1. Thin magnetic film in a static field of arbitrary orientation.

where $\mathbf{H}_1$ and $\mathbf{H}_N$ are not necessarily equal. Considering the spins semiclassically as vectors, we can expand $\mathbf{S}_{2,N-1}$ in terms of $\mathbf{S}_{1,N}$ and their derivatives.

$$\mathbf{S}_{2,N-1}=\mathbf{S}_{1,N}+a\frac{\partial\mathbf{S}_{1,N}}{\partial y}+\tfrac{1}{2}a^2\frac{\partial^2\mathbf{S}_{1,N}}{\partial y^2}+\cdots, \tag{5}$$

where we have assumed that the positive direction of y is the surface outward normal and where a is the lattice constant; and the direction of the spins varies only in the y direction. Strictly speaking, Eq. (5) should be a difference rather than differential equation since the spin locations are discrete. However, this distinction is unimportant for the continuum approximation considered below. Combining Eq. (5) with Eqs. (3) and (4), we obtain

$$\frac{\partial\mathbf{S}_{1,N}}{\partial t}=\frac{2J}{\hbar}\mathbf{S}_{1,N}\times\left(a\frac{\partial\mathbf{S}_{1,N}}{\partial y}+\tfrac{1}{2}a^2\frac{\partial^2\mathbf{S}_{1,N}}{\partial y^2}\right)+\gamma\mathbf{S}_{1,N}\times\mathbf{H}_{1,N}, \tag{6}$$

where we have neglected terms involving derivatives higher than the second.

Macroscopically, $\mathbf{S}_{1,N}$ may be replaced by the magnetization $\mathbf{M}_{1,N}$. By $\mathbf{M}_{1,N}$ we then mean the magnetization of the surface layers whose dimensions are large compared to the lattice constant but small compared to the pertinent dimensions of the sample. Thus, Eq. (6) becomes

$$\frac{\partial\mathbf{M}_{1,N}}{\partial t}=\frac{2J}{\hbar\gamma N_0}\mathbf{M}_{1,N}\times\left(a\frac{\partial\mathbf{M}_{1,N}}{\partial y}+\tfrac{1}{2}a^2\frac{\partial^2\mathbf{M}_{1,N}}{\partial y^2}\right)+\gamma\mathbf{M}_{1,N}\times\mathbf{H}_{1,N}. \tag{7}$$

where N_0 is equal to the number of spins per unit volume. The reason for the transformation to this approximation is for its obvious connection with macroscopic ferromagnetic resonance experiments. Furthermore, the components of the torque $\boldsymbol{\tau}=\gamma\mathbf{M}_{1,N}\times\mathbf{H}_{1,N}$ can now be easily identified and derived from the classical energy-density function:

$$E=\tfrac{1}{2}(4\pi M^2)\sin^2\theta\sin^2\phi-MH_0\sin\theta\cos(\phi_H-\phi)+E_k(\theta,\phi), \tag{8}$$

where θ and ϕ are the angles that the magnetization $\mathbf{M}$ makes with the z and x axis, respectively, with the film lying parallel to the xz plane. ϕ_H is the angle $\mathbf{H}_0$ makes with the x axis with $\mathbf{H}_0$ lying in the xy plane. This situation is depicted in Fig. 1.

THEORY

The torque may be found from a generalized force $\mathbf{F}=-\nabla E$ using the expression,

$$\mathbf{T}=\mathbf{r}\times\mathbf{F}=-\mathbf{r}\times\nabla E. \tag{9}$$

Assuming that the character of the surface energy is uniaxial with the easy axis parallel to the surfaces of the film, we have $E_k(\theta,\phi)=K_s'\sin^2\theta\sin^2\phi$. Thus, from Eq. (8) we find

$$\nabla E=\hat{\phi}\frac{1}{r}[(2\pi M^2+K_s')\sin\theta\sin2\phi-MH_0\sin(\phi_H-\phi)]+\hat{\theta}\frac{1}{r}[(2\pi M^2+K_s')\sin^2\phi\sin2\theta-MH_0\cos\theta\cos(\phi_H-\phi)], \tag{10}$$

where $\hat{\theta}$ and $\hat{\phi}$ are unit vectors in the θ and ϕ direction, respectively, and $K_s'a=K_s$ is the surface energy per unit area. It follows from Eqs. (9) and (10) that:

$$\mathbf{T}=\hat{\theta}[(2\pi M^2+K_s')\sin\theta\sin2\phi-MH_0\sin(\phi_H-\phi)]-\hat{\phi}[(2\pi M^2+K_s')\sin2\theta\sin^2\phi-MH_0\cos(\phi_H-\phi)\cos\theta]. \tag{11}$$

For small excursions about the equilibrium position $\theta_{\text{eq}}=\pi/2$ and ϕ_{eq}, we may let $\theta=\pi/2+\delta_\theta$ and $\phi=\phi_{\text{eq}}+\delta_\phi$, where $\delta_\theta\ll\pi/2$ and $\delta_\phi\ll\phi_{\text{eq}}$. Then Eq. (11) approximates to

$$\begin{aligned}\mathbf{T}=\hat{\theta}\{&(2\pi M^2+K_s')(\sin2\phi_{\text{eq}}+2\cos2\phi_{\text{eq}}\delta_\phi)\\&-MH_0[\sin(\phi_H-\phi_{\text{eq}})-\cos(\phi_H-\phi_{\text{eq}})\delta_\phi]\}\\-\hat{\phi}\{&-(2\pi M^2+K_s')2\delta_\theta(\sin^2\phi_{\text{eq}}+\sin^2\phi_{\text{eq}}\delta_\phi)\\&+MH_0\delta_\theta[\cos(\phi_H-\phi_{\text{eq}})+\sin(\phi_H-\phi_{\text{eq}})\delta_\phi]\}.\end{aligned} \tag{12}$$

Now, let $\mathbf{M}_{1,N}=\hat{r}M+\hat{\theta}m_{1\theta,N\theta}+\hat{\phi}m_{1\phi,N\phi}$ where $m_{1\theta,N\theta}=M\delta_{1\theta,N\theta}$ and $m_{1\phi,N\phi}=M\delta_{1\phi,N\phi}$. Combining Eqs. (7) and (12), we obtain the final component equations as

$$\begin{aligned}\frac{\partial m_{\theta1,N}}{\partial t}=&-\gamma\frac{2A}{M}\left(\frac{1}{a}\frac{\partial m_{\phi1,N}}{\partial y}+\frac{1}{2}\frac{\partial^2 m_{\phi1,N}}{\partial y^2}\right)\\&+\gamma\left(4\pi M+\frac{2K'_{s1,N}}{M}\right)\cos2\phi_{\text{eq }1,N}m_{\phi1,N}\\&+\gamma H_0\cos(\phi_H-\phi_{\text{eq }1,N})m_{\phi1,N}\\&+\gamma M\left[\left(2\pi M+\frac{K'_{S1,N}}{M}\right)\sin2\phi_{\text{eq }1,N}-H_0\sin(\phi_H-\phi_{\text{eq }1,N})\right]\end{aligned} \tag{13}$$

and

$$\frac{\partial m_{\phi 1,N}}{\partial t}=\gamma\frac{2A}{M}\left(\frac{1}{a}\frac{\partial m_{\theta 1,N}}{\partial y}+\frac{1}{2}\frac{\partial^2 m_{\theta 1,N}}{\partial y^2}\right)+\gamma\left(4\pi M+\frac{2K'_{s1,N}}{M}\right)\sin^2\phi_{\mathrm{eq}\ 1,N}m_{\theta 1,N}-\gamma H_0\cos(\phi_H-\phi_{\mathrm{eq}\ 1,N})m_{\theta 1,N}, \tag{14}$$

where we have replaced $JSMa^2/\gamma\hbar$ by its equivalent A, the exchange constant.

For the interior spins the terms linear in a and in K_s' vanish by symmetry while the term quadratic in a is doubled. Thus, Eqs. (13) and (14) becomes

$$\frac{\partial m_\theta}{\partial t}=-\gamma\frac{2A}{M}\frac{\partial^2 m_\phi}{\partial y^2}+\gamma 4\pi M\cos 2\phi_{\mathrm{eq}}m_\phi+\gamma H_0\cos(\phi_H-\phi_{\mathrm{eq}})m_\phi+\gamma M[2\pi M\sin 2\phi_{\mathrm{eq}}-H_0\sin(\phi_H-\phi_{\mathrm{eq}})] \tag{15}$$

$$\frac{\partial m_\phi}{\partial t}=\gamma\frac{2A}{M}\frac{\partial^2 m_\theta}{\partial y^2}+\gamma 4\pi M\sin^2\phi_{\mathrm{eq}}m_\theta-\gamma H_0\cos(\phi_H-\phi_{\mathrm{eq}})m_\theta. \tag{16}$$

The equilibrium condition for the magnetization, according to Eq. (15) is given by[9]

$$H_0\cos\phi_H\sin\phi_{\mathrm{eq}}=(H_0\sin\phi_H-4\pi M\sin\phi_{\mathrm{eq}})\cos\phi_{\mathrm{eq}}. \tag{17}$$

For a general orientation of $\mathbf{H}_0$, the rf magnetization will not be circularly polarized. Thus, we look for solutions of Eqs. (15) and (16) of the form,

$$\begin{aligned} m_\phi&=R(k)\cos\omega t(\alpha'\sin ky+\beta'\cos ky)\\ m_\theta&=\sin\omega t(\alpha\sin ky+\beta\cos ky). \end{aligned} \tag{18}$$

Substituting Eq. (18) into Eqs. (15) and (16), we obtain the dispersion relation for spin waves in a thin film as

$$\left(\frac{\omega}{\gamma}\right)^2=\left[H_0\cos(\phi_H-\phi_{\mathrm{eq}})-4\pi M\sin^2\phi_{\mathrm{eq}}+\frac{2A}{M}k^2\right]\times\left[H_0\cos(\phi_H-\phi_{\mathrm{eq}})+4\pi M\cos 2\phi_{\mathrm{eq}}+\frac{2A}{M}k^2\right] \tag{19}$$

and the expression for $R(k)$ as

$$R(k)=\left[\frac{H_0\cos(\phi_H-\phi_{\mathrm{eq}})+(2A/M)k^2-4\pi M\sin^2\phi_{\mathrm{eq}}}{H_0\cos(\phi_H-\phi_{\mathrm{eq}})+(2A/M)k^2+4\pi M\cos 2\phi_{\mathrm{eq}}}\right]^{1/2}. \tag{20}$$

Substituting Eq. (18) into Eq. (13) and (14) using Eqs. (19) and (20) and let $y=0$ for the first spin, we find for $\phi_{\mathrm{eq}}=\phi_{\mathrm{eq}1,N}$

$$\frac{\alpha'}{\beta'}=-\tfrac{1}{2}ka+\left(\frac{2K_{s1}'}{M}\bigg/\frac{2A}{M}k^2\right)ka\cos 2\phi_{\mathrm{eq}} \tag{21}$$

and

$$\frac{\alpha}{\beta}=-\tfrac{1}{2}ka-\left(\frac{2K_{s1}'}{M}\bigg/\frac{2A}{M}k^2\right)ka\sin^2\phi_{\mathrm{eq}}. \tag{22}$$

From Eq. (21), we see that there is a particular value of ϕ_{eq} whereby $\alpha'/\beta'=0$ and the ϕ component of the spin system becomes unpinned. Denoting this value of ϕ_{eq} by $(\phi_{\mathrm{eq}})_u$, we find from Eq. (21) that

$$(\phi_{\mathrm{eq}})_u=\tfrac{1}{2}\cos^{-1}\left[\frac{ka}{2}\left(\frac{2Ak}{2K_s}\right)\right], \tag{23}$$

where $K_s=K_s'a$ is the uniaxial surface energy constant in ergs/cm^2. For this value of $(\phi_{\mathrm{eq}})_u$ there is a corresponding value of ϕ_H denoted by ϕ_{Hu} as determined by Eq. (17) for a given value of H_0. However, for a given value of ω, H_{0u} and ϕ_{Hu} must be of such values as to satisfy both Eqs. (17) and (19). Thus, ϕ_{Hu} may be determined as a function of $2Ak^2/2K_s'$, the ratio of exchange to surface energy.

It is of interest to investigate the case where $K_s\to\infty$ corresponding to complete pinning of the surface spins. We see from Eq. (23) that under this condition $(\phi_{\mathrm{eq}})_u\to\pi/4$. Then, we find from Eq. (17) that $H_{0u}=4\pi M/\sqrt{2}(\sin\phi_H-\cos\phi_H)$. Substituting this expression into Eq. (19) for H_0 we readily find the quadratic

---

[9] For the atomic layers near the surfaces of the film, the equilibrium value of ϕ, i.e., $\phi_{\mathrm{eq}\ 1,N}$ is determined by the expression

$$H_0\cos\phi_H\sin\phi_{\mathrm{eq}\ 1,N}=\left[H_0\sin\phi_H-\left(4\pi M+\frac{2K_s'}{M}\right)\sin\phi_{\mathrm{eq}\ 1,N}\right]\cos\phi_{\mathrm{eq}\ 1,N}$$

obtained from Eq. (13). If the surface anisotropy field $2K_s'/M$ is small compared to the static magnetization $4\pi M$, as is usually the case, $\phi_{\mathrm{eq}\ 1,N}$ would be nearly the same as ϕ_{eq} as can be seen by comparing the above expression with Eq. (17). Under these conditions, the entire film is uniformly magnetized and our calculation is strictly correct. If $2K_s'/M$ is not small compared to $4\pi M$, $\phi_{\mathrm{eq}\ 1,N}$ would differ from ϕ_{eq}. In this case, due to the presence of exchange forces between spins of the surface layers and those of the film proper, a domain wall within which the angle that the spins make with the film surface varies gradually from ϕ_{eq} to $\phi_{\mathrm{eq}\ 1,N}$ will presumably be formed. In this case the magnetization distribution corresponding to the surface modes (discussed in the section entitled "Line Spectrum") would be rather complicated. However, so long as $2K_s'/M$ is not too large compared to $4\pi M$, the difference between ϕ_{eq} and $\phi_{\mathrm{eq}\ 1,N}$ is not too great and the domain wall width is correspondingly small. Under these circumstances the magnetization distribution calculated for the surface modes would still closely resemble that of the actual case providing that the characteristic decay distance of the rf magnetization $1/k$ is large compared to the domain wall width. In any case, the magnetization of the bulk of the film should be at an equilibrium angle ϕ_{eq} and our calculation of the resonance spectrum of the spin-wave modes should be rather insensitive to the slight variation of the equilibrium value of ϕ across the film in realistic cases.

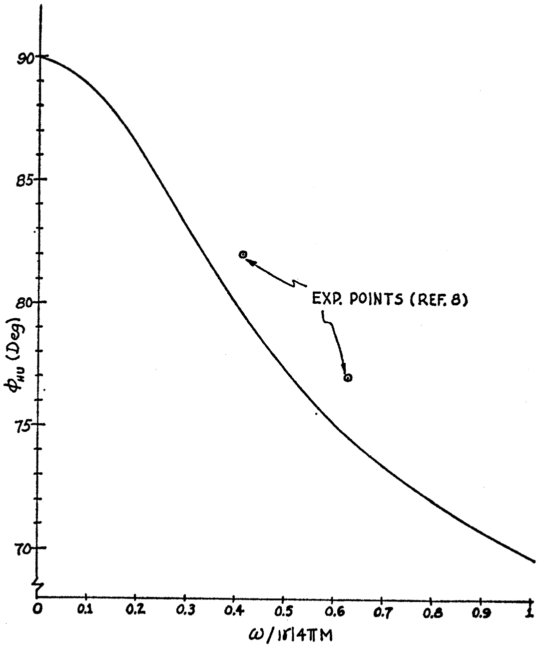

FIG. 2. Critical static field angle versus normalized frequency (complete pinning).

expression for ϕ_{Hu} to be

$$\phi_{Hu}=\tan^{-1}\left[1+\left(\frac{\gamma 2\pi M}{\omega}\right)^2 \pm\left[\left(1+\left(\frac{\gamma 2\pi M}{\omega}\right)^2\right)^2+2\left(\frac{\gamma 2\pi M}{\omega}\right)^2\right]^{1/2}\right]. \quad (24)$$

In the derivation of Eq. (24), we have made the observation that the exchange terms are usually negligible in comparison with others. ϕ_{Hu} is plotted in Fig. 2 as a function of $\omega/\gamma 4\pi M$.

If K_s is finite, we find the more general expression from Eqs. (17), (19), and (23) as

$$\left(\frac{\omega}{\gamma 4\pi M}\right)^2=[\sin\phi_{\mathrm{eq}\,u}\cos\phi_{\mathrm{eq}\,u}\cot(\phi_{Hu}-\phi_{\mathrm{eq}\,u})-\sin^2\phi_{\mathrm{eq}\,u}]$$
$$\times[\sin\phi_{\mathrm{eq}\,u}\cos\phi_{\mathrm{eq}\,u}\cot(\phi_{Hu}-\phi_{\mathrm{eq}\,u})-\sin^2\phi_{\mathrm{eq}\,u}+\cos^2\phi_{\mathrm{eq}\,u}], \quad (25)$$

where $\phi_{\mathrm{eq}\,u}$ is given by Eq. (23). ϕ_{Hu} for several values of $2Ak^2/2K_s'$ with k corresponding to the disappearance of the peaks with the sine distribution except the first, could also be plotted versus $\omega/\gamma 4\pi M$ similar to the $K_s\rightarrow\infty$ case of Fig. 2. For comparison with experiment, however, it may be more convenient to plot $2Ak^2/2K_s'$ versus ϕ_{Hu} with $\omega/\gamma 4\pi M$ as the constant parameter. This has been done in Fig. 3 for $\omega/\gamma 4\pi M=0.4$ and 0.6. These curves afford an accurate measurement of $2Ak^2/2K_s'$ by a single measurement of the angle ϕ_H.

If the surface anisotropy is uniaxial with the easy axis parallel to the film normal and hard planes perpendicular to it, $E_k(\theta,\phi)$ would be given by $E_k(1-\sin^2\theta\sin^2\phi)$. An entirely analogous calculation would show that as far as the motion of the spin system is concerned, we need only change the sign of K_s in the above equations to render it valid for this case. In a similar fashion we may plot the corresponding curves of ϕ_{Hu} versus $\omega/\gamma 4\pi M$ and $2Ak^2/2K_s'$ as is done in Figs. 2 and 3.

On the other hand, if the surface anisotropy is unidirectional with its easy axis in the direction of the inward normal to the film surfaces, $E_k(\theta,\phi)=K_s'(1-\sin\theta\sin\phi)/2$. Analogous calculation would show that the terms involving K_s' in Eqs. (13) and (14) should be replaced by $-\gamma K'_{s1,N}(M\cos\phi_{\mathrm{eq}1,N}-\sin\phi_{\mathrm{eq}1,N}m_{\phi 1,N})/2M$ and $-\gamma K'_{s1,N}\sin\phi_{\mathrm{eq}1,N}m_{\theta 1,N}/2M$, respectively. This change would lead to the corresponding expression for α'/β' as

$$\frac{\alpha'}{\beta'}=-\tfrac{1}{2}ka+\left(\frac{K_{s1}'}{2M}\Big/\frac{2A}{M}k^2\right)ka\sin\phi_{\mathrm{eq}} \quad (26)$$

and α/β is obtained from Eq. (26) by changing the sign of $\sin\phi_{\mathrm{eq}}$.

If the easy axis is in the direction of the surface outward normal instead, $E_k(\theta,\phi)=K_s'(1+\sin\theta\sin\phi)/2$ and the only effect as compared to the inward normal case is again the change of sign of K_s'. Of course, curves similar to those given in Figs. 2 and 3 could be plotted also for the unidirectional cases. However, as we shall see later, since the oxidation experiments indicate that the surface anisotropy energy is uniaxial rather than unidirectional, we shall not pursue this further.

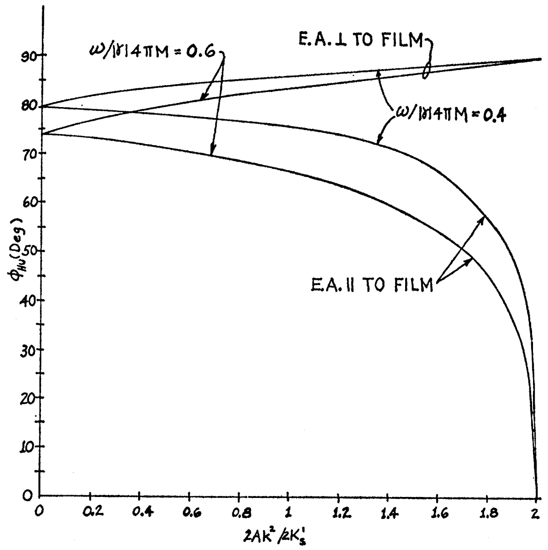

FIG. 3. Critical static field angle versus ratio of exchange to surface anisotropy energy (uniaxial case).

GENERAL EXCHANGE BOUNDARY CONDITION

In the continuum approximation, we must let $a \rightarrow 0$ in such a way that $K_s = K_s' a$, the surface-energy coefficient remains finite. In this case Eqs. (21) and (22) become

$$\frac{\alpha'}{\beta'} = \frac{2K_s}{2Ak} \cos 2\phi_{\text{eq}}$$
$$\frac{\alpha}{\beta} = \frac{2K_s}{2Ak} \sin^2 \phi_{\text{eq}}. \tag{27}$$

Combining Eq. (27) with Eq. (18), we find the macroscopic exchange boundary condition at $y=0$ for the uniaxial case with the hard axis in the direction of the film normal as

$$2A \frac{\partial m_{\phi 1}}{\partial y} - 2K_s \cos 2\phi_{\text{eq}} m_{\phi 1} = 0$$
$$2A \frac{\partial m_{\theta 1}}{\partial y} + 2K_s \sin^2 \phi_{\text{eq}} m_{\theta 1} = 0. \tag{28}$$

At $y=d$ where d is the thickness of the film, the exchange boundary condition is

$$2A \frac{\partial m_{\phi 1}}{\partial y} + 2K_s \cos 2\phi_{\text{eq}} m_{\phi 1} = 0$$
$$2A \frac{\partial m_{\theta 1}}{\partial y} - 2K_s \sin^2 \phi_{\text{eq}} m_{\theta 1} = 0. \tag{29}$$

The difference in sign for the second term of Eqs. (28) and (29) is due to the fact that the direction of the outward (or inward) normal changes sign for $y=0$ and $y=d$. Equations (28) and (29) are formally equivalent to the macroscopic expressions derived by Rado and Weertman[10] for the special case where $\phi_{\text{eq}} = \pi/2$. If the easy axis of the surface anisotropy is perpendicular rather than parallel to the surface of the film, similar calculation shows that the sign of K_s' or K_s is changed from plus to minus.

If the surface anisotropy is unidirectional with the easy axis in the direction of the surface inward normal, a similar calculation will show that the corresponding macroscopic boundary conditions are given by

$$2A \frac{\partial m_{\phi 1}}{\partial y} - \frac{K_s}{2} \sin \phi_{\text{eq}} m_{\phi 1} = 0, \tag{30}$$

at both $y=0$ and $y=d$. If the easy axis in the direction of the surface outward normal, calculation shows that K_s in Eq. (30) changes sign. For $m_{\theta 1}$ the sign of the second term in Eq. (30) should be changed.

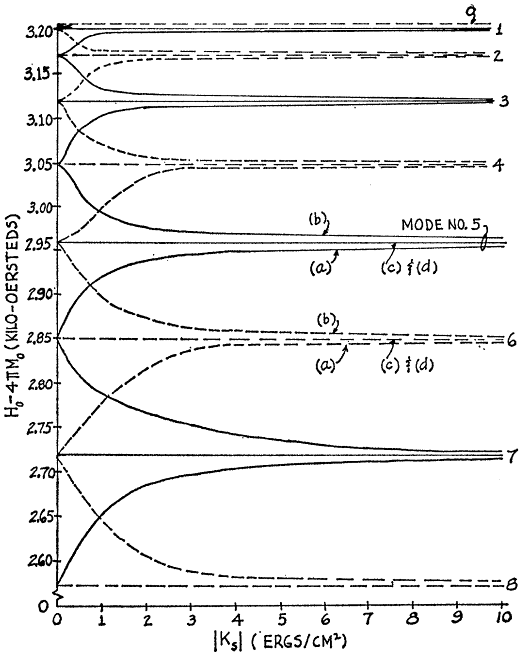

FIG. 4. Resonance field of spin-wave modes versus surface anisotropy energy of a thin insulating film ($d = 5 \times 10^{-5}$ cm, $4\pi M = 10^4$ G, $|\gamma| = 2.8$ Mc/sec, $A = 10^{-6}$ erg/cm³, and $f = 9$ kMc/sec). (a) uniaxial, easy axis ⊥ to film; (b) uniaxial, easy axis ∥ to film; (c) and (d) unidirectional.

LINE SPECTRUM

Let us consider the location of the various spin-wave resonance peaks on the static field axis for different shapes of the surface anisotropy energy surface. For the special case where $\phi_H = \phi_{\text{eq}} = \pi/2$, the boundary conditions for the θ and ϕ components are the same as is evident by an examination of Eqs. (28)-(29). For the uniaxial case with the hard axis in the direction of the film normal, we find by combining Eqs. (18), (28), and (29) the expression determining the location of the spin-wave peak as

$$\tan kd = \frac{-8AkK_s}{(2Ak)^2 - (2K_s^2)}. \tag{31}$$

Again, for the case where the easy axis is in the direction of the film surface normal, K_s in Eq. (31) should be replaced by $-K_s$.

For the unidirectional cases, we find by combining Eqs. (18) and (30) the expression determining the location of the spin-wave peaks as

$$\tan kd = 0. \tag{32}$$

Equations (31) and (32) have been plotted in Fig. 4 for different values of K_s. We note from the figure that, whereas the location of the spin-wave peaks move toward the right or left as K_s is changed for the uniaxial case, they are stationary for the unidirectional cases. These results may have been surmised by observing

---

[10] C. T. Rado and T. R. Weertman, J. Phys. Chem. Solids 2, 315 (1959).

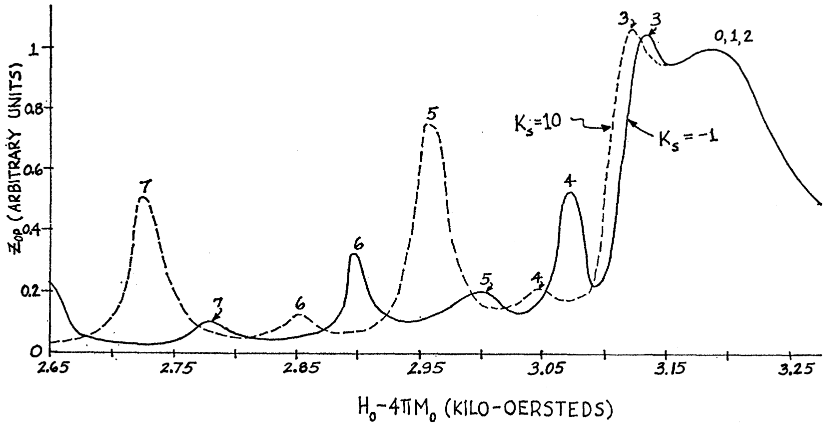

FIG. 5. Spin-wave absorption spectrum of a thin conducting film ($\rho=21\times10^{-6}$ Ω-cm and other film data same as that given in Fig. 4). Surface anisotropy is uniaxial with easy axis ⊥ to film.

that the direction of the equivalent surface fields are antisymmetric and symmetric, with respect to the median plane $y=d/2$ for the uniaxial and unidirectional cases, respectively. For the uniaxial case, an examination of Eqs. (28) and (29) will show that the direction of the equivalent field acting on the surface spins are in the $-y$ direction at $y=0$ and d for the case where the hard axis is in the direction of the film normal. For the case where the easy axis is in the direction of the film normal, the equivalent surface fields are in the $+y$ direction at $y=0, d$. On the other hand, for the unidirectional cases, the equivalent surface fields for the ϕ component are in the direction of the inward normal at $y=0, d$ for the case where the easy direction is parallel to the inward normal at the surfaces of the film. Correspondingly, if the easy direction is along the outward normal of the surfaces, the equivalent surface fields are also in the direction of the outward normals at $y=0, d$.

The foregoing results may be easily generalized to include the case of unequal spin pinning at the two surfaces of the film. Denoting the surface-energy density constants by K_{s1} and K_{sN} for $y=0$ and d, respectively, we find, for example, for the uniaxial case with the easy axis in the direction of the film normal the pertinent equation,

$$\left[\left(-\tfrac{1}{2}ka+\frac{2K_{s1}}{2Ak}\right)\left(-\tfrac{1}{2}ka+\frac{2K_{sN}}{2Ak}\right)+1\right]\tan kd = 2\frac{K_{s1}-K_{sN}}{2Ak}, \quad (33)$$

for the location of the spin-wave peaks. Both Eqs. (31) and (33) may be satisfied by real or imaginary values of k. The imaginary k solutions correspond not to the ordinary volume resonance modes (real k) but to surface modes. The rf magnetization of these modes should decrease rapidly from the surface and, therefore, may have an important influence upon the nature of the magnetization reversal process in thin films. Thus, the possible existence of these surface modes may contribute to prevent the magnetization from rotating in unison in the exterior and interior parts of the film. With reference to Fig. 4, we note that for the uniaxial cases, H_0 changes with K_s. According to the spin-wave dispersion relation (19) for the special case $\phi_H=\pi/2$, the relationship between k and H_0 is given by

$$k^2=\frac{\omega/|\gamma|-H_0+4\pi M}{2A/M}.$$

Thus, at a given ω, k changes with changes in K_s as H_0 required for resonance for a given spin-wave mode is dependent upon K_s for these cases. Thus, if the modes are numbered according to the asymptotic approach of H_0 as $K_s\rightarrow\infty$ so that $n=dk/\pi$ with n odd, the k^2 law for spin waves will be apparently violated as H_0 departs from its asymptotic values with finite K_s. This "numbering ambiguity"[11] is particularly significant as K_s is typically of the order unity[5] so that there is significant departure of H_0 from its $K_s\rightarrow\infty$ values. Furthermore, in as much as the substrate side of the film appears to be strongly pinned, presumably due to the presence of oxidized layer on the film-substrate interface, the curves of Fig. 4, according to Eq. (33), would vary somewhat as K_s on the nonsubstrate side is changed. This would introduce further complications into the determination of the exchange constant A by means of spin-wave resonance.

ABSORPTION SPECTRUM

Since most spin-wave resonance experiments are done with conducting Permalloy films, it would be pertinent to calculate the absorption spectrum including conductivity. However, relaxation damping will be neglected for simplicity.

For the special case where $\phi_H=\pi/2$ so that H_0 is perpendicular to the film, we have previously shown that the magnetization can be expressed in terms of a

---

[11] R. F. Soohoo, J. Appl. Phys. 34, 1149 (1963).

linear combination of four plane spin waves.[5,12] For the positive circularly polarized waves,

$$m_p=(m_3{}^+e^{-ik_3y}+m_4{}^+e^{-ik_4y}+m_3{}^-e^{ik_3y} \\ +m_4{}^-e^{ik_4y})e^{i\omega t}, \quad (34)$$

where the first two terms represent waves traveling in the positive y direction while the last two terms represent waves traveling in the negative y direction. The expression for h_p can be derived from Maxwell's equations. Imposing the exchange boundary condition (28) and (29) and the usually requirement of the continuity of the tangential component of **h** or **e** at the surfaces of the film, we find

$$Z_{p0}=i\frac{e_{p0}}{h_{p0}} \\ =\frac{i\omega\delta'^2}{2c}\frac{k_3C_{e3}(m_3{}^+-m_3{}^-)+k_4C_{e4}(m_4{}^+-m_4{}^-)}{C_{e3}(m_3{}^++m_3{}^-)+C_{e4}(m_4{}^++m_4{}^-)}, \quad (35)$$

where Z_{p0} is the impedance of the film at the surface $z=0$ and $C_{e3,4}=4\pi/[1-i\frac{1}{2}\delta'^2k_{3,4}{}^2]$ and $\delta'=-i2c^2/\omega^2\epsilon_e$ is the generalized skin depth where $\epsilon_e=\epsilon[1+(4\pi\sigma/i\omega\epsilon)]$ and ϵ and σ are the dielectric constant and conducting of the ferromagnet, respectively. For the uniaxial case, we have

$$D\frac{m_3{}^++m_3{}^-}{h_0}=-4C_{e3}[(K_s{}^2-4A^2k_4{}^2)\sin k_4d \\ -4Ak_4K_s\cos k_4d]\sin k_3d \\ +4C_{e4}\{(K_s\sin k_3d-2Ak_3\cos k_3d) \\ \times[K_s\sin k_4d-2Ak_4(\cos k_4d-1)] \\ -4A^2k_3k_4+2Ak_3(K_s\sin k_4d \\ +2Ak_4\cos k_4d)\}$$

$$D\frac{m_3{}^+-m_3{}^-}{h_0}=4iC_{e3}[(K_s{}^2-4A^2k_4{}^2)(\cos k_3d-1)\sin k_4d \\ -4Ak_4K_s(\cos k_3d-1)\cos k_4d] \\ -4iC_{e4}\{(K_s\cos k_3d+2Ak_3\sin k_{3d}) \\ \times[K_s\sin k_4d-2Ak_4(\cos k_4d-1)] \\ -K_s[2Ak_4+K_s\sin k_4d \\ -2Ak_4\cos k_4d]\}. \quad (36)$$

K_s is positive and negative, respectively, for the cases where the hard and easy axis are in the direction of the film normal. For the unidirectional case with the easy direction in the direction of the inward normal, the expression for $m_3{}^+\pm m_3{}^-$ has been given previously in Ref. 11 and is similar to the ones given above. To obtain the expressions for $m_4{}^+\pm m_4{}^-$, we need only change k_3 to k_4, C_{e3} to C_{e4} and vice versa on the right-hand side of the equations for $D(m_3\pm m_3{}^-)/h_0$, respectively. For the other sense of polarization we need only change k_3 to k_2 and k_4 to k_1.

A plot of Eq. (36) versus $H_0-4\pi M$ is given in Fig. 5 for two different values of K_s. The movement of the peaks as K_s is changed, shown in Fig. 4 for the uniaxial case, is clearly indicated. Furthermore, detailed numerical calculations show that the location of the absorption peaks are practically the same as those given in Fig. 4 for an insulator even in the presence of conductivity.

ORIGIN OF SURFACE ANISOTROPY

By observing the spin-wave spectrum of a thin film with various values of K_s, it should be possible to determine the nature, and in the uniaxial cases the value as well, of the surface anisotropy energy. Kooi, Holmquist, and Doherty have performed such experiments by repeatedly oxidizing and reducing the film surface not adjacent to the substrate.[7] By using their data, we found that the spin-wave resonance peaks move to lower values of the static field H_0 as K_s is increased by oxidation. It, therefore, appears, by comparison with the theoretical curves in Fig. 4, that the surface anisotropy is uniaxial in character with the easy axis of magnetization parallel to the film normal. This behavior could be accounted for by either a low magnetization layer as recently proposed by Wigen *et al.*[8] or an antiferromagnetic layer at the surfaces of the film with an easy axis along the film normal and a hard plane perpendicular to it. This is so because, according to Eq. (10), the existence of an uniaxial surface energy is mathematically equivalent to a difference in demagnetizing field for the surface and interior parts of the film. To the first order, this is equivalent to the case of a lower magnetization layer at the surface of the film and our theoretical results with regard to the disappearance of the spin pinning at some critical angle ϕ_{Hu} for a given $\omega/\gamma4\pi M$ is consistent with that observed by Wigen *et al.* as indicated in Fig. 2. The discrepancy between theoretical and observed values of ϕ_{Hu} may be attributed to incomplete pinning. However, according to Eqs. (21) and (22), only the ϕ component of the magnetization becomes unpinned at ϕ_{Hu} and $\phi_{\text{eq}}\simeq45°$, while m_θ remains pinned. To be consistent with experiments, one would have to assume that m_θ as well as m_ϕ becomes unpinned when the magnetization makes an angle of 45° with the film normal by exchange forces.

It is very likely that a combination of antiferromagnetic surface layer and a lower magnetization layer exists as the interface between ferromagnetic and antiferromagnetic layers could be rather complicated

---

[12] R. F. Soohoo, Phys. Rev. **120**, 1978 (1960).

and there is no assurance of complete ferromagnetic to antiferromagnetic order. Of course, the surface energy K_s must be sufficiently large and $4\pi\Delta M$ must be larger than the line width (so that the surface spins would be nonresonant) for effective pinning to occur. Although this phenomenon could be equally accounted for by inhomogeneous demagnetizing field due to the film's nonellipsoidal shape, our detailed calculations show that the inhomogeneity is only of order $(d/D)4\pi M$, where d/D is the thickness to diameter ratio of the film, entirely too small compared to the line width to account for pinning.

A further word on the experimental determination of the exchange constant A and the surface anisotropy energy density K_s is in order. Using the measured critical angle ϕ_{Hu} at which the spin system becomes unpinned, $2Ak^2/2K_s'$, the ratio of the exchange to surface energy, could be determined from Fig. 3. Then, using this ratio and curves similar to Fig. 4 plotted with A as a constant parameter, K_s and A may be determined simultaneously. Thus, we see that if the surface spins are not completely pinned, the exchange constant cannot be determined independent of the surface energy, as is usually done.

PHYSICAL REVIEW VOLUME 131, NUMBER 2 15 JULY 1963

Paramagnetic Resonance of Chromium in CdTe†

G. W. Ludwig and M. R. Lorenz
General Electric Research Laboratory, Schenectady, New York

(Received 19 March 1963)

Paramagnetic resonance has been studied for Cr in the $3d^5$ configuration substituting for Cd in CdTe. We find $S=5/2$, $g=1.9997\pm0.0003$, $|a|=(3.1\pm0.6)\times10^{-4}$ cm^{-1}, and $A=(+12.781\pm0.005)\times10^{-4}$ cm^{-1} for Cr^{53}. Using electron-nuclear double resonance the complete tensor describing the anisotropic hyperfine coupling with the nearest Cd neighbors has also been determined. Electrical measurements indicate that the Cr acceptor level lies within 0.6 eV of the conduction band edge.

I. INTRODUCTION

The technique of electron paramagnetic resonance has been used with moderate success for the study of defect centers, principally transition metal ions of the $3d$ group, in CdTe and related II–VI compounds. Data on manganese ions having a half-filled $3d$ shell are available for all of these compounds, while cobalt in the $3d^7$ configuration has been studied in most of them. Paramagnetic resonance associated with chromium has been reported only in ZnS and CdS.[1,2]

The purpose of the present paper is to report on the paramagnetic properties of chromium in the $3d^5$ configuration in CdTe, a cubic crystal having the zincblende structure. If chromium were simply to substitute for cadmium in the lattice with no charge unbalance, its configuration would be expected to be $3d^4$. The fact that one detects Cr($3d^5$) implies that chromium can act as an acceptor as it does in ZnS.[1,3] The resonance study of Cr($3d^5$) in CdTe has been unusually successful. It has been possible to determine not only the g factor and the cubic field splitting parameter, but also, using electron-nuclear double resonance (ENDOR) techniques, the hyperfine interaction with Cr^{53}, and the complete tensor describing the hyperfine coupling with the magnetic isotopes Cd^{111} and Cd^{113} occupying second-neighbor positions.

Sample preparation and properties and the resonance spectrum are described in II; III is devoted to a description of the ENDOR experiments; the results are presented and discussed in IV.

II. EXPERIMENTAL TECHNIQUES AND THE RESONANCE SPECTRUM

High-purity CdTe single crystals were prepared by techniques already described.[4] Samples were cut into oriented bars approximately $3\times3\times10$ mm^3 with a [110] axis parallel to the long dimension. The bars were etched in HF·HNO$_3$·2H$_2$O solution and chemically polished in a solution of 70 parts of saturated K$_2$Cr$_2$O$_7$

---

† The research reported in this paper was sponsored in part by the Air Force Aeronautical Research Laboratories, Office of Aerospace Research, under contract AF 33(616)-8264.

[1] R. S. Title, Bull. Am. Phys. Soc. 8, 23 (1963).

[2] For a more complete discussion of paramagnetic resonance of defects in II–VI compounds, including references, see G. W. Ludwig and H. H. Woodbury, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 223.

[3] The configuration of the free chromium atom is $3d^5 4s$. On an ionic model one writes CdTe as Cd^{2+}Te^{2-}; thus, at a chromium impurity site, assuming no charge unbalance, one would have Cr^{2+}($3d^4$). On a covalent model one writes CdTe as Cd^{2-}Te^{2+}, but the outer Cd electrons are used in the covalent bonding. On such a model one would have Cr^{2-}($3d^4 4s4p^3$) at a chromium site were there no charge unbalance. The $4s4p^3$ electrons participate in covalent bonding leaving the Cr core in the $3d^4$ configuration. Thus with either model Cr($3d^4$) is the configuration for no charge unbalance at the Cr site, while Cr($3d^5$) implies that the chromium impurity has accepted one electron.

[4] M. R. Lorenz and R. E. Halsted, J. Electrochem. Soc., **101**, 343 (1963).