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Magnetic Anisotropy in Single-Crystal Thin Films

Abstract: Thin, single-crystal films of Ni, Fe, Ni-Fe and Ni-Co have been grown by vacuum deposition onto heated rock salt. The cubic crystalline anisotropy constant, K_1, of these films has been measured at room temperature by a torque method. In the case of the Ni-Fe alloys, K_1 was found to be the same for thin films as for bulk materials of the same composition. The measured anisotropy in the Ni-Co films differs quantitatively but has the same qualitative variation with composition as is reported for bulk crystals. The results of one magnetic annealing experiment on a 75% Ni - 25% Fe film lends support to the short-range ordering model of uniaxial anisotropy in alloys. Pure nickel films exhibit a pronounced uniaxial anisotropy superimposed on the crystalline anisotropy. This uniaxial term disappears after the film is removed from the substrate, indicating that its origin is in an anisotropic stress in the deposited film.

Introduction

In recent years, considerable work has been done in measuring the coercive force, rotational threshold, and domain structure in ferromagnetic films, particularly films of the permalloy composition. While all of these properties are closely related to the magnetic anisotropy, it has been difficult to make direct comparison of the anisotropies in films and bulk materials because of the extremely complex crystalline structures usually found in films. For a clear understanding of these and related phenomena, a systematic study of the magnetic properties of single-crystal thin films is needed.

The growth of single-crystal films by vacuum deposition onto heated faces of single-crystal sodium chloride was first reported for silver by Brück[1] in 1932. This phenomenon, known as *epitaxy,* has since been investigated by many workers,[2-5] especially for the noble metals gold and silver. The term *epitaxial growth* refers to an atomic interaction between the substrate and the deposited atoms, which under suitable conditions can cause the deposited material to assume a single-crystal structure, generally with the same orientation as the substrate. However, neither the crystal structure nor the lattice constants of the substrate and deposited material need be the same, as is clearly illustrated by the growth of face-centered cubic gold or silver on simple cubic sodium chloride with lattice mismatch of about 30%.

The most recently reported epitaxial growth of ferromagnetic metals was that of Collins and Heavens,[6,7] who grew fcc nickel, bcc iron, and fcc cobalt on sodium chloride. Prior to the previous work of the author,[8] however, no work on the epitaxial growth of ferromagnetic alloys had been reported. This paper discusses the preparation of single crystals of Ni, Fe, Ni-Fe, and Ni-Co alloys and the measurement of the magnetic crystalline anisotropy by a torque balance. The anisotropy constants and some preliminary magnetic annealing studies are compared with those previously reported in bulk materials.

Preparation of thin-film crystals

Preparation of the pure metals and alloys was by vacuum deposition onto heated sodium chloride single crystals in a manner similar to that of previous workers. Sodium chloride crystals were cleaved on the (100) plane and placed in a chamber which was evacuated to a pressure of about 1×10^{-4} mm Hg. It was noted that the use of a radiation heater to produce the substrate temperature, rather than filaments under the substrate, was necessary for the formation of good crystals in this system. The substrate temperatures used are shown in Table 1 along with the magnetic measurements. In most cases the temperature was in the range of 490° to 520°C, as measured at the inside surface of the radiation heater. The heat cycle used was as follows: the substrate was raised to about 500°C and held there for one hour in vacuum; then the metal was evaporated from a tungsten filament, and alloying took place during deposition. In most cases, the film was then annealed for one hour at the same temperature, and cooled by turning off the heater. Pure Fe, Ni, and Co wires were used as source material. No special care was taken to control the rate of evaporation, which was between 20 and 100 A per second, because the results appeared to be independent of the evaporation rate within the indicated range.

Metal films formed on microscope slides in the chamber during the evaporation provided material for photometric analysis of composition. Film thickness was determined by an optical interference method on the samples used for magnetic measurements. Portions of each film were removed from the sodium chloride by floating them onto a water surface. These were studied by transmission electron diffraction and by transmission electron microscopy. Figure 1 is the diffraction pattern and Fig. 2 the micrograph of a pure Ni film which was cooled immediately following evaporation. The diffraction pattern shows satellites at each principal reflection which are due to stacking faults and microtwins in the (111) planes of the crystal.[2]

The micrograph shows a gross effect as bands of contrast change and a detail effect as small regions of intensity change. Both of these variations in intensity may be explained by the local depletion of the central beam of electrons by diffraction of a portion of the beam. In a micrograph such as Fig. 2, only this central beam is viewed, and all singly diffracted electrons are lost. Thus, if a portion of the crystal is set so that the incident beam makes a Bragg angle with the lattice, this region will appear dark, since most of the electrons passing through will be diffracted. The gross bands of contrast in Fig. 2 can occur only in a well aligned crystal and are due to bending of the crystal out of a plane normal to the incident beam. The small regions of contrast change are due to stacking faults and twins which produced the satellites in the diffraction pattern. A count of these defects suggests that there are between 10^{11} and 10^{13} lattice imperfections per square centimeter of film crystal.

Figure 3 is the diffraction pattern of a nickel film similar to that of Fig. 1, except that it has been annealed for one hour at 500°C immediately following evaporation. There is no noticeable difference between this pattern and that of Fig. 1. The transmission micrographs of this film in Figs. 4-8 show that the anneal has changed the structure of the film in a striking manner from that of Fig. 2. The series of micrographs were made by rotating the plane of the film so that the electron beam passed through the film at angles of from 7° on one side of normal to 5° on the other side, in equal steps. The sketch in Fig. 9 may be used as a key to various regions in the micrographs which change radically in intensity during the rotation. The region marked (1) in Fig. 9 retains its boundary during the rotation, and thus may be called a grain. The rest of the noted regions change so markedly that they cannot be considered as being grains in the usual sense.

Figures 1 to 9 follow. Text is continued on page 127.

Table 1 **A comparison of the crystalline anisotropy constant K_1 of single crystal thin films with previously published data[11] for bulk materials of similar composition.**

Composition %Ni	%Fe	%Co	*Substrate Temp.*	*Anneal Time*	*Thickness*	*K_1 Film*	*K_1 Bulk*
100			500°C	1 hour	750 A	-42×10^3	-50×10^3
100			519°C	2 hours	880 A	-40×10^3	-50×10^3
100			523°C	1 hour	720 A	-36×10^3	-50×10^3
100			497°C	—	800 A	-45×10^3	-50×10^3
92	8		500°C	—	600 A	-17×10^3	-20×10^3
87	13		497°C	1 hour	700 A	-8×10^3	-10×10^3
81	19		526°C	1 hour	900 A	-1.6×10^3	-3×10^3
74	26		497°C	1 hour	700 A	$<0.5\times10^3$	0
74	26		495°C	1 hour	500 A	$<0.5\times10^3$	0
68	32		520°C	1 hour	200 A	$+10\times10^3$	$+4\times10^3$
	100		504°C	¾ hour	200 A	$+450\times10^3$	$+500\times10^3$
97		3	544°C	1 hour	600 A	$<0.5\times10^3$	0
94		6	497°C	1 hour	800 A	$+34\times10^3$	$+16\times10^3$
77		23	520°C	1 hour	1400 A	$+20\times10^3$	-4×10^3
67		33	506°C	½ hour	400 A	-40×10^3	-30×10^3

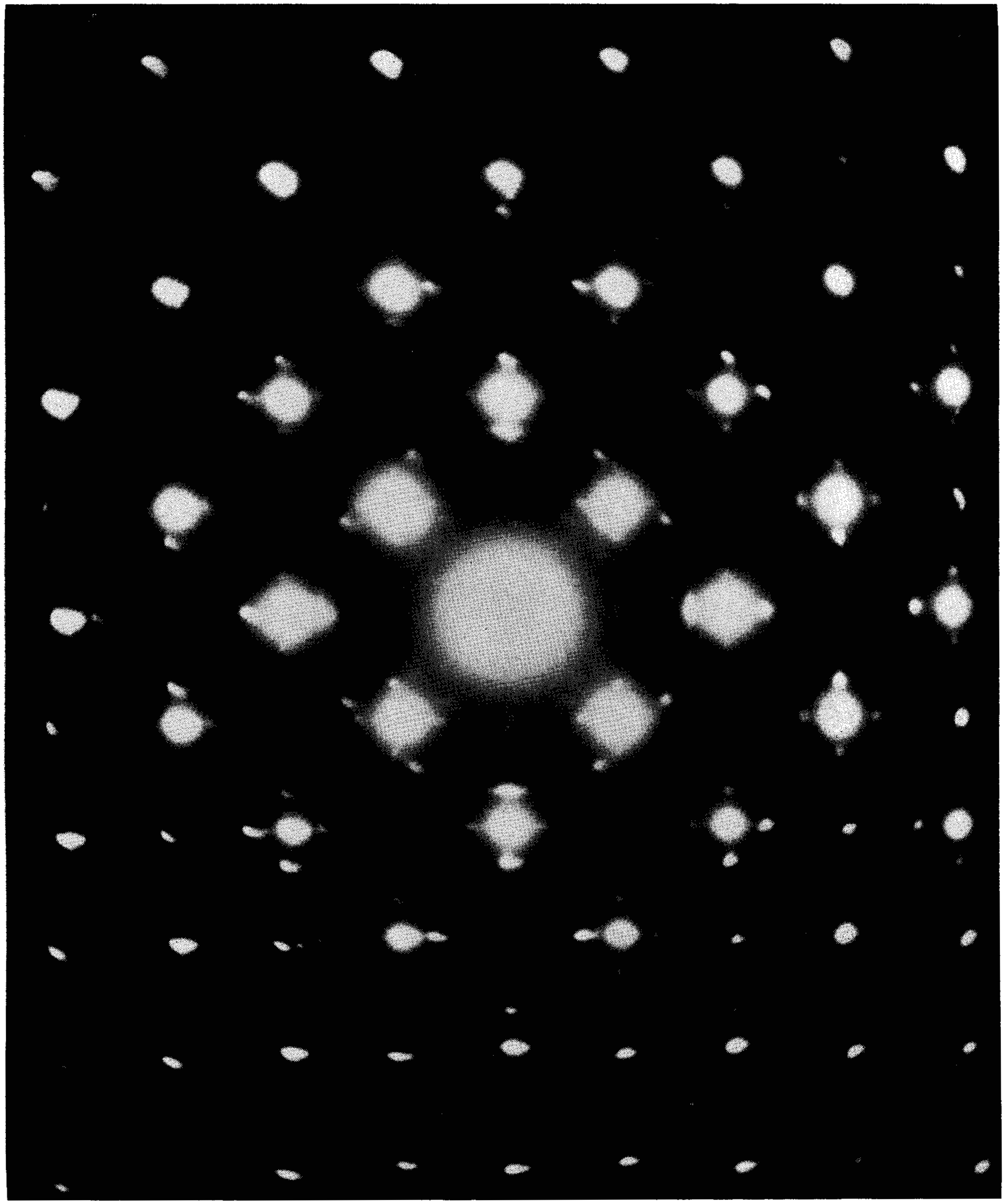


Figure 1 **Transmission electron diffraction pattern of an unannealed single-crystal nickel film. Note the satellite spots due to stacking faults.**

Figure 2 **Transmission electron micrograph of the film shown in Fig. 1. The small regions of contrast change are due to defects in the lattice.**

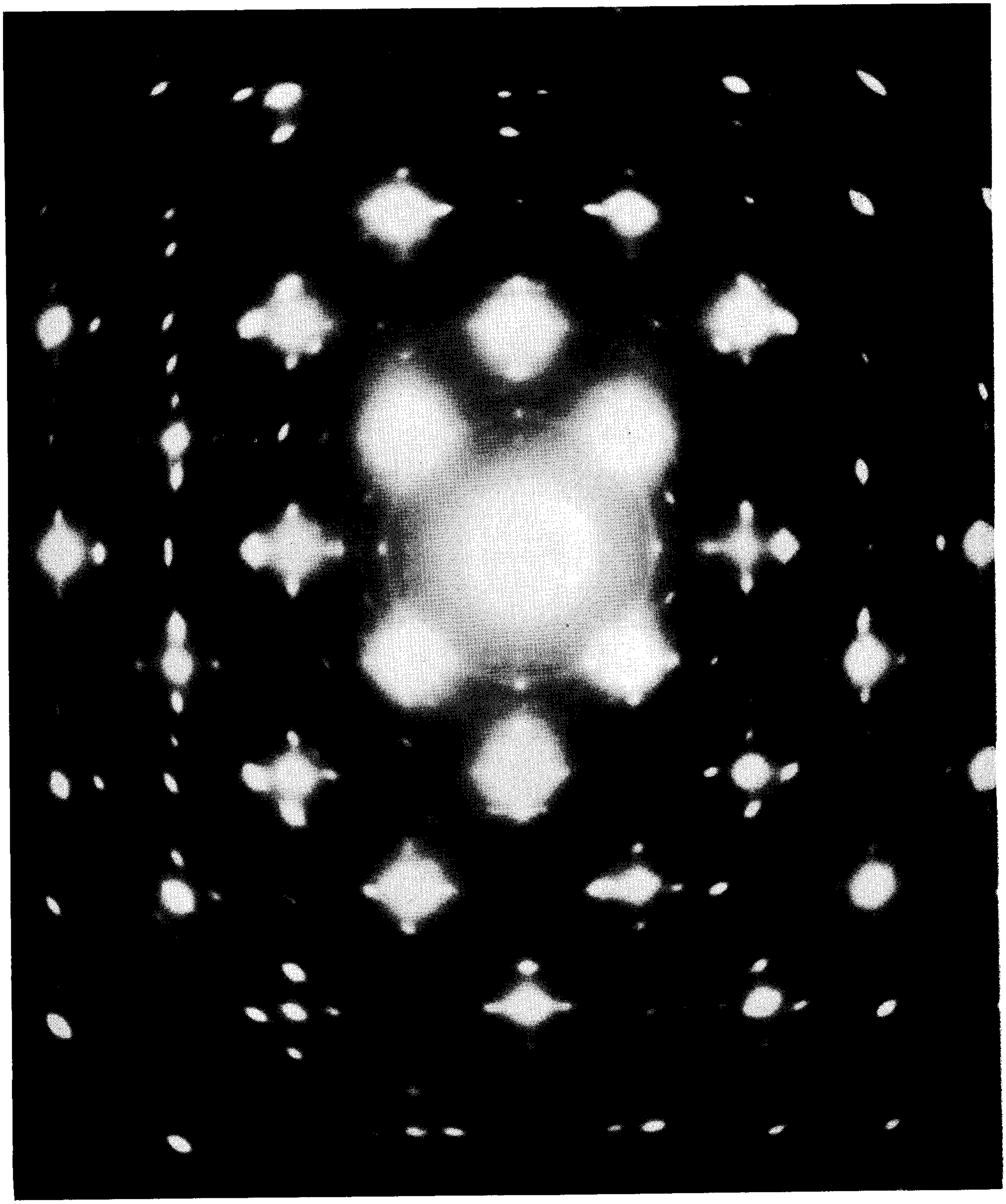


Figure 3 **Transmission electron diffraction pattern of an annealed single-crystal nickel film. Note the similarity to Fig. 1.**

Figure 4 **Transmission electron micrograph of the annealed nickel crystal of Fig. 3.**
One of a series (Figs. 4 to 8) made by rotating the sample in the electron beam so that the beam went from $-7°$ (Fig. 4) on one side of the normal to theplane of the film to $+5°$ (Fig. 8) on the other side.

Figure 5 **−4° from the normal to the plane of the film.** *See caption to Fig. 4.*

Figure 6 **−1° from the normal to the plane of the film.**
See caption to Fig. 4.

Figure 7 **+2° from the normal to the plane of the film.**
See caption to Fig. 4.

Figure 8 **+5° from the normal to the plane of the film.**
See caption to Fig. 4.

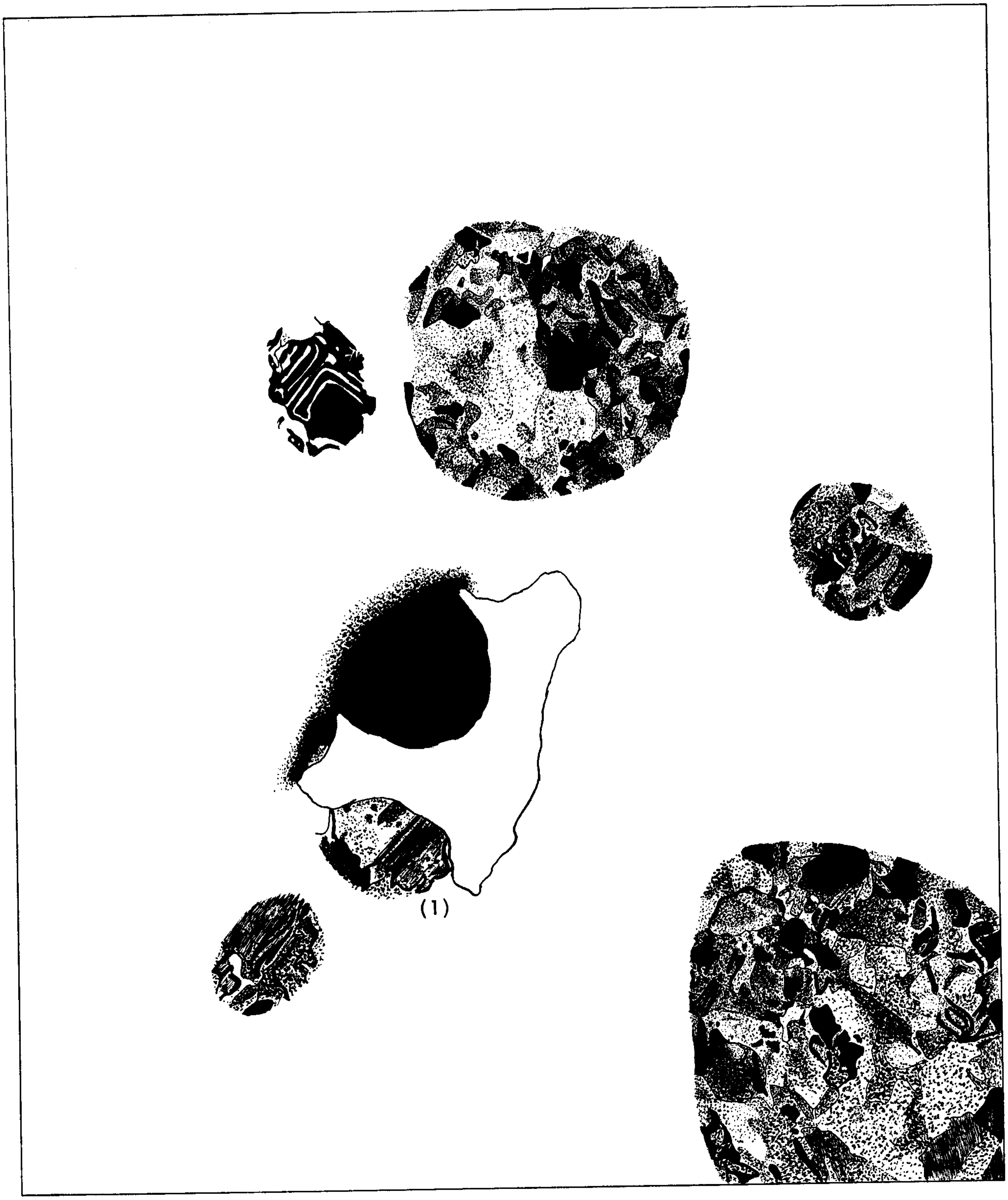


Figure 9 **Sketch of the regions in Figs. 4 to 8 which are of interest because of the great contrast changes that occur as the film is rotated.**
Region (1) retains its boundary during the rotation, and thus may be called a grain. The other regions change so markedly that they cannot be considered grains in the usual sense.

Differences in film thickness cannot result in the great contrast variations which appear in these photographs. A strong possibility is that the faults which appeared in the unannealed film in Fig. 1 have been collected into subgrain boundaries on anneal, and that the annealed film is really a mosaic structure with a very slight ($\approx 2°$) misorientation of the subgrains.

While the foregoing pictures and discussions were related to a nickel film, they apply equally well to all alloy films reported here. All films before anneal are characterized as large crystals with many small faults. After anneal, they become mosaic structures consisting of subgrains. Either structure is sufficiently aligned to permit a good determination of the anisotropy constant, K_1.

For the magnetic measurements, these crystals were transferred to Vycor disks by a flotation process. They were found to adhere tightly to the new substrate upon transfer.

Magnetic measurements

An expression for that portion of the free energy of a single-domain cubic crystal which depends on the direction of the magnetization may be written as[9]

$$
\begin{aligned}
E_M &= K_1(\alpha_1^2\,\alpha_2^2+\alpha_2^2\,\alpha_3^2+\alpha_3^2\,\alpha_1^2)\\
&\quad +K_2(\alpha_1^2\,\alpha_2^2\,\alpha_3^2)\\
&\quad -3/2\lambda_{100}(C_{11}-C_{12})(\alpha_1^2\,e_{xx}+\alpha_2^2\,e_{yy}+\alpha_3^2\,e_{zz})\\
&\quad -3\lambda_{111}C_{44}(\alpha_1\alpha_2e_{xy}+\alpha_2\alpha_3e_{yz}+\alpha_3\alpha_1e_{zx}),
\end{aligned}
$$

provided there is no directional ordering of atoms as could occur in an alloy. In this expression, the α's are the direction cosines of $\mathbf{M}$; K_1 and K_2 are the first and second order crystalline anisotropy constants; λ_{100} and λ_{111} are the magnetostriction constants; C_{11}, C_{12}, and C_{44} are the elastic coefficients; and e_{ii} and e_{ij} are the extension and shear strains. If the magnetization is confined to a plane in the crystal, then this expression may be written in terms of one angle, θ. In the case of a (100) crystallographic plane, the above expression reduces to

$$
\begin{aligned}
E_M &= K_1(\sin^2\theta-\sin^4\theta)\\
&\quad -3/2\lambda_{100}(C_{11}-C_{12})(e_{xy}\cos^2\theta+e_{yy}\sin^2\theta)\\
&\quad -3/2\lambda_{111}C_{44}[\sin 2\theta e_{xy}].
\end{aligned}
$$

The first derivative of the energy with respect to position of $\mathbf{M}$ is a torque, $L=-\partial E/\partial\theta$. In the (100) plane, this derivative reduces to a sin 4θ variation of K_1, and a sin 2θ variation arising from either an anisotropic extension strain or a shear strain. For the experiments reported here, a (100) crystallographic plane was chosen, both for ease of measurement and because the (100) plane is easy to grow on NaCl.

Since the torque measured depends on the volume of material measured as well as the magnitude of the anisotropy, and since the samples measured were as small as 5×10^{-6} to 5×10^{-5} cc of material, a very sensitive torque balance was required to make the measurements. Figure 10 is a schematic diagram of this instrument, which is based on a design of Penoyer's.[10] The basic difference between this balance and the one reported by Penoyer is the support of the sample by a fiber instead of a bearing. Lateral vibration is damped by the two oil baths along the shaft. A photocell feedback network supplies current to a coil mounted on the shaft which bucks out the torque of the sample. This current is then displayed on an X-Y recorder as a function of angle of the applied field. The balance is capable of resolving torques of 0.5×10^{-3} dyne-cm, and of making continuous plots of L vs θ. For best resolution, point-by-point data were taken to eliminate eddy-current effects. Because of the shape anisotropy out of the plane of the film, which tends to hold $\mathbf{M}$ in that plane, no special care was necessary in the centering of the sample in the field.

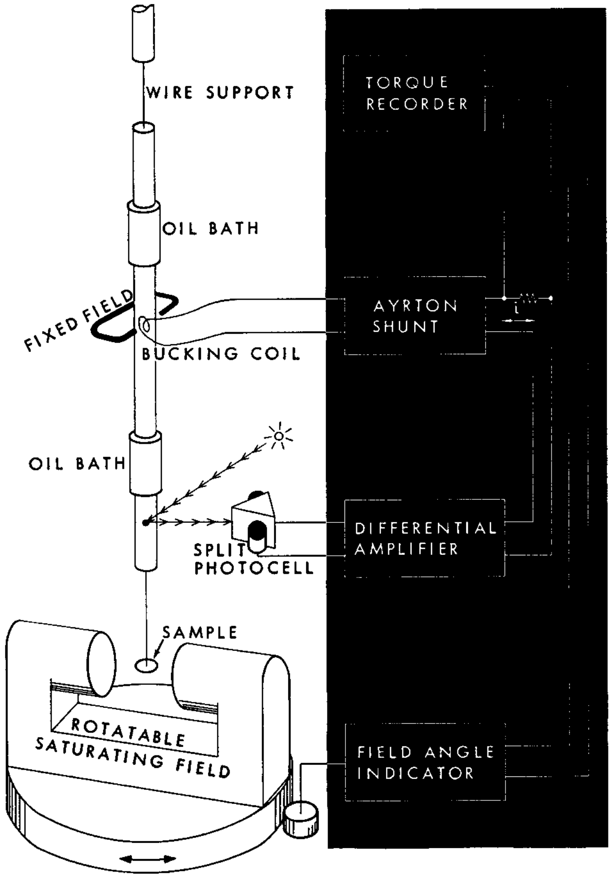


Figure 10 **Schematic diagram of the torque balance used to measure anisotropy in thin films.**
The current, i, in the circuit between the Ayrton shunt and differential amplifier is proportional to the torque between the magnetization and anisotropy of the sample.

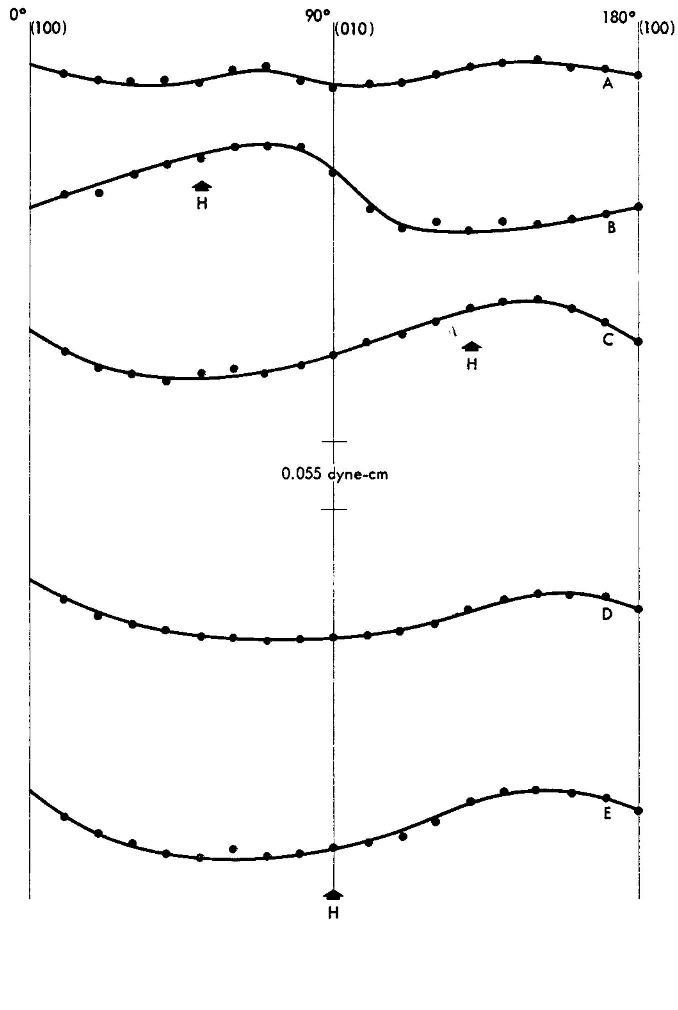
Table 1 contains the results of measurements of K_1 for films of Ni, Fe, and Ni-Fe and Ni-Co alloys. These results are compared with previously published data taken on bulk single crystals.[11] The Ni-Fe series of films are in good agreement with published data in the case of K_1. The Ni-Co alloys are not in good agreement as to magnitude of K_1 but do show the same variation with composition. A possible explanation for this difference could be that the state of atomic order is different in the films from that in bulk.

Films with compositions in the neighborhood of 75% Ni - 25% Fe were thermally annealed both in vacuum and in forming gas in an attempt to produce the ordered phase Ni_3Fe. Of these only the 81% Ni - 19% Fe sample responded to the heat treatment. One portion of the original crystal was annealed in forming gas for 10 hours at 300°C. As a result of this treatment, K_1 increased from -1.6×10^3 to -3.9×10^3 erg/cc. Another portion of this same crystal, annealed in vacuum for 90 hours at 490°C, then cooled at $\approx$8°C/min, acquired a K_1 value of -4.5×10^3 erg/cc. Electron diffraction of these samples after anneal shows no noticeable change in the structure except for the loss of stacking faults. Electron microscopy indicates that the number of major defects such as those shown in Figs. 4-8 increased during the anneal. It may be that the inability to increase K_1 significantly by thermal anneal in many of the Ni-Fe films is due to the large number of defects. In bulk material, defects have reportedly prevented the formation of large, ordered regions within an alloy.

One sample of 75% Ni - 25% Fe was anealed in the presence of an externally applied field at 450°C. When this field was along either [110] direction, the material became uniaxial with the easy direction in the direction of the field. When the field was in a [100] direction, no change in the anisotropy was noted. Figure 11 shows plots of torque vs θ for this film as a function of anneal. The measured uniaxial anisotropy constant K_u is 2.7×10^3 erg/cc in this case. It has been proposed[12-14] that the uniaxial anisotropy magnetically annealed into alloys of nickel-iron around the 75% nickel composition is due to the directional ordering of like atom pairs along the [110] crystallographic directions. The magnetic annealing experiment on the thin film supports this in two ways: first, anneals with the applied field in the [110] direction produce a large uniaxial anisotropy (K_u= 2.7×10^3 erg/cc) which agrees in magnitude with published[14] (1.5×10^3 erg/cc) values, and second, an anneal with **H** in the [100] direction has little effect on the state of the sample. The anneal with **H** in the [100] direction rules out the possibility of magnetostriction as a cause of the magnetic annealing effect, since this would presumably result in an anisotropic extension strain and thus a uniaxial anisotropy, which is not observed in this case.

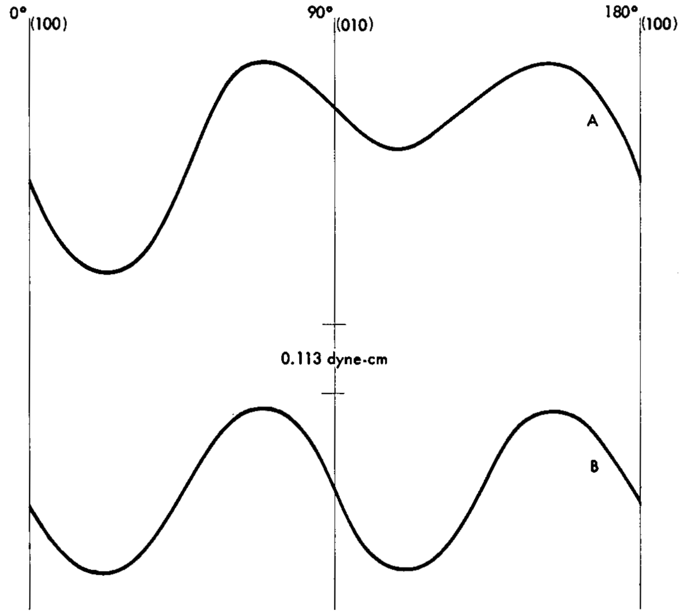
Lastly, measurements made on pure nickel crystals, while still on the sodium chloride substrate, and after the transfer to Vycor, indicate that the crystals are strained anisotropically upon evaporation but that this strain disappears upon transfer. Figure 12 is a set of torque curves of a pure Ni film before and after the transfer. Before transfer there is a sin 2θ torque equivalent to a K_u of 15×10^3 erg/cc; after transfer this sin 2θ component is barely resolved and may be neglected. This uniaxial anisotropy probably has its origin in the 15° angle which the incident vapor beam makes with a normal to the film. The magnitude of the anisotropy, however, is at least an order of magnitude larger than would be predicted from angle-of-incidence data obtained at lower temperatures. Furthermore, the anisotropy of films deposited at the lower temperatures does not disappear after removal from the substrate.[16] The origin of the high-temperature effect would appear to be best explained in terms of anisotropic stresses which are relieved during the transfer from the original NaCl substrate to Vycor.

Figure 11 **Torque curves of a 75% Ni - 25% Fe crystal.**
Curve A, unannealed film on a Vycor substrate. Curves B and C, film annealed one hour and two hours at 450°C in vacuum with a field applied along the [110] direction, as shown. Curve D, film annealed four hours at 450°C, then 10 minutes at 550°C in vacuum, with no field applied. Curve E, film annealed one hour at 450°C in vacuum with the field along the [010] direction, as shown.



The author wishes to thank those who helped him in various phases of this work: D. P. Cameron and C. F. Aliotta in the electron microscope work, G. L. Evans and R. C. DiBenedetto in chemical analysis, O. C. Wortham in torque measurement and J. C. Slonczewski in discussion of the various aspects of the experiment.

Figure 12 **Torque curves of the pure nickel crystal.** *Curve A: as the crystal is on the sodium chloride substrate. Curve B: the same crystal after transfer to a Vycor substrate. Note that Curve A contains a sin 2θ component which is missing in Curve B.*



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Received November 10, 1959