Thin Films of Ferromagnetic Materials*

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Experimental observations are reported on the magnetic properties of thin evaporated films of nickel. The saturation magnetization follows the general prediction of Klein and Smith after somewhat arbitrary modifications on the basis of fitting the Weiss curve for bulk specimens, as suggested by Drigo. Qualitatively observed properties due to domain structure follow the predictions of Kittle. The surface roughness of the specimens has been carefully controlled. Measurements of temperature coefficient of resistance have led to modification of the theory of electron mean free path in thin films. The mean free path is found to vary at small thicknesses, rather than remaining constant as assumed by Fuchs and Sondheimer. The surface roughness has been estimated with the help of this theory. The films of nickel behave as if surface variations extend into the film approximately 3 angstroms from each surface.

THERE are several theories of ferromagnetism which agree well with experimental evidence for bulk samples.[1] It appears, however, that if a magnetic specimen is made thin in one dimension while remaining large in the others, important differences develop between the theories.[2] In this respect investigation of the ferromagnetic properties of thin films has the nature of a critical experiment with regard to the theory of ferromagnetic behavior.

The Bloch spin-wave theory predicts that a three-dimensional lattice is ferromagnetic, but a two-dimensional one is not. Klein and Smith have extended the spin-wave method to obtain a quantitative prediction of the manner in which the magnetization should vary with thickness and with temperature. The temperature dependence of magnetization varies from a $T^{\frac{3}{2}}$ law for thick films to a linear dependence for very thin films. The Bloch theory is not considered to be valid except in the region where the magnetization is near its maximum value, I_0. This rather naturally persists in the extension to thin films. This is unfortunate since the interesting region for a thin film is the region where its magnetization falls decidedly below I_0. For lack of quantitative extension into this region based on any other model, an empirical modification of the Klein-Smith theory has been made for comparison with the experimental results.

The observations reported here have been made on evaporated films of nickel, extending down to a thickness of 10.2 angstroms. Experimentally the most serious problems have been those of being certain that the films were pure metallic nickel and of controlling and measuring the flatness. A number of details concerned with the experimental techniques of preparation will be discussed to dispel doubts concerning the nature of such extremely thin films.

Magnetic measurements have also been made by Drigo[3] on thin films of electroplated nickel, iron, and cobalt. These are shown later for comparison. However, it seems difficult to avoid the presence of impurities in the electroplated nickel and to control and determine the magnitude of surface roughness in the very thin films.

It is recognized that evaporated metal films have acquired a bad reputation as far as being specimens of metal which may be directly compared with pure bulk specimens of the same material. A number of effects have contributed to this reputation. Ordinarily the pressures used in evaporation are not low enough to avoid contamination. Connected with this is the lack of true protection offered by vacuum of the order of 10^{-5} mm of mercury, for which each surface atom is hit approximately once every half-second by a residual gas molecule. Evaporated films also tend to form in lumps or to agglomerate when the temperature is increased. In addition, they are formed with a high density of crystal imperfections, especially if the condensing surface is cold and the condensation rate high. On heating, these imperfections disappear and their loss leads to the development of a high tensile stress in the film which may cause rupture of the film. Evaporated films are polycrystalline with a small crystal size. Preferred orientation or oriented overgrowth may be present under some conditions. However, with due attention to these effects, evaporated films can be well behaved specimens of normal metal.

Nickel was chosen as the material for study because the energy of magnetization is not highly anisotropic and strain induced anisotropy is not strongly dependent on crystal orientation relative to the strain. This allows a polycrystalline thin specimen to act as one domain.

Specimens are prepared in the equipment shown diagramatically in Fig. 1. The substrate material is fire polished glass cut from microscope slides. Williams and Backus[4] have shown such glass to be smooth to less than 5 angstroms as regards sudden discontinuities. The glass substrate strips are approximately $\frac{1}{4}$ inch

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[1] J. H. Van Vleck, Revs. Modern Phys. **17**, 27 (1945).

[2] M. J. Klein and R. S. Smith, Phys. Rev. **81**, 378 (1951).

[3] A. Drigo, Nuovo cimento **8**, 498 (1951).

[4] R. C. Williams and R. C. Backus, J. Appl. Phys. **20**, 98 (1949).

by 3 inches. Silver current and potential contacts are fired on in advance to allow measurement of electrical conductivity. The conductance of the specimen in the "rate furnace" is recorded continuously and used to control the filament source of nickel vapor so that the film grows at a uniform rate of 60 angstroms per second. The rate furnace is kept at 250°C. This high a temperature for nickel leads to deposition of a polycrystalline film in which the microcrystals are essentially free of imperfections. This temperature is, however, not so high as to produce grain growth. The shutters are not opened until a thick layer is already present on the rate furnace specimen. This avoids trouble with electron surface scattering effects in the rate specimen. Timing of the shutters determines the thickness deposited on the specimen. Immediately after deposition of the nickel, a third shutter, not shown, is opened and a layer of about 200 angstroms of SiO evaporated over the specimen to prevent oxidation. The two filament sources are so arranged that no cross transfer occurs between them.

The source of nickel vapor is a tungsten filament electroplated with nickel. The entire system is outgassed for about 12 hours before evaporation takes place. The filament is operated at a temperature where very slow evaporation takes place during this 12 hours to remove dissolved hydrogen present in the electroplated nickel. Evaporation takes place in vacuum ranging between 5×10^{-7} and 3×10^{-6}. This gives a maximum possible gas contamination of 0.15 percent, taking the residual gas to be N_2.

The film thickness is determined from the rate of change of conductance of the monitor specimen in the rate furnace and from the time interval between opening and closing of the specimen shutters. Absolute calibration was obtained by chemical means. The specimen was dissolved and the mass of nickel determined by quantitative colorimetry using a spectrophotometer. The thickness agreed well with multiple beam interferometry results for thick films (2000A) where that technique is valid.

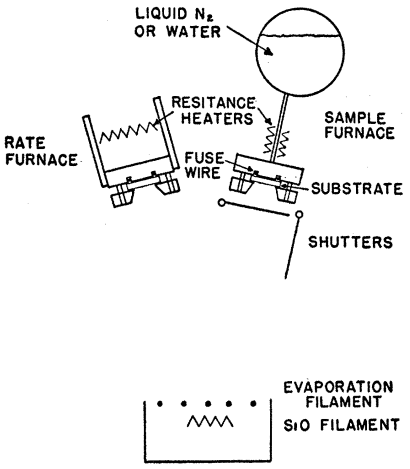

FIG. 1. Diagram of evaporation system.

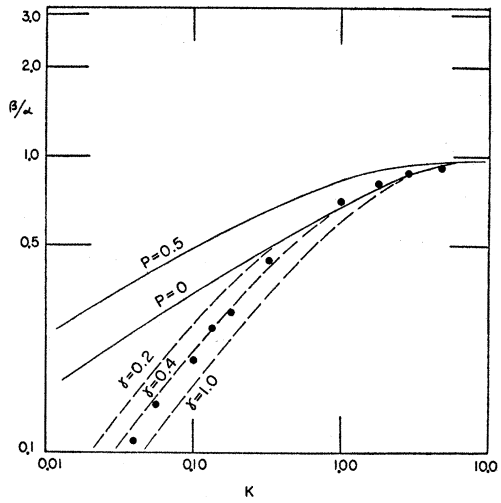

FIG. 2. Graph of temperature coefficient of resistance *vs* k, the ratio of thickness to electron mean free path. The solid curves result from the theory of Fuchs and Sondheimer for total inelastic scattering ($P=0$) and 50 percent inelastic scattering ($P=0.5$). The dotted curves are the result of introducing a variable mean free path for various values of the parameter γ.

The specimen temperature during deposit is held at 75°C. Temperatures somewhat lower than this (about 10°C) lead to cracking of the films because of very high tensile stress in the film. In general, the lowest temperature possible is desirable in order to reduce surface migration of the first arriving atoms. A high surface mobility leads to nucleation of a small number of crystals and a consequent increase in "lumpiness" of the initial deposit. For nickel 75°C was found to be satisfactory. Such films, however, have a high density of crystal imperfections. On heating, the resistivity falls irreversibly. Annealing at 275°C for four hours brings the specimens to a reproducible state.

An interesting point is illustrated by annealing very thin films. An intact, though rough, slab of metal should flatten out on annealing if the temperature is high enough to give some surface mobility. By flattening, the surface energy is reduced. However, a specimen consisting of isolated islands of metal or a cracked slab should tend to pull into spheres to reduce its surface energy. A film of apparent thickness, 5A, was deposited and coated with SiO. This film was just on the threshold of being an electrical conductor, i.e., "thinner" films consist of isolated crystals which do not touch. On annealing, the resistance of this film increased, indicating that it was pulling into isolated spheres. On the other hand, slightly thicker films became decidedly better conductors on annealing, indicating that they are becoming flatter. This effect is in addition to the loss of internal crystal imperfections which is occurring simultaneously. The thinnest specimen used for magnetic measurements was 10.2A, well above the thickness, 5A, at which agglomeration set in.

As a quantitative means of observing roughness, the electrical resistivity of these films was studied as

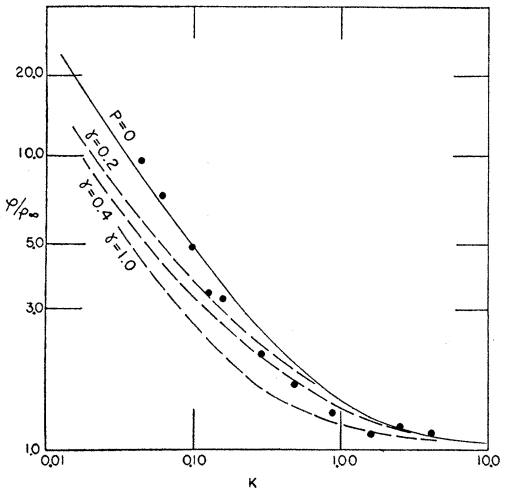

FIG. 3. Graph of resistivity *vs* k. The solid curve is that given by Fuchs and Sondheimer. The dotted curves result from introducing a variable mean free path.

a function of thickness. Surface scattering of the conduction electrons causes the resistivity to rise as thickness decreases. Experimentally the resistivity is difficult to observe with precision because the observed resistance must be divided by the thickness to obtain resistivity. On the other hand, the temperature coefficient of resistivity is a quantity which is independent of specimen geometry. Both quantities were determined on all specimens. Theoretical calculations of resistivity *vs* thickness have been made by Fuchs[5] and later by Sondheimer.[6] Both authors assumed a constant mean free path for conduction electrons. Their results can be readily extended to predict the temperature coefficient of resistance. However, the experimental data fails to fit their theoretical predictions for very small thickness. This is especially apparent for the temperature coefficient of resistance which falls far too fast as thickness decreases. Invoking elastic scattering at the surface for some fraction of the electrons, as suggested as a possibility by Fuchs, gives a poorer fit. In attempting to explain this, it was realized that the surfaces should have still another effect on the electrons besides scattering.[7] Since one must satisfy the boundary condition that the electron density falls to zero for any appreciable distance outside the specimen, one is forced to a standing wave pattern for ψ inside the metal. This limits the possible values of electron momentum normal to the specimen surface. The Brillouin zone structure, which for a large specimen of simple material has its filled region in the form of a sphere, is now crossed by a system of planes representing allowed momenta. This reduces the scattering probability for electrons moving in the film. The resistivity of the "material of the film" thus decreases as the film becomes thinner. The surface scattering is of course still present and is a large effect, so that the observed resistivity still rises as thickness falls. The temperature coefficient of resistivity is affected more markedly than the resistivity. Figure 2 shows the temperature coefficient as a function of thickness as observed and as predicted by both theories. The corresponding values of resistivity are shown in Fig. 3. An adjustable parameter γ enters which represents, in effect, the width of the "planes" crossing the Brillouin zone structure.

It will be noticed in Fig. 2 that the points for the smallest thickness begin to fall below the new theoretical curve. It seems reasonable to interpret this as an effect of specimen roughness. The point plotted at a thickness $\kappa=0.04$ (22.0A) would fall on the curve if displaced approximately 6 angstroms toward smaller thicknesses. The same displacement also places other points on the curve, although the importance of displacement rapidly disappears at higher thickness because of the logarithmic scale. The values of the resistivity plotted in Fig. 3 have not been corrected for the roughness. Adjustment for the roughness not only changes the thickness at which the points are plotted but also the value of the resistivity. If a 6-angstrom correction is made, the experimental points fall on the theoretical curve for $\gamma=0.4$. The 6A displacement possibly means that scattering points protrude frequently to the order of 3A into the film from each surface. It seems likely that this is nearly as flat a film as is possible, since the atomic diameter of nickel is 2.5A. It should also be noted that the height of the nickel unit cell is 3.5A, so that a detailed model of the roughness seems risky.

The magnetic measurements have been made in air whereas the electrical resistivity and temperature coefficients have been measured in vacuum. Although the films are coated with about 200A of SiO, some slight oxidation occurs on admitting air to the system. Each individual specimen was separately corrected for its oxidation on the basis of resistivity changes, the correction varying from 0.1A to 20A. The film continued to oxidize at a slow rate for long periods so that the correction necessary varied with the elapsed time before magnetic measurements were made.

The magnetic measurements were made with an instrument which displays the magnetic hysteresis loop on the screen of a cathode-ray oscillograph.[8] The measurement of saturation magnetization has an uncertainty of about 1A expressed as magnetic thickness for films 50A thick. By this is meant the apparent thickness assuming the specimen to have the flux density of normal bulk nickel at room temperature (6050 gauss). The applied magnetic field attainable is ± 400 oersteds.

As prepared, the thin films of nickel are in a state of tensile stress of 2.5×10^9 dynes/cm^2 at room tempera-

[5] K. Fuchs, Proc. Cambridge Phil. Soc. **34**, 100 (1938).
[6] E. H. Sondheimer, Phys. Rev. **80**, 401 (1950).
[7] Crittenden, Hoffman, and Layer, Phys. Rev. **86**, 657 (1952).
[8] Crittenden, Hudimac, and Strough, Rev. Sci. Instr. **22**, 872 (1951).

ture.[9] This stress is isotropic in the plane of the film. A small part of this stress results from simple differential expansion in cooling from deposition temperature to room temperature, but the principal part results from loss of crystal imperfections during deposition and during the annealing cycle. In the case of measurements made at much lower temperature than room temperature, differential expansion appreciably increases the stress. The associated strain causes uniaxial anisotropy of the energy of magnetization with an axis of easy magnetization perpendicular to the surface of the film. Since the film is polycrystalline, the strain induced anisotropy developed by each individual crystal is not truly uniaxial, but for all orientations the anisotropy figure has the general nature of uniaxial anisotropy. Under these conditions the films would be expected to behave as predicted by Kittel.[10] The general features of the predictions are born out. The hysteresis loop is rectangular for thin films, becoming more sharply rectangular as the films become thinner. This is consistent with the existence of a single domain magnetized parallel to the film surface for the thin films. Addition of a small static cross field in the plane of the film but at right angles to the oscillating large magnetizing field of the instrument drastically reduces the coercive force. The same small cross field applied perpendicular to the film has no effect. These observations also indicate the existence of a single domain magnetized in the plane of the film. Thicker films possess hysteresis loops that are more rounded and less sensitive to small cross fields. Presumably here the domain structure in zero applied field has the nature of that discussed by Kittel, in which domains are magnetized perpendicular to the plane of the film. On cooling a film of intermediate thickness, its hysteresis loop shifts from a sharp rectangular loop to a rounded loop. This indicates transition from a single domain parallel to the film to a domain system containing domains magnetized at right angles to the film, in zero field. Cooling the film increases the uniaxial anisotropy by virtue of increased tension due to differential expansion.

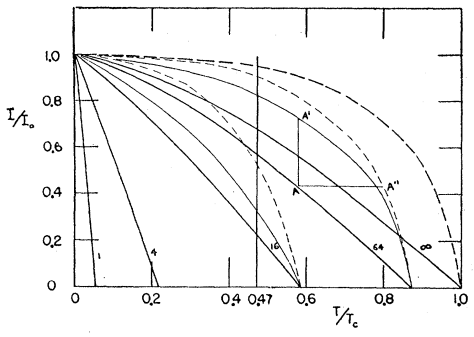

FIG. 4. Graph of intensity of magnetization *vs* temperature. The heavy dotted curve is the Weiss curve. The heavy solid curves are the theoretical results of Klein and Smith, setting $T_B = T_C$. The light solid curves result by adjusting magnetization at constant temperature. The light dotted curves are the result of adjusting the temperature at constant magnetization.

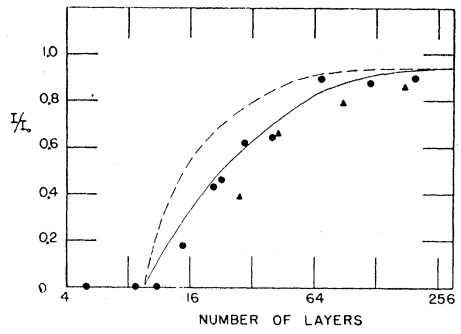

FIG. 5. Graph of magnetization *vs* thickness. The curves are the modified results of Klein and Smith. The solid curve corresponds to adjusting the magnetization at constant temperature. The dotted curve results from adjusting the temperature at constant magnetization. The points in triangles are the results of Drigo on electroplated films.

It is fortunate that thin films have rectangular hysteresis loops, as this simplifies the measurement of saturation magnetization. In case of the data to be reported, very thick films presented a problem because of lack of saturation at 400 oersteds.

Before presentation of the experimental data, the necessary modification of the theory of Klein and Smith[2] should be presented. Their theoretical results are reported in Fig. 4 as a plot of I/I_0 *versus* T/T_B, where T_B is the characteristic Bloch temperature. A family of curves for various values of the number of layers is shown. Since the Bloch $T^{\frac{3}{2}}$ law is not followed experimentally for bulk specimens, a modification of either the theoretical or experimental results must be found so that both can be compared on a common ground. One method would be to plot the experimental results as a function of T/T_B using the experimentally determined value of 2210°K for T_B.[11,12] However, it was felt that a more advantageous method would be to modify the theory to fit the Weiss curve, which agrees well with experiment for bulk specimens. Results can then be quoted in terms of T/T_C where T_C is the Curie temperature. One can set $T_B = T_C$ and plot both the theoretical curve and the Weiss curve on the same temperature scale T/T_C. Two simple, but arbitrary, methods for adjusting the theoretical curves to the Weiss curve for the case of an infinite number of layers will be illustrated. The first method, that used by Drigo,[3] is to adjust the magnetization of the infinite thickness curve at constant temperature to fit the Weiss curve. The magnetization of all the curves for smaller thickness was adjusted by the ratio of the Weiss magnetization to the Bloch curve at a given temperature. The second method is to adjust the temperature at constant

[9] R. W. Hoffman and E. C. Crittenden, Jr., Phys. Rev. **78**, 349 (1950).
[10] C. Kittel, Phys. Rev. **70**, 965 (1946).
[11] P. Weiss and R. Forrer, Ann. phys. **12**, 279 (1929).
[12] P. Weiss, Compt. rend. **198**, 1893 (1934).

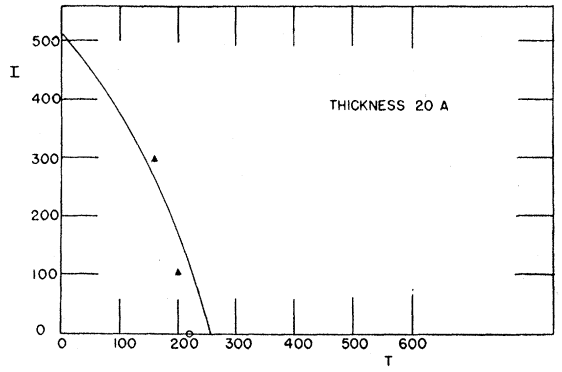

FIG. 6. Graph of intensity of magnetization in gauss *vs* temperature in degrees Kelvin for a 20A nickel film. The solid curve is the theoretical result of Klein and Smith modified by adjusting the magnetization.

magnetization. In this case each curve is adjusted by the ratio of the temperature of the Weiss curve to the Bloch curve at a given magnetization. The two methods of adjustment yield somewhat different results for the adjusted I/I_0 *versus* T/T_C curves. Figure 4 shows the Klein and Smith theoretical curves, and the two sets of adjusted curves, all plotted against T/T_C. The solid heavy curves are the theoretical curves obtained by Klein and Smith for different numbers of layers. The number with each family of curves corresponds to the number of atomic layers in a simple cubic lattice for which this theory was developed. The heavy dotted curve is the Weiss curve. The light solid line is the result of adjusting the magnetization at constant temperature. The light dotted lines are the result of adjusting the temperature at constant magnetization.

To illustrate the two methods of adjusting the theoretical curves, point A in Fig. 4 is transformed in both ways. Point A moves to A' if the magnetization is adjusted at a given value of the temperature. Point A is translated to A'' if the temperature is adjusted at a given magnetization.

Measurements of the saturation magnetization have been made with two models of the magnetic instrument

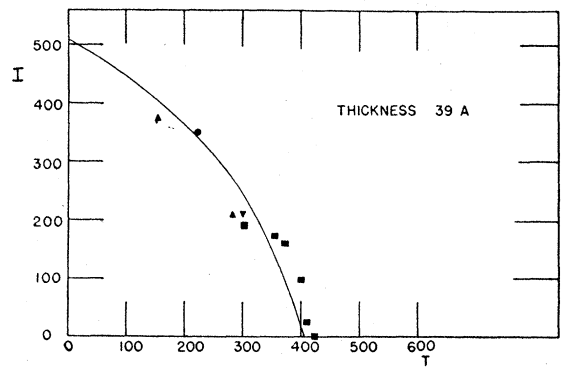

FIG. 7. Graph of intensity of magnetization in gauss *vs* temperature in degrees Kelvin for a 39A film.

mentioned earlier. One model was specifically designed for precision measurements at room temperature, the other was designed to provide measurements over the temperature range -190°C to $+200$°C. The results obtained with the two instruments will be described separately as the latter is subject to some additional uncertainties.

Measurements made at 25°C are plotted in Fig. 5. The theoretical curves are taken from Fig. 4 for $T/T_C=0.47$, the ratio for nickel at room temperature. The number of atomic layers has been obtained by dividing the thickness by 2A, the approximate distance between the 111 planes in the face-centered cubic nickel crystal. The points seem to fall rather close to the solid line representing the theoretical results of Klein and Smith after adjusting the magnetization by the Weiss curve at constant temperature. The thickness at which magnetization ceases at this temperature is in surprising agreement with the theoretical prediction.

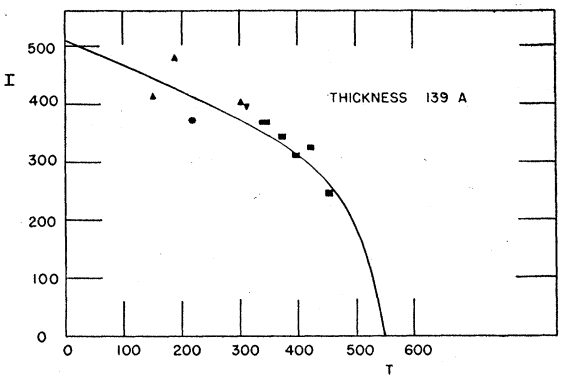

FIG. 8. Graph of intensity of magnetization in gauss *vs* temperature in degrees Kelvin for a 139A film.

The points for small thickness have less uncertainty than for the higher thicknesses because of difficulty at high thickness with saturating the specimen. The results of Drigo[3] plotted on the same figure seem to fall low. This might be due to surface roughness or oxidation of the electroplated films.

Measurements made as a function of temperature are shown in Figs. 6, 7, and 8. Figure 6 represents the specimen plotted at 10 atomic layers in Fig. 5. This specimen is not ferromagnetic at room temperature but becomes so at lower temperature. Figure 7 represents the specimen plotted at 19.5 atomic layers in Fig. 5. This specimen is weakly ferromagnetic at room temperature, and it has been possible to follow it to its Curie temperature. Figure 8 is a much thicker specimen, 69.5 atomic layers, for which the Curie temperature is nearly that of bulk nickel, but the curve still shows a definite flattening compared to the Weiss curve for bulk nickel.

A new instrument is under construction with which it

is hoped that curves such as Figs. 6–8 can be obtained with much better precision.

The general agreement between the observations and the modified theory of Klein and Smith is quite surprising. This may be largely fortuitous, as the modifications based on the Weiss curve are quite arbitrary. In addition, the theory was developed for the case of a simple cubic crystal whereas nickel is face-centered cubic. This has required the rather arbitrary guess that the distance between the 111 planes in the face-centered cubic crystal should be substituted for the distance between 100 planes in the simple cubic crystal. Nevertheless, the general features of the behavior appear to be well described by the theory of Klein and Smith.

It is hoped that the availability of experimental observations in this field will stimulate further theoretical work, particularly in the extension of other models of ferromagnetic behavior into this range.

The authors wish to thank Mr. Edwin H. Layer and Mr. John D. Groselle of this laboratory for their contributions to the experimental data reported. The work has been assisted by a fellowship provided by the Standard Oil Company of Ohio which was held by one of the authors (RWH).

DISCUSSION

T. L. GILBERT, *Armour Research Foundation, Chicago, Illinois:* It is commonly accepted that the Bloch spin wave method, which is based on the Heitler-London-Heisenberg model of a ferromagnet, predicts that two-dimensional arrays of atoms are always nonferromagnetic. This prediction is inferred from the fact that an integral which appears in the constant A in the theoretical magnetization-temperature curve, $M(T)/M(O)=1-AT^{3/2}$, is divergent.[1]

This inference is unjustified, for the divergence may be the result of entirely extraneous reasons. It is in disagreement with predictions based on the Ising model of a ferromagnet. This disagreement is, by itself, not too significant because the Ising model is, admittedly, a poor one. However, it has been shown by Ekstein[2] that, if one refines the spin-wave method by taking into account the interaction between reversed spins, using a perturbation approach, the integral appearing in the constant A may converge to a finite value for certain two-dimensional arrays. One infers from this that two-dimensional arrays can be ferromagnetic if the Heitler-London-Heisenberg model is valid.

Recent developments, as reported at this conference, indicate that the Heitler-London-Heisenberg model is inadequate, and so the matter is not fully settled; but this result does show that the present theory of thin films, in so far as it is based on the spin-wave method as used by Bloch, is open to serious question.

C. J. GORTER, *Leiden University, The Netherlands:* At the Grenoble Conference, two years ago, I pointed out that according to Nernst's law the spontaneous magnetization should have a horizontal tangent with respect to T at $T=0$. I was not able then to extract a satisfactory explanation from Professor Stoner and Professor Néel, who presented curves in disagreement with this requirement.

I am now getting really worried about Nernst's law, since the theoretical curves shown by Dr. Crittenden also seem to violate it.

R. W. HOFFMAN, *Case Institute of Technology, Cleveland, Ohio:* (in answer to questions) No line broadening determinations were made with x-rays. However, electron diffraction line width measurements have been made by E. K. Halteman at this laboratory. Since the stress broadening and the broadening caused by particle size depend in different ways on the angle of reflection, the two parts may be separated experimentally.

C. GUILLAUD, *Centre National de la Recherche Scientifique, Bellevue, France:* In very thin films it is possible to obtain nonferromagnetic hexagonal nickel, which can be transformed to ferromagnetic cubic nickel by annealing.[1]

[1] Sommerfeld and Bethe, *Handbuch der Physik* (Julius Springer, Berlin, 1926), Vol. 24/2.
[2] H. Ekstein, Phys. Rev. **80**, 122 (1950).

[1] A. Colombani, Ann. phys. **19**, 272–326 (1944).