Thin Ferromagnetic Films*

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The spontaneous magnetization of thin films of ferromagnetic materials has been studied by means of spin-wave theory. Results have been obtained for the magnetization as a function of temperature and film thickness for body-centered and face-centered cubic materials, generalizing earlier calculations by Klein and Smith. The approximations in the theory are critically discussed, and the relevant experimental material is briefly reviewed.

I. INTRODUCTION

THE spin-wave theory of ferromagnetism as developed by Bloch[1] states that ferromagnetism is an essentially three-dimensional phenomenon, and that two-dimensional lattices do not show spontaneous magnetization. This theory suggests then that films of ferromagnetic materials should show an interesting transitional behavior as the thickness of the film is reduced. Klein and Smith[2] calculated the spontaneous magnetization for films of simple-cubic structure using the spin-wave theory. These calculations of magnetization as a function of temperature and film thickness predict deviations from the Bloch $T^{\frac{3}{2}}$ law, which holds at low temperatures for the bulk ferromagnetic material, and these deviations are appreciable for sufficiently thin films, thinner than about one hundred atomic layers for the case considered.

These deviations from the Bloch law have been observed in a number of experiments,[3–7] and the existence of the thin film-effect is now well established.[8,9] Although the experimental results show the predicted type of magnetic behavior, there is no quantitative agreement between theory and experiment. The principal reason for the lack of quantitative agreement is that the experiments were done at room temperature[10] which is surely outside the range of validity of the spin-wave theory, since this theory requires for its validity that the spin system be almost completely magnetized. A second reason for the lack of quantitative agreement is that the materials studied experimentally are not simple cubic. It is this latter reason which prompted the calculation described below.

In this paper the calculations of I have been extended to body-centered and face-centered cubic structures. The results differ from those for simple-cubic films only in detail; the general form of the results is unchanged by the change in lattice type. The method of calculation is described in the following section. The results of the calculations are expressed as graphs ofthe magnetization as a function of thickness and of temperature for face-centered and body-centered lattices. The final sections of this paper contain a general discussion of the results, some critical remarks on the sensitivity of the results to particular assumptions made in the theory, and a brief comparison of the results with experiment.

II. CALCULATIONS

We consider a cubic lattice which has N spins located on its lattice sites. Each spin interacts with an external magnetic field $\mathbf{H}$, and with its nearest neighbors through the Heisenberg exchange interaction. The Hamiltonian $\mathcal{H}$ is then given by the equation[11]

$$\mathcal{H}=-2\beta\mathbf{H}\cdot\sum_{\mathbf{l},i}\mathbf{S}_{\mathbf{l},i}-J\sum_{\mathbf{l},i}\sum_{\mathbf{m},r}\mathbf{S}_{\mathbf{l},i}\cdot\mathbf{S}_{\mathbf{m},r}. \tag{1}$$

In this equation J is the exchange integral, β is the Bohr magneton, and $\mathbf{S}_{\mathbf{l},i}$ is the spin operator of the ith atom within the simple-cubic cell indexed by $\mathbf{l}$. The sum on $\mathbf{m}$ and r runs over the nearest neighbors of atom $\mathbf{l},i$.

If we make the assumption, basic to all spin-wave calculations, that the system is almost completely magnetized, then the approximate eigenvalues of $\mathcal{H}$ can be determined. They take on the form[11]

$$E(n_{\mathbf{k},j})=-2\beta HSN-zNJS^2+4JS\sum_{\mathbf{k},j}n_{\mathbf{k},j}\mu_{\mathbf{k},j}. \tag{2}$$

In this equation S is the spin quantum number of any atom and z is the number of nearest neighbors of an atom. The first two terms give the energy of the com-

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[1] F. Bloch, Z. Physik **61**, 206 (1930).
[2] M. J. Klein and R. S. Smith, Phys. Rev. **81**, 378 (1951). This paper is referred to as I.
[3] A. Drigo, Nuovo cimento **8**, 498 (1951).
[4] E. C. Crittenden and R. W. Hoffman, Revs. Modern Phys. **25**, 310 (1953).
[5] H. H. Jensen and A. Nielsen, Trans. Danish Acad. Tech. Sci. No. 2, 3 (1953).
[6] W. Reincke, Z. Physik **137**, 169 (1954).
[7] R. L. Conger and F. C. Essig, Phys. Rev. **104**, 915 (1956).
[8] H. Mayer, *Physik Dünner Schichten* (Wissenschaftliche Verlagsgesellschaft M.B.H., Stuttgart, 1955), Part 2, pp. 324–327, 343–346.
[9] A. Colombani, *Propriétés Magnétiques des Lames Métalliques Minces* (Mémorial des Sciences Physiques, Fascicule LVIII, Gauthier-Villars, Paris, 1954), pp. 49–60.
[10] See, however, R. W. Hoffman and A. M. Eich, *Conference on Magnetism and Magnetic Materials, Boston, 1956* (American Institute of Electrical Engineers, New York, 1957), p. 78. This work is discussed in Sec. IV of this paper.
[11] See T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940). Our Hamiltonian omits dipole-dipole interactions which can be treated approximately by spin-wave methods as shown by Holstein and Primakoff. These interactions are not expected to have any important effect on our results. This may be seen by the arguments in Sec. IIB of the paper, C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).

pletely magnetized system (the ground state energy), and the third term is the energy of excitation of the spin waves. The number of quanta, or excitation strength, of the spin wave whose quantum of energy is $4JS\mu_{\mathbf{k},j}$ is $n_{\mathbf{k},j}$ which takes on non-negative integer values. The $\mu_{\mathbf{k},j}$ have the following forms for the three cubic lattices.[12]

$$\mu_{\mathbf{k}}=\alpha+3-\cos k_1-\cos k_2-\cos k_3, \quad \text{(simple cubic)}$$

$$\mu_{\mathbf{k},\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}}=\alpha+4[1\{\pm\}\cos(k_1/2)\cos(k_2/2)\cos(k_3/2)], \quad \text{(body-centered cubic)}$$

$$u_{\mathbf{k},\left\{\begin{smallmatrix}1\\2\\3\\4\end{smallmatrix}\right\}}=\alpha+2\left[3+\left\{\begin{matrix}-\\-\\+\\+\end{matrix}\right\}\cos(k_1/2)\cos(k_2/2)+\left\{\begin{matrix}-\\+\\-\\+\end{matrix}\right\}\cos(k_2/2)\cos(k_3/2)+\left\{\begin{matrix}-\\+\\+\\-\end{matrix}\right\}\cos(k_3/2)\cos(k_1/2)\right], \quad \text{(face-centered cubic)}. \tag{3}$$

In these equations α is $(\beta H/2JS)$, and k_i is $2\pi\lambda_i/G_i$ $(i=1, 2, 3)$ with G_i equal to the number of cubic cells in the ith direction of our crystal, whose shape is a rectangular parallelepiped. The λ_i are integers which take on the values $0, 1, \cdots, G_i-1$, or equivalently $-\frac{1}{2}G_i+1, \cdots, 0, \cdots \frac{1}{2}G_i$. Periodic boundary conditions have been assumed. Note that N is equal to $\rho G_1G_2G_3$ where ρ is the number of atoms in a cubic unit cell; ($\rho=1, 2, 4$ for the s.c., b.c.c., and f.c.c. cases).

Following the usual procedures of the spin-wave theory, i.e., treating the excitation numbers $n_{\mathbf{k},j}$ as independent quantum numbers which take on all non-negative integer values, the total magnetic moment M of the system is found to be

$$\frac{M}{M_0}=1-(SN)^{-1}\sum_{\mathbf{k},j}\left[\exp\left\{\left(\frac{4JS}{kT}\right)\mu_{\mathbf{k},j}\right\}-1\right]^{-1}, \tag{4}$$

where $M_0=2\beta SN$, the magnetic moment for complete alignment.

We illustrate the evaluation of M/M_0 from Eq. (4) for the case of a body-centered cubic film. We assume that the film normal is in the direction of one of the cubic axes, and we set both G_1 and G_2 equal to G, where G is a large number ($\sim10^7$ or more) which measures the linear dimensions of the film in units of the cubic cell. The thickness of the film measured in the same way is G_3 which need not be large. We now replace the sums on k_1 and k_2 by integrals, and M/M_0 takes the form

$$\frac{M}{M_0}=1-(SN)^{-1}\sum_{\lambda_3=0}^{G_3-1}\left(\frac{G^2}{\pi^2}\right)\int_{-\pi/2}^{\pi/2}\int_{-\pi/2}^{\pi/2}\times\sum_{j=1}^{2}\left[\exp\left\{\left(\frac{4JS}{kT}\right)\mu_{\mathbf{k},j}\right\}-1\right]^{-1}d\kappa_1d\kappa_2, \tag{5}$$

where $\kappa_i=k_i/2$. If we examine the form of $\mu_{\mathbf{k},j}$ for the case $H=0$, since we are concerned with the spontaneous magnetization, we observe that only $\mu_{\mathbf{k},2}$ gives an important contribution to the integral. (Important contributions come from values of κ_1, κ_2 which make the integrand large, that is, from values near the origin in the κ_1, κ_2 plane.) We therefore drop the term in $\mu_{\mathbf{k},1}$ and expand the cosines of $(k_1/2)$ and $(k_2/2)$ in $\mu_{\mathbf{k},2}$. After we transform to polar coordinates our expression for M/M_0 becomes

$$\frac{M}{M_0}=1-(\pi SG_3)^{-1}\sum_{\lambda_3=0}^{G_3-1}\times\int_{\pi/G}^{\sqrt{\pi}}\frac{\kappa d\kappa}{\exp\{(8JS/kT)(2-2\cos\kappa_3+\kappa^2\cos\kappa_3)\}-1}. \tag{6}$$

(We have used the fact that $N=2G_3G^2$.) The lower limit on κ is not zero since the states $k_1=k_2=k_3=0$ have been omitted. (This omission is justified and discussed in some detail in the appendix of I.) The upper limit on κ is the radius of a circle whose area is equal to that of the square which was the original domain of integration. This approximation should not matter as the integrand is already small at this limit, but not small enough for us to run the limit out to infinity in all cases.

The integration is now straightforward, and we obtain the result

$$\frac{M}{M_0}=1-(16\pi S^2G_3)^{-1}\left(\frac{kT}{J}\right)\sum_{\lambda_3=0}^{G_3-1}(\cos\kappa_3)^{-1}\times[\ln(1-e^{-B})-\ln(1-e^{-A})], \tag{7}$$

where

$$A=(16JS/kT)[1-(1-\pi^2/2G^2)\cos\kappa_3],$$

and

$$B=(16JS/kT)[1-(1-\pi/2)\cos\kappa_3].$$

Similar calculations for the face-centered cubic film lead to an equation like Eq. (7), but with minor changes, namely,

$$\frac{M}{M_0}=1-(16\pi S^2G_3)^{-1}\left(\frac{kT}{J}\right)\sum_{\lambda_3=0}^{G_3-1}(1+\cos\kappa_3)^{-1}\times[\ln(1-e^{-B'})-\ln(1-e^{-A'})], \tag{8}$$

where

$$A'=(16JS/kT)[(1+\pi^2/4G^2)-(1-\pi^2/4G^2)\cos\kappa_3],$$

and

$$B'=(16JS/kT)[(1+\pi/4)-(1-\pi/4)\cos\kappa_3].$$

[12] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, pp. 601–613. See also J. M. Luttinger, Phys. Rev. **81**, 1015 (1951).

III. RESULTS AND DISCUSSION

The results of the analytical work are summarized above in Eqs. (7) and (8). These expressions have been evaluated numerically for reasonable values of the parameters. The results of these computations are best seen in graphical form, and they are shown in Figs. 1–4. In Figs. 1 and 2 we have plotted the ratio of the spontaneous magnetization to its saturation value, M/M_0, as a function of the temperature in units of J/k for the face-centered and body-centered cases, respectively. In each figure a family of curves has been plotted, each curve corresponding to a value of G_3, the film thickness measured in units of the cubic lattice parameter. Figures 3 and 4 show the same information in another way, as we have plotted the relative magnetization, M/M_0, as a function of thickness, G_3, with temperature, kT/J, as parameter. In all cases we have taken $S=\frac{1}{2}$ and $G=3\times 10^7$; the latter figure corresponds to a film of surface area about 1 cm^2.

There are a number of separate comments to be made on the results portrayed in the figures, and it is convenient to take them up in turn.

(1) The principal conclusion to be drawn from the results is that the body-centered and face-centered cubic films have magnetic properties qualitatively similar to each other and to the properties of the simple cubic films previously studied. That is, the spontaneous magnetization at any given temperature falls off rather sharply from its value for bulk material as the film thickness decreases below a particular value of G_3, G_3 about 50 in the cases considered. Or, to put it another way, the magnetization falls off more sharply with increasing temperature for sufficiently thin films, so that the effective Curie temperature of a thin film may be only a small fraction of the Curie temperature of the bulk material.

(2) It will be observed that the scale for M/M_0 covers only the range from 1.0 to 0.75. The latter figure is an arbitrary cutoff which has been chosen to emphasize the point that the spin-wave theory is valid only when the magnetization is near its saturation value. It is well known that the spin-wave theory, the Bloch $T^{\frac{3}{2}}$ law, correctly describes the M *vs* T curves of bulk material only at low temperatures where M/M_0 is near one.[13] We have perhaps been optimistic in extending our curves to relative magnetizations as low as 0.75.

(3) The curves for bulk material are those labeled $G_3=\infty$ in Figs. 1 and 2. These curves were computed by replacing the sums on λ_3 in Eqs. (7) and (8) by integrals which were evaluated numerically. This procedure was used instead of making use of the known $T^{\frac{3}{2}}$ law for the following reason. The $T^{\frac{3}{2}}$ law involves mathematical approximations slightly different from those used in the film calculations and these approximations lead to results inconsistent with our results. More specifically, in the usual derivation of the $T^{\frac{3}{2}}$ law the sums on the k_i in Eq. (4) are replaced by infinite integrals. The contributions to these integrals from the regions outside $-\pi$ to π are small but important enough to lead to an intersection of the $T^{\frac{3}{2}}$-law magnetization curve and those for some of the films. This nonphysical result which, taken literally, would mean that the film could have a larger magnetization than the bulk material at the same temperature, is avoided by our self-consistent mathematical procedure. It should be mentioned that the inconsistency referred to occurs for values of T and M where the use of spin-wave theory is already questionable.

(4) Our results have been obtained for a particular value of G, the linear dimension of the film, and it is clear from Eq. (7) that the magnetization does depend on G. It is easy to see, however, that this dependence is very weak. It is only the term with $\lambda_3=0$ in Eqs. (7) and (8) in which the G dependence is significant, and

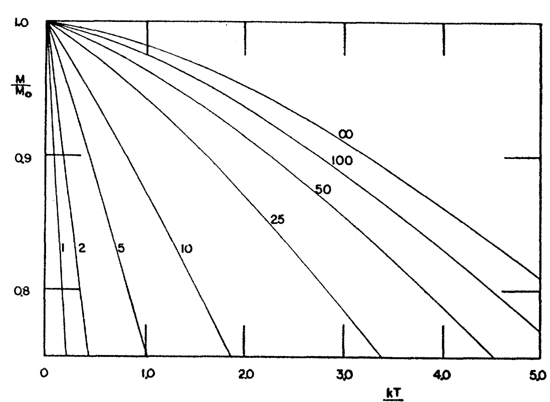

FIG. 1. The relative magnetization for face-centered films as a function of the reduced temperature, kT/J, for films of different thickness. The integers on the curves represent the thickness of the film in units of the cubic lattice parameter. The film is square, 3×10^7 lattice parameters on a side.

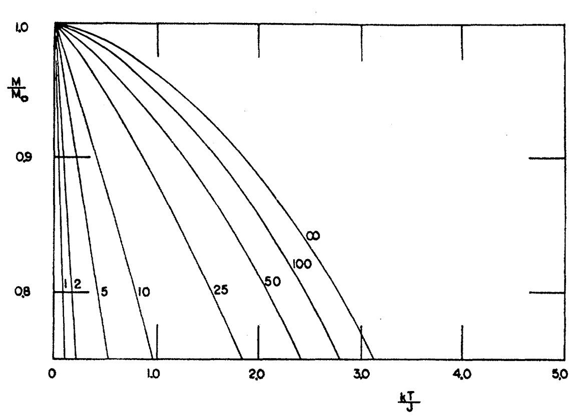

FIG. 2. The relative magnetization for body-centered films as a function of the reduced temperature, kT/J, for films of different thickness. The integers on the curves represent the thickness of the films in units of the cubic lattice parameter. The film is square, 3×10^7 lattice parameters on a side.

[13] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, Cambridge, 1955), pp. 496–501. Also L. F. Bates, *Modern Magnetism* (Cambridge University Press, Cambridge, 1948), pp. 239–248, and R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), pp. 448–449, 713–720.

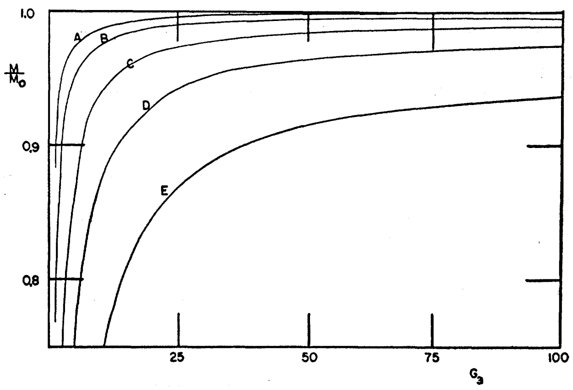

FIG. 3. The relative magnetization for face-centered films as a function of thickness in units of the cubic lattice parameter. The letters on the curves represent the reduced temperature, kT/J. A, B, C, D, E represent the reduced temperatures 0.10, 0.19, 0.49, 0.97, 1.94, respectively.

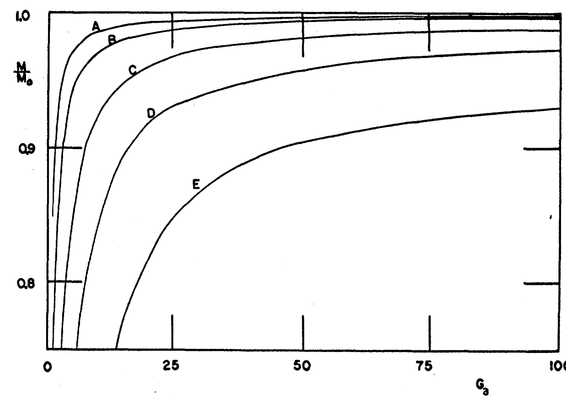

FIG. 4. The relative magnetization for body-centered films as a function of thickness in units of the cubic lattice parameter. The letters on the curves represent the reduced temperature, kT/J. A, B, C, D, E represent the reduced temperatures 0.06, 0.12, 0.31, 0.61, 1.22, respectively.

from this term, in the body-centered case, we can easily calculate that $\partial(M/M_0)/\partial G = -(kT/J)G^{-1}(8\pi^2 SG_3)^{-1}$. Hence for large G the variation of the magnetization with G is unimportant. (See the discussion in Sec. III of I.)

(5) Our calculations have used periodic boundary conditions as a convenience. Since these boundary conditions are questionable for very thin films we have checked in some special cases by allowing for the changed number of nearest neighbors of the boundary layer atoms. The results for films a few layers thick (where periodic boundary conditions should be most influential) differ by negligible amounts from those already quoted when we are well within the region of validity of spin-wave theory.

(6) The calculations described above have assumed that the film plane is perpendicular to one of the basis vectors of the cubic lattice. This is an unfortunate limitation on the theory when we want to compare with experiment since the films studied experimentally are normally polycrystalline with more or less randomly oriented crystallites. We have not been able to remove this limitation, but preliminary calculations for films a few layers thick, whose base plane is a (110) plane, suggest that only small changes in the magnetization curves would be found if the magnetization of the polycrystalline film could be calculated.

(7) It will be noted that curves for films whose thickness is one cubic lattice spacing are included in Figs. 1 and 2. These essentially two-dimensional films are ferromagnetic only at very low temperatures, and their ferromagnetism comes from the nonzero lower limit in the integral of Eq. (6). For a discussion of this lower limit and of the linear nature of these curves we refer to I (Appendix and reference 9).

IV. CONCLUSIONS

In conclusion we shall discuss briefly the comparison of our theoretical work with experiment. The older experimental results are summarized and are also compared with the theory of I by Mayer and by Colombani in their monographs on thin films.[8,9] These experiments, which were done at room temperature, confirm the existence of the thin-film effect, but the results are not in quantitative agreement with the theory which is applicable only at low temperatures. When the curves of I are adjusted by a more or less *ad hoc* procedure, introduced by Drigo[3] and used by Crittenden and Hoffman,[4] which was designed to account for the inadequacy of spin-wave theory for bulk material at room temperature, the agreement is quite impressive but not very significant.

Experiments have recently been carried out in this Laboratory by Hoffman and Eich[10] in order to put the theory to a more stringent test. In these experiments the saturation magnetization of evaporated nickel films, whose thicknesses ranged from 35 A to 1350 A, was measured over a range of temperatures from 10°K to 300°K. Experimental difficulties gave rise to a problem of lack of reproducibility in the data, but the smoothed results may be summarized as follows. The smoothed experimental curves of relative magnetization *vs* temperature agree very well with our f.c.c. theoretical curves, Fig. 1, if a value of the exchange integral J is determined by using one experimental point. Unfortunately, however, the values of J so determined vary from one film to another, the extreme values being $75k$ and $140k$. Furthermore all of these J values differ seriously from Fallot's[14] value for J, $230k$, which was obtained from the $T^{3/2}$-law curve for nickel at low temperatures.

Further experimental work at low temperatures, free of the difficulties described by Hoffman and Eich, would be desirable for a fuller understanding of the relationship between the theory given above[15] and the actual behavior of thin ferromagnetic films.

[14] M. Fallot, Ann. phys. **6**, 305 (1936).

[15] For an alternative and different theoretical discussion based on spin-wave theory see G. Heber, Ann. Physik **13**, 44 (1953).