

Saturation Magnetization of Nickel Films of Thickness Less Than 100 Å

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Nickel films varying in thickness from 200 to 3 Å were prepared by evaporation on glass substrates in a vacuum sufficiently high to prevent gas adsorption on the film during preparation and measurement. Their magnetization was measured as a function of field up to 10 000 oe using a vacuum torsion magnetometer. The saturation magnetization of these films was determined as a function of their thickness at 300°K and 77°K. No decrease in saturation magnetization from that of bulk nickel has been observed for films of thickness down to 20 Å, at room temperature. The Curie temperature of a 27 Å film was found to coincide with that of bulk nickel. The magnetic behavior of films in the thickness range below 20 Å suggests superparamagnetism rather than a decrease in the saturation magnetization. Measurements of the magnetostrictive anisotropy constant indicate that the films as originally prepared are in a state of high tensile strain, which can be relieved by annealing. The thin film nature of some specimens was ascertained by examination in the electron microscope.

INTRODUCTION

SEVERAL investigators¹⁻⁴ have studied the magnetic behavior of small, ferromagnetic particles down to 15 Å radius. In these studies, the saturation magnetization of superparamagnetic cobalt and iron particles was measured either directly at different temperatures, or its variation with temperature was inferred from the temperature dependence of the magnetocrystalline anisotropy. In no case has there been any evidence for a saturation magnetization of cobalt or iron particles different from that of the bulk material at any temperature down to a 15 Å radius, within an accuracy of about 10%.

In sharp contrast to this striking independence of the saturation magnetization with particle size, even at room temperature, are the results of various workers on thin films.⁵⁻¹² According to this work, the saturation magnetization of films thinner than about 100 Å decreases much more rapidly with increasing temperature than that of the bulk material. Thus, a nickel film of thickness in the neighborhood of 20 Å has no ferromagnetism at room temperature. The saturation magnetization of a 40 Å film at 300°K is only about half that of the bulk value. Such a dependence of saturation magnetization on temperature and film thickness has been predicted by a theory of Klein and Smith,¹³ who used the Bloch spin-wave approach.

Seavey and Tannenwald¹⁴ found from microwave resonance absorption in permalloy films that magnetism drops sharply at 60 Å, and ferromagnetism disappears between 8 and 12 Å.

These results would imply that, if a 15 Å radius particle of a ferromagnetic material is incorporated into a 30 Å, continuous film of the same material, its saturation magnetization would drop from the bulk value to a small fraction of it in the process.

This investigation on thin films was undertaken in order to reconcile this difference in the magnetic behavior between fine, ferromagnetic particles on the one hand, and thin films of ferromagnetic materials in the thickness range less than 100 Å on the other.

TECHNIQUES USED

Since the magnetic fields required to saturate thin films are often quite high, a field strength of up to 10 000 oe was utilized. Also, in order to eliminate the uncertain effects on the magnetic properties of gas adsorption and oxidation during the preparation and measurement, which often necessitated sizable corrections in previous work, the films were prepared and kept in an ultra-high vacuum system at pressures of the order of 10^{-9} mm of Hg or less. This vacuum is sufficiently high to insure that, within the period of measurement, the film remained essentially free from adsorbed gases.

In addition, since all results depend most critically on an accurate knowledge of the thickness of the films, a method had to be found whose accuracy would not deteriorate as a function of thickness in the less than 100 Å range. Film thickness was measured in each case by x-ray emission spectrography (x-ray fluorescence analysis). In this measurement a polychromatic x-ray beam excites the K_{α} line of nickel ($\lambda=1.658$ Å), whose intensity is measured by scintillation counting. The intensity increases linearly with the thickness of the

¹ Bean, Livingston, and Rodell, *J. phys. radium* **20**, 298 (1959).

² C. P. Bean and I. S. Jacobs, *J. Appl. Phys.* **27**, 1448 (1956).

³ F. Luborsky, *Phys. Rev.* **109**, 40 (1958).

⁴ J. J. Becker, *Trans. Am. Inst. Mining Met. Engrs.* **209**, 59 (1957).

⁵ A. Drigo, *Nuovo cimento* **8**, 498 (1951).

⁶ E. C. Crittenden, Jr., and R. W. Hoffman, *Revs. Modern Phys.* **25**, 310 (1953).

⁷ L. Reimer, *Z. Naturforsch.* **12a**, 550 (1957).

⁸ W. Ruske, *Ann. Physik* **2**, 274 (1958).

⁹ H. J. Bauer, *Z. Physik* **153**, 484 (1959).

¹⁰ Colombani, Goureaux, and Huet, *J. phys. radium* **20**, 303 (1959).

¹¹ W. Hellenthal, *Z. Naturforsch.* **13a**, 566 (1958).

¹² W. Reincke, *Z. Physik* **137**, 169 (1954).

¹³ M. J. Klein and R. S. Smith, *Phys. Rev.* **81**, 378 (1951).

¹⁴ M. H. Seavey, Jr., and P. E. Tannenwald, *J. Appl. Phys.* **29**, 292 (1958).

film up to several thousand angstroms. A typical count rate is 80 counts/ $\mu\text{g}/\text{sec}$. The spectrometer was calibrated against known weights of solutions of nickel salts. The maximum error in the method is about 10% of the measured film thickness. The validity of the method has been demonstrated by Liebhfsky and Zemany,¹⁵ and Rhodin.¹⁶

The Magnetic Measurement

The films are prepared by evaporation from a 99.99% pure nickel filament obtained from the Sigmund Cohn Company on to 5 cm^2 glass microscope slides kept at room temperature. This substrate is suspended on a calibrated torsion wire, and, while still in vacuum, can be placed in a variable magnetic field between the pole pieces of an isthmus electromagnet. When the film is positioned at an angle θ° to the field direction, its energy, at saturation, is given by¹⁷

$$E = -M_s H \cos\theta + \frac{1}{2} N M_s^2 \sin^2(\theta^\circ - \theta) + K \sin^2(\theta^\circ - \theta), \quad (1)$$

where M_s denotes the saturation magnetization of the film, H is the external field, θ is the angle between the magnetization vector and the field direction, θ° is the angle between the film and the field direction, N is the demagnetizing factor for the film and is equal to 4π , and K is an anisotropy constant inserted to accommodate a possible easy or hard direction of magnetization perpendicular to the plane of the film.

The energy is a minimum with respect to θ when

$$\partial E / \partial \theta = 0 = M_s H \sin\theta - 2(2\pi M_s^2 + K) \times \sin(\theta^\circ - \theta) \cos(\theta^\circ - \theta). \quad (2)$$

If $\theta^\circ = 45^\circ$, solving for $\sin\theta$:

$$\sin\theta = \frac{-M_s H \pm [M_s^2 H^2 + 8(2\pi M_s^2 + K)^2]^{1/2}}{4(2\pi M_s^2 + K)}. \quad (3)$$

The torque exerted on the torsion wire by a film of unit volume in a field H is:

$$L = M \times H,$$

$$L = M_s H \sin\theta \text{ at saturation.}$$

In general,

$$L = M_s V H \sin\theta, \quad (4)$$

where V is the volume of the film. This equation can be readily solved for three different values of the field H :

A. At low fields. Here the H^2 term can be ignored, and a linear relation is obtained:

$$\frac{L}{H} = - \left[\frac{M_s^2 V}{4(2\pi M_s^2 + K)} \right] H + \frac{1}{2} \sqrt{2} M_s V. \quad (5)$$

¹⁵ H. A. Liebhfsky and P. D. Zemany, *Anal. Chem.* **28**, 455 (1956).

¹⁶ T. N. Rhodin, *Anal. Chem.* **27**, 1857 (1955).

¹⁷ This treatment is due to C. P. Bean and R. B. Fritz of this Laboratory.

Thus the intercept of a L/H versus H plot yields $(L/H)_0 = 0.707 M_s V$.

From the experimentally measured value of this intercept, the known area of the film A , the torque constant of the torsion wire α , and assuming the bulk value for M_s (485 emu at 300°K and 505 emu at 77°K), a "magnetic thickness" of the film can be calculated:

$$d_m = \frac{\alpha (L/H)_0}{0.707 M_s A}. \quad (6)$$

If $d_m = d_x$, the actual film thickness obtained from x-ray spectroscopy, then the saturation magnetization M_s of the film was indeed that for bulk nickel.

In general

$$\frac{M_s (\text{film})}{M_s (\text{bulk nickel})} = \frac{d_m}{d_x}.$$

B. At a field $H = (2\pi M_s^2 + K)/M_s$. The solution of the torque equation (4) then is:

$$L/H = 0.707 (L/H)_0. \quad (7)$$

This relation allows easy evaluation of the anisotropy constant K , by finding the field corresponding to the value of the ordinate $0.707 (L/H)_0$.

Figure 1 illustrates the use of these relationships in calculating d_m , M_s , and K from the experimental torque curve for a 91 Å film.

C. At high fields. First, $\sin\theta$ can be rewritten

$$\sin\theta = \frac{M_s H}{4(2\pi M_s^2 + K)} \pm \left[\frac{M_s^2 H^2}{16(2\pi M_s^2 + K)^2} + \frac{1}{2} \right]^{1/2}.$$

Letting

$$a = \frac{M_s H}{4(2\pi M_s^2 + K)},$$

then

$$\sin\theta = a \pm (a^2 + \frac{1}{2})^{1/2} = a \pm a(1 + 1/2a^2)^{1/2},$$

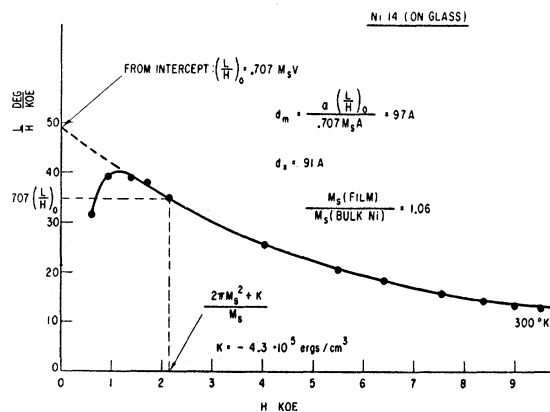


FIG. 1. L/H versus H for a 91 Å film, illustrating use of Eqs. (5), (6), (7).

which can be expanded if $\frac{1}{2}a^2 < 1$. This condition is met if $H > 9$ koe at $K=0$; or if $H > 6$ koe at $K = -5 \times 10^5$ ergs/cm³. Expanding and substituting

$$L = -(2\pi M_s^2 + K)V + 2(2\pi M_s^2 + K)^3 V / M_s^2 H^2 \quad (8)$$

for very high fields. When L is plotted against $1/H^2$, the intercept of the straight line yields the saturation torque,

$$L_\infty = (2\pi M_s^2 + K)V.$$

Actually, the torque at 10 koe is within 15% of L_∞ at $K=0$:

$$\frac{L_{10}}{L_\infty} = \frac{10\,000 \sin\theta}{2\pi M_s} = 0.85,$$

and if $K = -5 \times 10^5$ ergs/cm³, $L_{10}/L_\infty = 0.93$. Also, extrapolation of torque from 6 to 10 koe, although not always strictly valid in this range, nevertheless yields a value of L_∞ which is at most 7% too low. Also, at higher temperatures, where M_s is small, L_{10} is very close to the value of L_∞ .

The saturation magnetization at different temperatures is given by:

$$2\pi M_s^2(T) + K(T) \propto L_\infty(T).$$

If now K is small,

$$M_s(T) \propto [L_\infty(T)]^{1/2}. \quad (9)$$

The Vacuum Torsion Magnetometer

A sketch of the experimental apparatus is shown in Fig. 2. The substrate and film are oriented at 45° with respect to the field direction. A mirror and lamp-scale combination allows detection of any changes in that position. When a field is applied, the film tends to twist itself parallel with the field. This tendency is

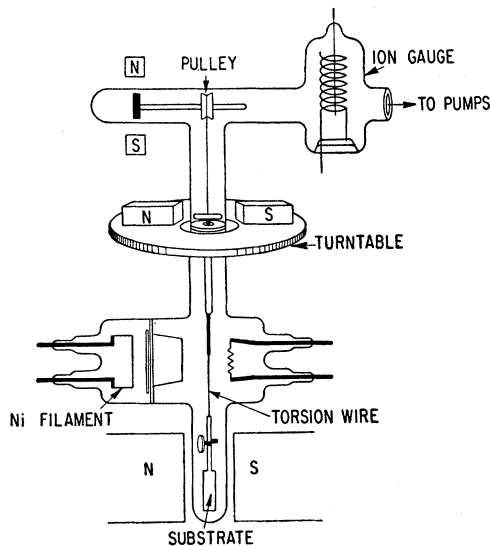


FIG. 2. Vacuum torsion magnetometer.

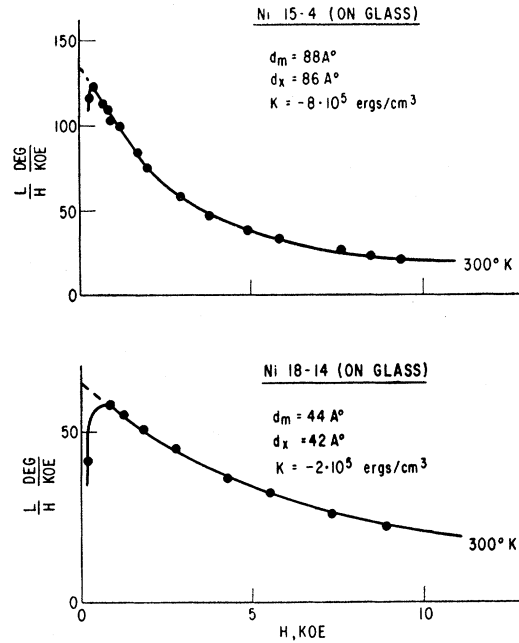


FIG. 3. L/H versus H curves for an 86 and 42 A film.

counteracted by applying an equal and opposite torque by twisting the torsion wire through the required number of degrees. This is accomplished by adjusting a calibrated turntable on which are positioned two magnets which transmit the angular motion by coupling with a third magnet in the vacuum, which in turn transmits it to the torsion wire. By observing this torque required to keep the film at 45° to the field direction as a function of increasing field, a L/H versus H curve can be constructed.

By means of a magnetically operated pulley, the substrate can be raised and positioned in front of the evaporation slit. Before depositing nickel on the substrate, a portion of the filament is evaporated to coat the glass walls with nickel and getter residual gases, until the pressure drops to 10^{-9} mm of Hg while the filament is still evaporating. A shutter in front of the slit is then opened for the required length of time to give a film of the desired thickness. The rate of film growth has been varied from 2 A/min to about 100 times that. The final thickness of the film is determined after all the magnetic measurements are completed and the system is broken open.

In order to obtain a vacuum of the order of 10^{-9} mm of Hg, the system has to be baked out at 450°C for 16 hours, and metal parts must be carefully outgassed.¹⁸

RESULTS

Some typical torque curves are shown in Figs. 1, 3, and 4. The temperature at the base of each curve denotes the temperature at which the film was kept

¹⁸ D. Alpert, J. Appl. Phys. 24, 860 (1953).

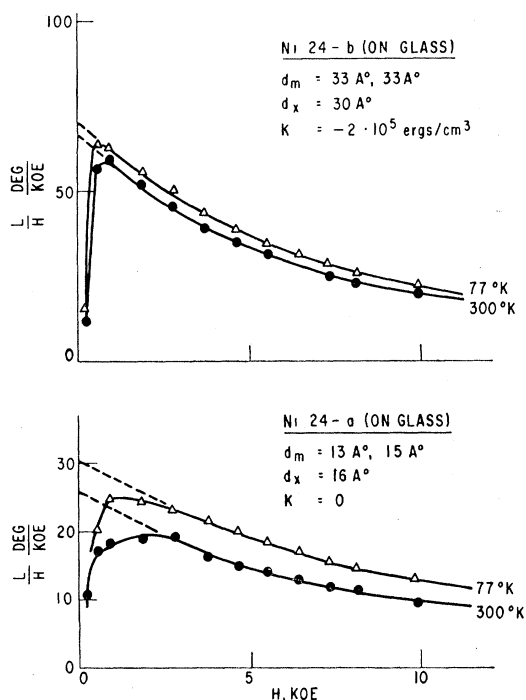


FIG. 4. L/H versus H curves for a 30 A film (upper graph) and a 16 A film (lower graph).

during the torque measurements. At very low fields, $M < M_s$, and the values of L/H are too low. The temperature dependence of the intercept $(L/H)_0 = 0.707M_sV$ is that expected from the temperature variation of the saturation magnetization of bulk nickel for films of 20 A thickness or thicker. For a 16 A film, lower graph, Fig. 4, the intercept becomes more temperature dependent. This is treated further in a later section.

Figure 5 shows the effect of annealing a film at 300°C for 15 min. Apparently only K is affected, but not M_sV . If K is associated with the magnetostrictive anisotropy constant, then its negative sign indicates that the film is under a tensile stress, which is relieved

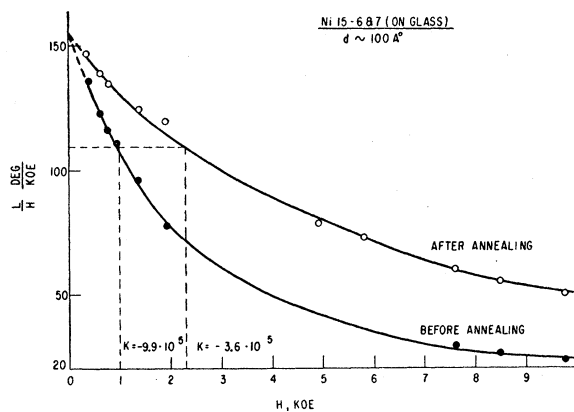


FIG. 5. The effect of annealing on the anisotropy constant K .

somewhat on annealing. Taking a typical observed value of K , one can calculate the corresponding stress in the film. Using the values $K = -5.5 \times 10^5 \text{ ergs/cm}^3$, $\lambda = \text{magnetostriction constant for nickel} = -34 \times 10^{-6}$, and the relation $K = (3/2)\sigma\lambda$, the stress $\sigma = 1.08 \times 10^{10} \text{ dynes/cm}^2$. By the way of comparison, a reasonable maximum stress which nickel can sustain might be about $2 \times 10^{10} \text{ dynes/cm}^2$.

Table I summarizes the results obtained on thin films between 171 and 15 A thick. The ratio $M_s(\text{film})/M_s(\text{bulk nickel})$ applies to 300°K. Within experimental error ($\sim 10\%$), this ratio can be seen to be unity for each film.

The relative saturation magnetization of a 27 A film was determined as a function of temperature between 77°K and 640°K, using formula (9). The results are plotted in Fig. 6. The full line gives the relative saturation magnetization for bulk nickel as a function of

TABLE I. Saturation magnetization and anisotropy constant of nickel films as a function of thickness.

d_x	Thickness of film, A	$M_s(\text{film})/$ $M_s(\text{bulk Ni})$		$K \text{ ergs/cm}^3$
		This work	C & H ^a	
171	195	1.14	1.0	$-(8 \pm 2) \times 10^5$
91	97	1.07	0.7	
86	88	1.02	0.7	
42	44	1.05	0.4	
34	37	1.09	0.3	
32	32	1.00	0.2	
30	33	1.10	0.2	
27	27	1.00	0.2	
25	23	0.93	0.1	
24 (On W)	27	1.12	0.1	
21	20	0.95	0.0	
21	22	1.05	0.0	
16	14.5	0.91	0.0	
15	13	0.87	0.0	

^a See reference 6.

temperature.¹⁹ Within experimental error, the Curie temperature of the film is identical to that of bulk nickel (615°K as compared to 631°K).

Several films have been prepared in the less than 10 A range as determined by x-ray emission. In the usual L/H versus H plot the torques measured at 300°K fall appreciably below those taken at 77°K. The upper curve in Fig. 7 is a typical example. Two interpretations are possible: A. One can extrapolate to an intercept $(L/H)_0$ in the usual manner and obtain a value for M_sV much lower at 300°K than at 77°K. This could imply an abnormally temperature dependent saturation magnetization in this thickness range. However, even for the very thinnest films measured, of apparent thickness of about 3 A, ferromagnetism did not vanish at 300°K. B. One is not dealing with a continuous film, but with an array of small, superparamagnetic particles. In that case, one can easily distinguish

¹⁹ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), first edition, Vol. 6, p. 377.

between two possibilities: (1) The magnetization vector is readily pulled out of the plane of the "film" even at low fields. The temperature dependence of the torque in such a case is given, at low fields, by the relation.²⁰

$$L = -\frac{2\pi n H^2 V_P^3 M_s^4}{15 k^2 T^2} \sin 2\theta^\circ, \quad (10)$$

where n is the number of particles, and V_P is an average particle volume for the superparamagnetic particles. Then, if the above conditions are fulfilled, the various values of the torque L , if plotted against H^2/T^2 , should superimpose for different temperatures, and the low field slope should be linear.

(2) The magnetization vector stays essentially in the plane of the "film" at low fields. Now the temperature dependence of the torque is given by the relation

$$L = -\frac{n V_P^2 M_s^2 H^2 \sin 2\theta^\circ}{4 k T}, \quad (11)$$

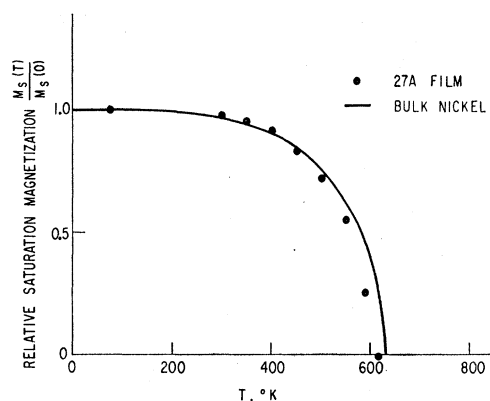


FIG. 6. The relative saturation magnetization of a 27 Å film as a function of temperature.

where n is the number of superparamagnetic particles. If this relationship applies, L should superimpose at different temperatures when plotted against H^2/T or $L^{\frac{1}{2}}$ versus $H/T^{\frac{1}{2}}$. This type of superposition is illustrated in the lower graph of Fig. 7, and has indeed been found for all films in the thickness range below 10 Å. An estimate of the average particle size from the low field slope of the $L^{\frac{1}{2}}$ versus $H/T^{\frac{1}{2}}$ curves yields 1000 (Å)^3 to $30\,000 \text{ (Å)}^3$ for the various films. The number of these particles is of the order of $10^{12}/\text{cm}^2$. This interpretation does not require that the saturation magnetization be abnormally temperature dependent or different from that of bulk nickel.

Several nickel films were prepared by evaporation on rocksalt at room temperature, so that the substrate could be easily dissolved to give the free film. These

²⁰ Equations (10) and (11) have been derived by J. D. Livingston of this Laboratory.

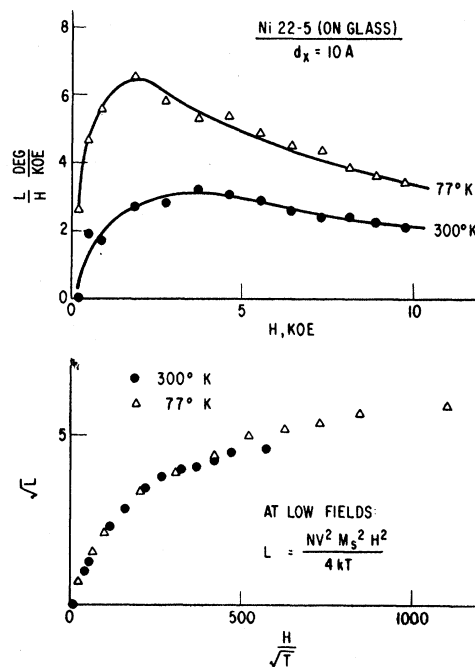


FIG. 7. A 10 Å film plotted L/H versus H (upper graph), and \sqrt{L} versus H/\sqrt{T} (lower graph).

films were then examined in the electron microscope by transmission.

A 30 Å film gives identically the same appearance in the microscope at 80 000 mag. as a 105 Å film. There is no evidence for aggregation into islands, and the films appear entirely continuous.

Examination of a 13 Å film at 40 000 mag. gave evidence which could be interpreted as island formation, less than 100 Å in diameter. However, these particles are so close together that an unambiguous interpretation is not possible.

CONCLUSIONS

A. The saturation magnetization of thin, evaporated nickel films in the 100 to 20 Å range is the same as that of bulk nickel, at a temperature of 300°K or lower.

B. Thin films less than 100 Å thick have a Curie temperature equal to that of bulk nickel, at least down to a thickness of 27 Å.

C. Although the data presented do not exclude the possibility of an abnormally low saturation magnetization at higher temperatures in films less than 20 Å thick, this interpretation is not unique. If these films consist of an array of superparamagnetic particles, the observed temperature dependence of the magnetization can be readily explained without postulating an abnormally low saturation magnetization at room temperature.

D. At least about 90% of the nickel in the various films was ferromagnetic. Electron diffraction work

indicated only face centered cubic nickel. Nonferromagnetic (hexagonal, amorphous) nickel has been reported in the literature.²¹⁻²³

E. A ferromagnetically dead surface layer, because

²¹ A. Colombani, *Mém. sci. phys. acad. sci. Paris* **58**, 32 (1954).

²² L. Reimer, *Physik. Verhandl.* **8**, 98 (1957).

²³ L. Reimer, *Z. Physik* **149**, 425 (1957).

of a lack of nearest neighbors, can be at most one half atom thick.

ACKNOWLEDGMENTS

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Electrical Resistivity of Yttrium Single Crystals*

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Two samples of yttrium cut from the same single crystal were used to determine the electrical resistivity parallel and perpendicular to the c -axis of the hexagonal close-packed metal. Measurements were made over the temperature range from 1.3 to 300°K. A large anisotropy was observed, with $\rho_{\perp}/\rho_{\parallel}=2.1$ at room temperature. Values for the polycrystalline resistivity over the temperature range indicated were computed from these data and were found to fit a Grüneisen law with $\theta=187.5^{\circ}\text{K}$. The computed polycrystalline values were also in good agreement with the measured resistivity of a polycrystalline sample.

PROCEDURE

IN order to obtain single crystals of yttrium for the electrical resistivity measurements reported here, a polycrystalline cylinder of the metal 2 cm in diameter and 3 cm long was machined from an arc-melted slug. It was then carefully polished and subsequently annealed in a vacuum at 1200°C for 24 hours. Nearly all of the cylinder comprised a single crystal after the anneal. The original metal was prepared by a method described by Carlson, Schmidt, and Spedding in a report summarizing work on yttrium at the Ames Laboratory.¹

Two samples were cut from this single crystal, one along the c -axis (yttrium is hexagonal close-packed), the other in the basal plane. The resistivities of these samples, plus that of a polycrystalline sample, were measured between 1.3 and 300°K. The single crystals were rods of rectangular cross section with dimensions about $1.8 \times 2.1 \times 16.3$ mm. The polycrystalline sample was a rod of circular cross section with a diameter $\frac{3}{16}$ of an inch and length of 2 inches. A four-probe system was used for the resistivity measurements with the potential knife edges 6.9 mm apart for the single crystals, and about one inch for the polycrystalline sample. The probable errors in measurement are estimated as 1.5% of the resistivity at room temperature, and 0.1 $\mu\text{ohm-cm}$ at 1.3°K.

* Contribution No. 786. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

¹ Banks, Carlson, Daane, Fassel, Fisher, Olson, Powell, and Spedding, Atomic Energy Commission Report IS-1, 1959 (unpublished).

RESULTS

The residual resistivities of the samples were found to be 1.5, 2.6, and 5.4 $\mu\text{ohm-cm}$ for the c -axis, basal plane and polycrystalline samples, respectively. With these residual resistivities subtracted, the results were as shown in Fig. 1. The lowest curve shows the resistivity with the current flowing along the c -axis, and the highest curve gives the basal plane resistivity. The anisotropy ratio ($\rho_{\perp}/\rho_{\parallel}=2.1$ at room temperature), is abnormally large for a metal.² A prediction was made

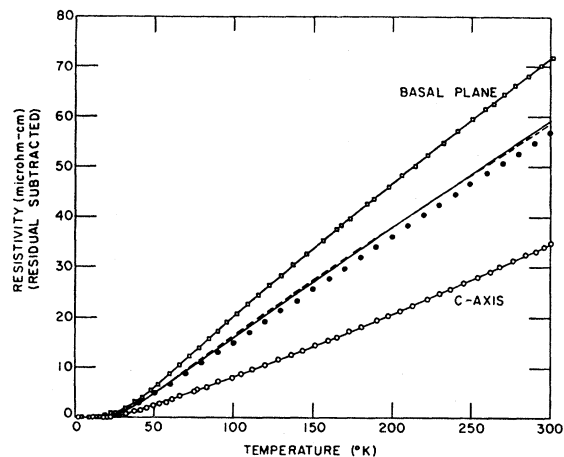


FIG. 1. Resistivity of yttrium. The highest curve shows the basal plane resistivity. The lowest curve gives the c -axis resistivity. The solid curve is a prediction for polycrystalline yttrium according to Eq. (1). The dashed line is a fit of Grüneisen's relation to this prediction. The dots represent the measured resistivity of a polycrystalline sample.

² Compare A. N. Gerritsen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 19.