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Magnetic Analysis of Nickel Films Deposited by Evaporation*

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The magnetic properties of nickel films deposited from vapor on surfaces at several temperatures and, in some cases, annealed to various degrees have been studied at room temperature. Films deposited at room temperature are magnetically hard, having low initial susceptibility (χ_0). For films deposited on a metal with a higher coefficient of linear expansion than nickel, raising the temperature of deposition or annealing at higher temperatures increases χ_0. For films on a metal with a lower coefficient of linear expansion than nickel χ_0 first increases with deposition or annealing temperature but decreases upon high temperature annealing. The results are explained on Becker's theory by assuming that the films are deposited under strain, these deposition strains becoming less at higher temperatures.

SORENSON,[1] Edwards[2] and Miller[3] measured the magnetic properties of thin films of nickel, deposited by evaporation on aluminum, finding the temperature of deposit important in fixing the course of magnetization. Howey[4] later evaporated films onto various backings, under better vacuum conditions, at deposition temperatures from 125°C to 320°C. Differences in films on Al, Cu, Pt and Mo, all measured at room temperature, were explained as due to differential contraction of film and backing in cooling after deposit. All these investigators found their films magnetically hard; the initial susceptibilities (χ_0) were small. Nickel films deposited by electrolysis,[5] or by sputtering,[6] are also hard to magnetize, but here interpretation is more difficult because of the greater probability of gaseous inclusions during deposit.

The effect of strain upon magnetization has been discussed by Becker,[7] who proposes that, in the absence of an external magnetic field, the stability of the direction of I (intensity of magnetization) in each domain is determined by the stress to which that domain is subject. (This neglects the effect of crystal structure which is found to be small in comparison with that of supportable stresses.) Experiments by Becker and Kersten,[8] and by Kersten[9] on nickel variously strained agree well with the theory. Their curves for nickel wires under tension are very similar to the usual magnetization curves for nickel films.

The purpose of the present investigation was to extend temperatures of deposit down to room temperature and to study the effects of annealing. The results have been examined in the light of Becker's theory to ascertain the internal state of the films at various stages. A similar study of electrolytic films has recently been reported by Elenbaas.[5]

THE STILL

The still, in which the nickel films were formed, had to meet three requirements. First, rapid evaporation must be possible so that relatively thick films could be built up in reasonable times. Second, means must be furnished for heating or cooling the surface on which deposition occurred, and for measuring the temperature of this surface. Third, vacuum conditions must be good enough to minimize any effects of residual gases. The still, as constructed to meet these requirements, is

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[1] A. J. Sorenson, Phys. Rev. **24**, 658 (1924).

[2] R. L. Edwards, Phys. Rev. **29**, 321 (1927).

[3] K. J. Miller, Phys. Rev. **32**, 689 (1929).

[4] J. H. Howey, Phys. Rev. **34**, 1440 (1929).

[5] W. Elenbaas, Zeits. f. Physik **76**, 829 (1932).

[6] L. R. Ingersoll and S. S. deVinney, Phys. Rev. **26**, 86 (1925) reported films sputtered in hydrogen to be non-magnetic.

[7] R. Becker, Zeits. f. Physik **62**, 253 (1930).

[8] R. Becker and M. Kersten, Zeits. f. Physik **64**, 660 (1930).

[9] M. Kersten, Zeits. f. Physik **71**, 553 (1931).

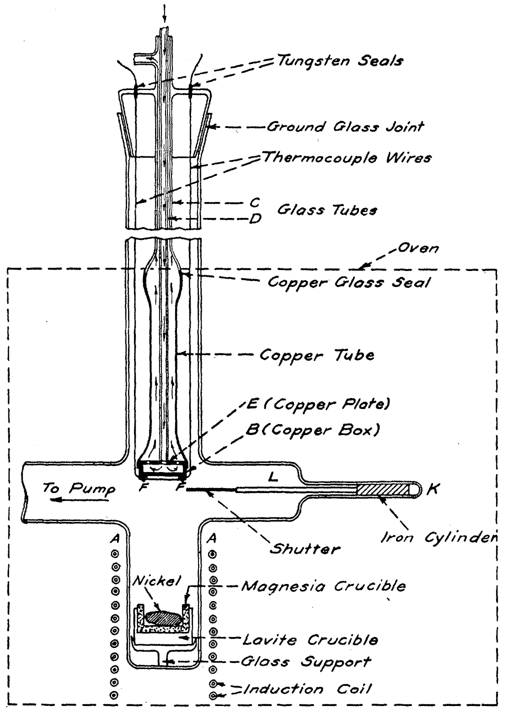

FIG. 1. Design of tube for deposition of nickel films.

shown in cross section in Fig. 1. The vertical tube, of Pyrex, was 5 cm in diameter. The metal disk upon which a film was to be deposited was clamped by small screws between the nickel ring *F* and the water-cooled copper box *B*. Copper parts were silver-soldered together to permit baking out before the water was circulated. The shutter could be moved by a solenoid slid over the side tube *K* so as to protect the prepared surface from nickel vaporized in preliminary operations. A Gaede two stage steel mercury vapor pump backed by a Cenco Hyvac oil pump and protected by a large bore liquid air trap was used and pressures were measured by an ionization manometer. The tube could be baked out or operated at higher than ordinary room temperature by surrounding it with an oven placed as indicated. With a 3 kva high frequency generator the nickel could be melted in from four to five minutes under the usual good vacuum conditions, pressures ranging, except as noted below, between 10^{-4} and 10^{-5} mm Hg. A chromel-alumel thermocouple gave the temperature of *B*.

The crucibles were made of pure MgO, which has been shown[10] to introduce only very slight impurities into a nickel melt. The nickel was prepared electrolytically by the method of Fink and Rohrman[11] and melted under hydrogen into a pellet of the desired shape in a molybdenum-wound furnace.

The film supports were thin disks of Cu, Mo, glass, and mica, 2.54 cm in diameter. Each was initially cleaned with benzene, alcohol and ether, dried in a desiccator and weighed. It was then mounted in the still and the ground glass joint sealed with low vapor pressure Boltwax. To ensure low pressure, surface cleanliness and minimum gas evolution during deposit the following procedure was followed. With shutter closed the nickel was melted and kept molten until the pressure fell below 10^{-4} mm. The tube was then baked at 500°C for from 4 to 10 hours, during which time the nickel was repeatedly frozen and remelted until melting caused no rise in pressure. The still was then allowed to cool to the desired temperature, water circulated if this was room temperature, the shutter drawn aside and a final melting for a controlled time gave the desired deposit. When the melt had cooled the film support was removed and weighed to find its thickness. It was assumed that the film density was that of pure bulk nickel.

MAGNETIC MEASUREMENTS

The torsion magnetometer used for magnetization curves and hysteresis loops has been described elsewhere.[12] Some of the films, initially magnetized, had to be demagnetized before the magnetization curves could be found. Complete loops were taken and agreement between values of *I* at loop tips was taken as proof of initial demagnetization. Only magnetization curves and the upper parts of the descending branches of hysteresis loops are shown in the figures.

RESULTS

Limiting magnetization curves and (partial) loops for films deposited on metals at room

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[10] W. H. Swanger and F. R. Caldwell, Bur. Standards J. Research **6**, 1131 (1931).

[11] C. J. Fink and F. A. Rohrman, Trans. Am. Electrochem. Soc. **57**, 325 (1930); **58**, 403 (1930).

[12] H. N. Otis, Rev. Sci. Inst. **4**, December (1933).

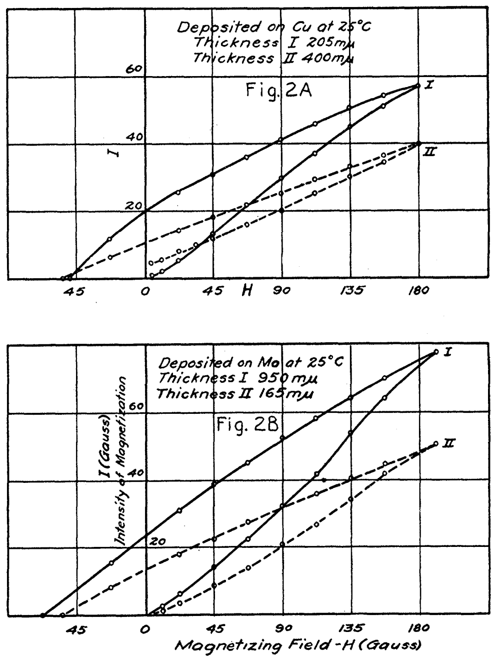

FIG. 2. Magnetization curves for nickel films deposited at room temperature.

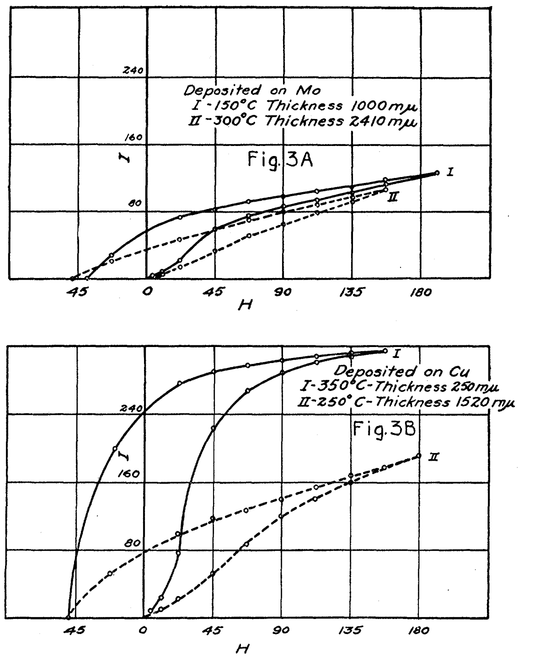

FIG. 3. Magnetization curves for nickel films deposited on molybdenum and copper at from 150° to 350°.

temperature are shown in Figs. 2A and 2B. All results fell between curves I and II.

These films were all relatively thin because peeling always occurred as soon as the thickness exceeded 800 to 1000 mμ. Direct observation showed that peeling over the entire surface occurred suddenly. This peeling might be due to (1) evolution of gases from the support, (2) entrapping of residual gases by the vapor stream, (3) temperature changes of the support. To test (1) and (2) a Mo disk was outgassed in vacuum at 1500°C for 15 hours, then quickly mounted in the still and extreme precautions taken to keep the pressure during deposit below 10^{-5} mm. Peeling occurred as usual. To test (3) a typical run was carried out with the thermojunction soldered to the face of a film support and thus exposed to the stream of nickel vapor. Its temperature rose less than 10°C. In a further test of (3) a film was deposited directly on box B, but still peeled at about the critical thickness. Furthermore, a film deposited on a nickel disk peeled as usual. To test (2) by itself the rate of deposit was reduced to one-tenth its usual value —this required only a slight change in the temperature of the molten nickel—without changing the thickness at which peeling occurred. It must be concluded that peeling results from some intrinsic property of nickel condensed at room temperature.

Figs. 3A, B are typical of films deposited on Mo and Cu at from 150° to 350°C (magnetic measurements at 25°C). Peeling never occurred when the temperature of deposit exceeded 100°C.

Figs. 4A, B, C, D show the effects of annealing, in vacuum for 6 hours at the temperatures indicated, films deposited on Mo and Cu at low and at high temperatures.

Figs. 5A, B show typical magnetic behavior for films on glass and mica. Such films never peeled, and it seems likely that this immunity is due to the higher temperature attained by films on these poor thermal conductors.

Fig. 6 presents magnetization curves for magnetically soft and magnetically hard films up to $H = 1300$. The latter is still far from saturation to judge by its terminal slope.

DISCUSSION

Suppose the stresses in any magnetic domain are resolved into a hydrostatic stress of either

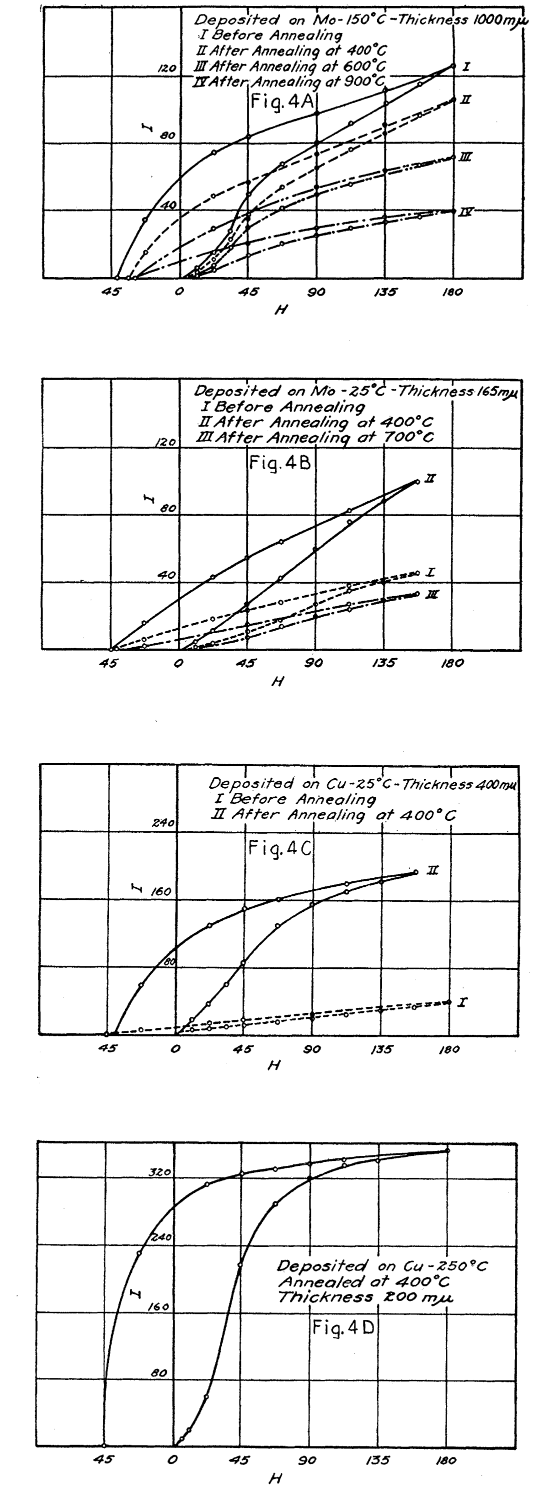

FIG. 4. Magnetization curves which show the effects of annealing.

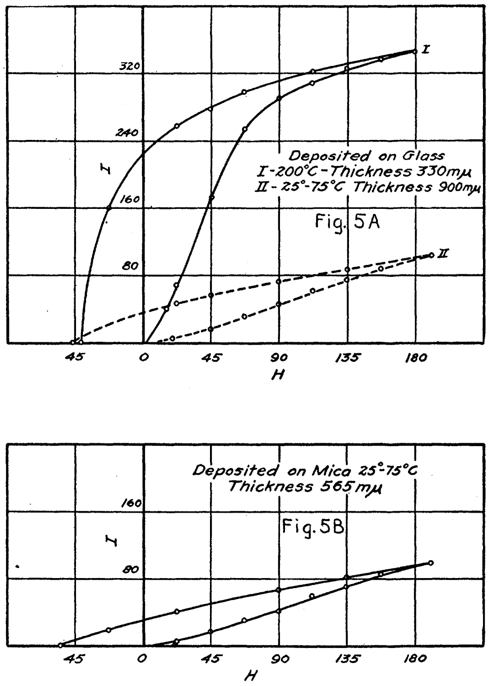

FIG. 5. Magnetization curves for nickel films deposited on glass and mica.

sign and a tension or compression. Becker's theory now states that in nickel, wherein the longitudinal magnetostriction is negative for all crystallographic directions, the magnetization I is parallel to the directed stress if the stress is compressional, at right angles thereto if the stress is tensile. The initial susceptibility for a specimen is then[9]

$$\chi_0=(I_\infty^2/3\sigma)\overline{\lambda^{-1}}\cdot\overline{\sin^2\epsilon} \qquad (1)$$

where $I_\infty\equiv$ saturation intensity of magnetization, $\sigma\equiv$ directed stress, $\lambda\equiv$ magnetostrictive strain, $\epsilon\equiv$ angle between the strain-determined direction of I in a domain and the direction of the applied H. Bars indicate mean values of the quantities under them. Substituting known values for I_∞ and $\overline{\lambda^{-1}}$ and expressing σ in kg·mm^{-2} we get

$$\sigma=(23.9/\chi_0)\,\overline{\sin^2\epsilon}. \qquad (2)$$

In a film with free upper surface any tension or compression must have its axis in the plane of the film. It will be shown that these stresses are probably tensile, so we take $\overline{\sin^2\epsilon}=1$ and (2) becomes

$$\sigma=23.9/\chi_0. \qquad (3)$$

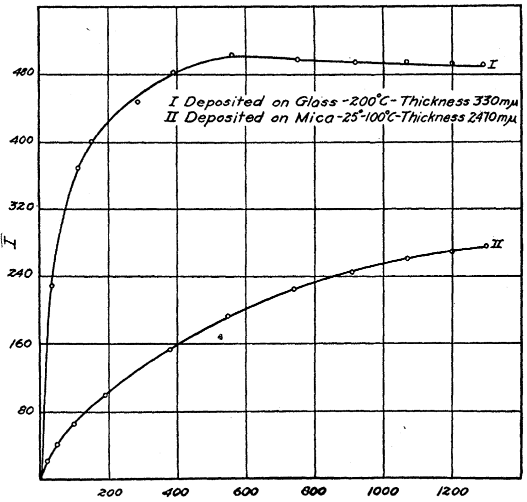

FIG. 6. Magnetization curves for magnetically soft and magnetically hard films.

Values of σ thus computed for the films of Figs. 2, 3, 4 are given in column 6 of Tables I, II.

We first note the similarity (Fig. 2) of films deposited on cold Mo and on cold Cu. The striking differences observed by Howey[4] have disappeared with the suppression of differential contraction of film and support.

TABLE I. *Column 3 gives the kind of metallic support used, column 4 the temperature of deposit, column 5 the initial susceptibility, and column 6 the stress, in* $kg \cdot mm^{-2}$ *computed from (3).*

Film No.	Fig.	Support	T_D	χ_0	σ
1	2A I	Cu	25°C	0.18	133
2	2A II	Cu	25	0.16	149
3	2B I	Mo	25	0.21	114
4	2B II	Mo	25	0.14	171
5	3B II	Cu	250	0.75	32
6	3B I	Cu	350	1.60	15
7	3A I	Mo	150	0.50	48
8	3A II	Mo	300	0.40	60

The magnetic analysis supports the opinion, already suggested by peeling, that in cold deposited films stresses exceed the breaking strength (about 30 $kg \cdot mm^{-2}$) of bulk nickel. That this stress is tensile was shown by the curvature of very thin mica on which a film was deposited. When peeling occurs the flakes are convex toward the support, which may mean either that the nickel first deposited is under least tension or that the flake suffers further cold work as it lets go. If the former is the correct explanation it might arise from slow annealing at room temperature of the highly overstrained metal.

TABLE II. *Column 3 gives the kind of metallic support used, column 4 the temperature of deposit, column 5 the annealing temperature, column 6 the initial susceptibility, column 7 the stress in* $kg \cdot mm^{-2}$ *computed from (3).*

Film No.	Fig.	Support	T_D	T_A	χ_0	σ
7	4A I	Mo	150°C		0.50	48
	4A II			400°C	0.36	66
	4A III			600	0.20	119
	4A IV			900	0.13	184
9	4B I	Mo	25		0.15	159
	4B II			400	0.36	66
	4B III			700	0.14	170
2	4C I	Cu	25		0.16	149
	4C II			400	1.60	15
10	4D	Cu	250	400	1.50	16

The Becker stresses in films deposited at higher temperatures should show the effect of any differential thermal contraction of film and support. Nickel films on copper would be subjected to edgewise compression, films on molybdenum would be stretched.[13] If the tensile stresses due to deposition are unaltered by rise in temperature of deposit films on copper should become magnetically softer, films on molybdenum magnetically harder as the temperature of deposit increases. These changes do occur after the temperature of deposit exceeds about 150°C, but up to that point, at least, χ_0 increases for films on Mo (cf. film 7 at 150°C with films 3, 4 at 25°C) though not as rapidly as for films on Cu. Furthermore the increase for films on Cu (cf. film 5 at 250°C with film 1 at 25°C) is too rapid to be due only to the compression of the hot deposited films by differential contraction. It is apparent that deposition stresses themselves vary with the temperature of deposit and that, if tensile, they decrease as this temperature rises.

Comparison of films 5 and 6 shows that deposition stresses are not completely absent at 250°C,

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[13] A rough calculation, neglecting shears, assuming no flow taking place during cooling, and taking the elastic constants of the films to be those for bulk nickel, gives a compressional stress of 12 $kg \cdot mm^{-2}$ per 100°C change in temperature for nickel on copper, and a tensile stress of 27 $kg \cdot mm^{-2}$ per 100°C change in temperature for nickel on molybdenum.

for if they were the value of σ would be higher for film 6 than for film 5. (Since both would be compressive we should have $\overline{\sin^2 \epsilon} = 1/2$ and $\sigma = 12/\chi_0$, but this would not alter *relative* values.) We must therefore conclude that in film 5, at least, the stress is still tensile, and *a fortiori* it must be tensile in film 7. The difference between σ for these two films is then seen to be smaller than that calculated on our simple assumption of homogeneous stresses, though the values fall in the expected order.

Howey,[4] whose curves for nickel deposited at elevated temperatures agree well enough with Figs. 3A, B, found that for deposit at 125°C a film on Mo was magnetically harder than a film on Cu. Values of σ calculated from his χ_0 values are greater than can be accounted for by differential contraction so that both films must have been in tension when at room temperature and deposit strains must also have been tensile.

The results of annealing (Table II) are, for anneals at 400°C, similar to the results of deposit at 300° or 350°C (cf. films 9 and 8, 2 and 6). This is taken to mean that deposit strains are relieved at these temperatures even during the process of condensation. The apparent anomaly presented by films on Mo which have higher χ_0 if deposited at 150°C than if deposited at room temperature or at 300°C, or if annealed at 400°C and upward, is due to the fact that deposit stresses decrease more rapidly than the thermal stretching increases in the lower range of temperatures, and do not decrease at all in the upper range. As before, however, the simple assumptions regarding thermal contraction are seen to be quantitatively inadequate on comparing σ for films 2 and 9 which should, on this basis, differ more than they do.

The peeling of films deposited on cold metal is now naturally attributed to stresses, mainly tensile, arising during deposition. To explain peeling at a critical thickness it must also be supposed that the breaking strength is greater for thin films than for bulk nickel and greater the thinner the film, so that the stretched thin film becomes unstable when its thickness exceeds about 800 mμ. Cracks, traces of gas, or temperature gradients can then initiate break-up.

Tension in electrodeposits has frequently been observed,[14] and it has often been assumed that such stresses were due to inclusion of gas within the metal lattice. The present work suggests that the mere formation of a metallic lattice, atom by atom, at a sufficiently low temperature, creates intense stresses.

For films on glass and mica χ_0 increased as the deposition temperature was raised. This is consistent with the low coefficient of expansion for these supports. The absence of peeling is attributed partly to the higher surface temperatures resulting from poor thermal conductivity, but since this temperature probably did not exceed 100°C there must be some other difference between these films and those on metals. The superior smoothness of glass and mica probably increases the tensile strength of the films since films on metals often started to peel at fine scratches in the supports.

The flattening of magnetization curves well below the saturation value for bulk nickel ($I = 480$) calls for explanation. Four possible sources of error in I have been considered. (1) The film weight may be incorrect, especially when of the order of 10^{-4} g. (2) Magnesia may evaporate and condense with the nickel. This seems unlikely at melt temperatures below 1800°C, since the vapor pressure of MgO is said to be negligible up to this point. (3) The nickel may be partly oxidized. The low gas pressure makes this improbable. (4) The nickel may alloy with the support. This should cause larger defects in I for thinner films, which was not observed. A chemical analysis of a thick film (4500 mμ), deposited on copper at 400°C, which gave a magnetization curve similar to Fig. 4D, gave a nickel content agreeing within 0.5 percent with the weight of the film. This virtually disposes of (1), (2) and (3) above. To get additional information regarding (4) a thin film (200 mμ) was deposited on copper at 350°C and annealed in the still for 6 hours at 400°C. The I-values were not lower than usual—the film was chosen for Fig. 4D as completely typical—where-

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[14] e.g., G. Gore, Phil. Trans. **148**, 185 (1858); **152**, 323 (1858). E. J. Mills, Proc. Roy. Soc. **A26**, 504 (1877). G. G. Stoney, Proc. Roy. Soc. **A82**, 172 (1907). R. M. Bozorth, Phys. Rev. **26**, 390 (1925).

as alloying should have been especially effective here if ever. It is suggested that the defects in I point to the existence of portions of the film subject to such great stresses or so imperfectly crystallized as to be nonmagnetizable even in relatively intense magnetic fields.

Magnetically soft films show magnetic saturation at about the expected value of I, as is seen in Fig. 6 which contrasts the two sorts of film up to $H=1300$.

No regular variation of magnetic properties with thickness of film was disclosed in these experiments. Results at the lower deposit temperatures, which were the most consistent, show that any effect of thickness must be small.

More extended application of Becker's theory to the data here collected does not seem justified in view of the uncertainty of I and the numerous evidences of local variations in the harder films.

It is a pleasure to acknowledge indebtedness to Professor L. W. McKeehan, who suggested the investigation, and whose advice and encouragement have been invaluable. The author wishes also to thank Dr. J. H. Howey for many helpful discussions, and Mr. L. H. Ott for collaborating in preparing the nickel.