THE ORIENTATIONS OF CRYSTALS IN ELECTRODEPOSITED METALS*

BY RICHARD M. BOZORTH

ABSTRACT

If a metallic film is placed in the path of a circular beam of x-rays, the Debye-Scherrer circles obtained on a photographic plate will each be nearly uniform in intensity if the crystals are oriented at random. If the circles contain spots of greater intensity, certain crystal planes must be oriented so as to make an average angle α with the normal to the film. (1) A *graphical method of determining the orientations* is described, a modification of that given by Polanyi and by Uspenski and Konobejewski, together with charts of the values of α corresponding to the location of intense spots for three values of the angle β of the beam with the normal to the film, and also a table of the values for α for different planes for the cubic system. (2) *Electrodeposited films of copper, zinc and cadmium* were found to have crystals oriented at random, but *films of iron, nickel and cobalt* show special orientations. For Fe, the (111) planes tend to lie parallel to the surface; for Ni the (100) or (211) planes tend to be parallel to the surface. The orientation was less marked for Co and only slightly evident for *silver*. In the case of Ni, the degree of special orientation was found to increase with the thickness of the films studied (2 to 130×10^{-4} cm) and at the same time the size of some of the crystal grains greatly decreased, reflecting more general radiation. A magnetic field had no influence on the amount of orientation. (3) *Association of the effect with strain in the films.* It is known that electrodeposited films are in a state of stress, presumably because of the hydrogen deposited with the metal, and that strained metals tend to have oriented crystals. It is suggested, therefore, that the orientation in this case is associated with the strain developed during deposition.

1. INTRODUCTION

THE crystalline structures of rolled metals and hard-drawn wires were first explained by Polanyi, Weissenberg, Mark and Ettisch,[1] independently by Uspenski and Konobejewsky,[2] and more recently by Jeffries[3] and others. All of these observers deduced from x-ray photographs the distribution in angle of the principal crystal axes in the minute grains constituting these substances. This paper describes a

---

* Reported in part at the Washington Meeting of the American Physical Society, April 25, 1924. (See abstract in Phys. Rev. **23**, 764, June 1924).

[1] See especially M. Polanyi, Zeits. f. Phys. **7**, 149-180 (1921); K. Weissenberg, Ann. der Phys. (4) **69**, 409-435 (1922); M. Polanyi and K. Weissenberg, Zeits. f. techn. Phys. **4**, 199-208 (1923).

[2] N. Uspenski and S. Konobejewski, Zeits. f. Phys. **16**, 215-27 (1923).

[3] Z. Jeffries, Trans. Am. Inst. Min. Eng. **70**, 303-327 (1924).

similar study of the orientations of the crystals in electrolytically deposited metals, those examined being Fe, Co, Ni, Cu, Zn, Ag and Cd.

2. Method of X-ray Examination

The metals were examined in the form of foils. These were deposited on cathodes of polished copper or iron which, just before the deposition, were coated with a thin film of selenium, making it easy to strip the foil from the cathode for subsequent examination. The foil was now mounted in the path of a beam of x-rays of circular cross section. The x-rays were supplied by a molybdenum target water-cooled tube, run at 40 kv peak, and were filtered through a zirconia screen. The photographic plate (Eastman X-Ray 5″×7″) was placed 5 cm behind the sample, perpendicular to the incident beam.

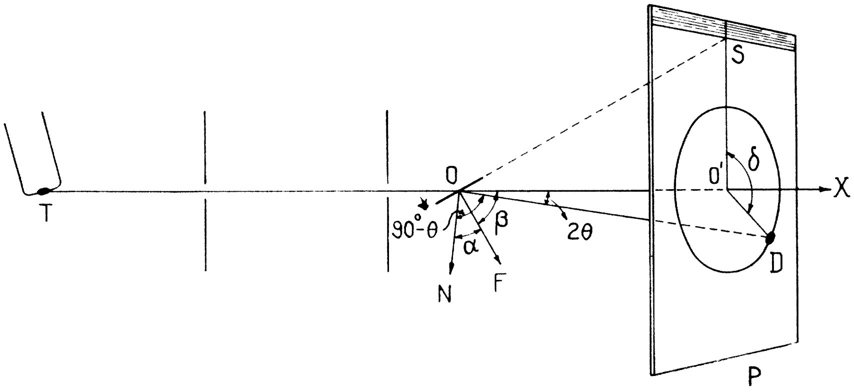

Fig. 1. Diagram showing refraction of beam to photographic plate *P*.

If the crystals in the foil were oriented at random each of the usual Debye-Scherrer circles would be of uniform intensity around its circumference except for the effect of absorption in the foil, which, in general, would be different for different directions of emergence and would produce differences of intensity between widely separated points. Regions of conspicuous intensity, such as those seen in Fig. 5, indicate, therefore, the existence of a special orientation of the individual crystals. In electrolytic foils it is to be expected that the distribution of equivalent crystallographic directions will have axial symmetry about a line perpendicular to the foil; that this is true is proved by the fact that when the foil is perpendicular to the beam each Debye-Scherrer circle is of uniform intensity around its circumference, although the consecutive circles have relative intensities greatly different from those known to correspond to random distribution.

In Fig. 1, the x-ray beam TX, cuts the sample at O and the photographic plate at O'; OF is the normal to the surface of the sample on the side from which the primary beam emerges; ON is the normal to the family of atom-planes which reflects x-rays in accordance with the equation $n\lambda = 2d \sin\theta$ on to the photographic plate P at D; the line $O'S$, chosen for reference, lies in the plane P and in the plane $O'OF$, on the opposite side of OO' from OF. The following relation[1,2] then exists between the angles marked in Fig. 1

$$\cos\alpha = \cos\beta \sin\theta + \sin\beta \cos\theta \cos\delta.$$

Of these quantities, θ is known from the crystal structure and the wavelength of the x-rays, and δ is measured on the plate; β can be determined most accurately from the relation $\tan\beta = OO'/O'S$, where OO' is calculated from the measured distances $O'D$ and the known values of θ,

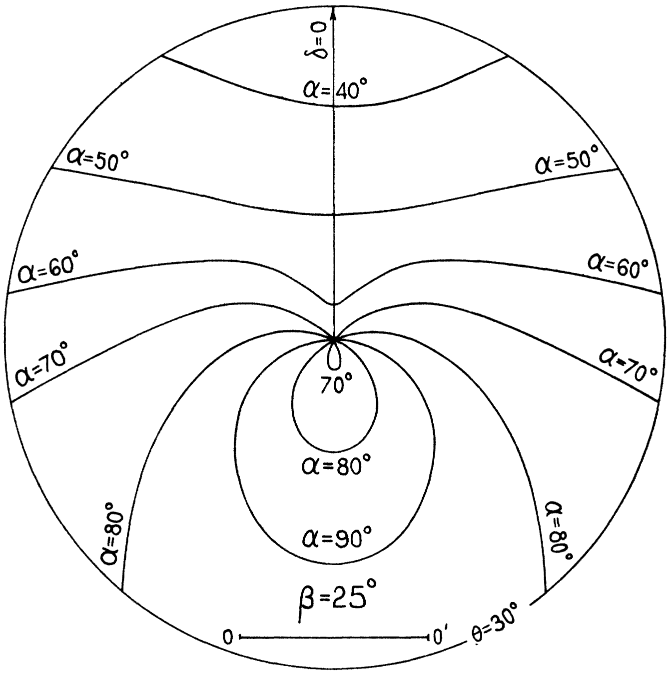

Fig. 2. Chart showing lines of constant α for $\beta = 25°$.

and $O'S$ is the distance on the plate from the central image to the edge of the unexposed streak on the plate due to the maximum absorption of scattered radiations in the plane of the sample.

In practice, the crystallographic direction $[hkl]$ which coincides with the normal to the foil, is determined with the aid of a chart and a table. The chart is constructed for the chosen value of β, a different chart being required for each inclination of the foil to the beam. For any arbitrary value of α a curve is drawn giving δ as a function of θ, where δ is plotted in azimuth and θ is plotted radially in such a way that a line of constant θ is a circle having the radius OO' tan 2θ, the radius of the Debye-Scherrer circle produced on the plate by x-rays reflected from crystal planes inclined at the angle θ to the incident beam (see Fig. 1). The chart is completed by drawing in a similar manner curves for other values of α chosen to facilitate interpolation, e. g. at intervals of 10°. Charts for several values of β (25°, 50°, 75°) are shown in Figs. 2, 3, and 4, and may be copied for use in determinations of this kind by so enlarging them that the length of the line labeled OO' is equal to the distance from the sample to the photographic plate.

In using a chart to determine α, the photographic plate is placed over it and values of α read off for each point of maximum intensity on each Debye-Scherrer circle. A table is now constructed giving the angles between simple planes of the same or different indices. Table I has been so constructed for the cubic system. For the Debye-Scherrer circle produced by reflection from planes whose indices are (HKL), the planes (hkl) are found for which the angles tabulated are equal to the values of α just determined. Repeating the process for the other Debye-Scherrer circles, the crystallographic plane (hkl) whch coincides with the plane of the foil is, in general, uniquely determined and the determination confirmed.

TABLE I

Angles between crystallographic planes in crystals of the cubic system.

(HKL)	(hkl)	Values of α, the angle between (HKL) and (hkl)				
100	100	0°	90°			
	110	45°	90°			
	111	54°44′				
	210	26°34′	63°26′	90°		
	211	35°16′	65°54′			
	221	48°11′	70°32′			
	310	18°26′	71°34′	90°		
	311	25°14′	72°27′			
	320	33°41′	56°19′	90°		
	321	36°43′	57°42′	74°30′		
110	110	0°	60°	90°		
	111	35°16′	90°			
	210	18°26′	50°46′	71°34′		
	211	30°	54°44′	73°13′	90°	
	221	19°28′	45°	76°22′	90°	
	310	26°34′	47°52′	63°26′	77° 5′	
	311	31°29′	64°46′	90°		
	320	11°19′	53°58′	66°54′	78°41′	
	321	19° 6′	40°54′	55°28′	67°48′	79° 6′

TABLE I—continued

Angles between crystallographic planes in crystals of the cubic system.

(*AKL*)	(*hkl*)	Values of α, the angle between (*HKL*) and (*hkl*)						
111	111	0°	70°32′					
	210	39°14′	75° 2′					
	211	19°28′	61°52′	90°				
	221	15°48′	54°44′	78°54′				
	310	43° 5′	68°35′					
	311	29°30′	58°31′	79°58′				
	320	61°17′	71°19′					
	321	22°12′	51°53′	72° 1′	90°			
210	210	0°	36°52′	53° 8′	66°25′	78°28′	90°	
	211	24° 6′	43° 5′	56°47′	79°29′	90°		
	221	26°34′	41°49′	53°24′	63°26′	72°39′	90°	
	310	8° 8′	58° 3′	45°	64°54′	73°34′		
	311	19°17′	47°36′	66° 8′	82°15′			
	320	7° 7′	29°45′	41°55′	60°15′	68° 9′	75°38′	82°53′
	321	17° 1′	33°13′	53°18′	61°26′	70°13′	83° 8′	90°
211	211	0°	33°33′	48°11′	60°	70°32′	80°24′	
	221	17°43′	35°16′	47° 7′	65°54′	74°12′	82°12′	
	310	25°21′	49°48′	58°55′	75° 2′	82°35′		
	311	19° 8′	42°24′	60°30′	75°45′	90°		
	320	25° 9′	37°37′	55°33′	63° 5′	83°30′		
	321	10°54′	29°12′	40°12′	49° 6′	56°56′		
		70°54′	77°24′	83°44′	90°			
221	221	0°	27°16′	38°57′	63°37′	83°37′	90°	
	310	32°31′	42°27′	58°12′	65° 4′	83°57′		
	311	25°14′	45°17′	59°50′	72°27′	84°14′		
	320	22°24′	42°18′	49°40′	68°18′	79°21′	84°42′	
	321	11°29′	27° 1′	36°42′	57°41′	63°33′	74°30′	
		79°44′	84°53′					
310	310	0°	25°51′	36°52′	53° 8′	72°33′	84°16′	
	311	17°33′	40°17′	55° 6′	67°35′	79° 1′	90°	
	320	15°15′	37°52′	52° 8′	74°45′	84°58′		
	321	21°37′	32°19′	40°29′	47°28′	53°44′	59°32′	
		65°	75°19′	85° 9′	90°			
311	311	0°	35° 6′	50°29′	62°58′	84°47′		
	320	23° 6′	41°11′	54°10′	65°17′	75°28′	85°12′	
	321	14°46′	36°19′	49°52′	61° 5′	71°12′	80°44′	
320	320	0°	22°37′	46°11′	62°31′	67°23′	72° 5′	90°
	321	15°30′	27°11′	35°23′	48° 9′	53°37′	58°45′	63°36′
		72°45′	77° 9′	85°45′	90°			
321	321	0°	21°47′	31°	38°13′	44°25′	50°	60°
		64°37′	69° 4′	73°24′	81°47′	85°54′		

The pattern due to an electrolytic foil of nickel, reproduced in Fig. 5A, may serve to illustrate the method. For this photograph β was made 50°. The values of α found from the chart are given in the second column of Table II; the values taken from Table I for $(hkl) = (211)$ are given in the third column and this is the only value of (hkl) which gives even approximate agreement between columns 2 and 3. It will be noted that column 3 contains one value not found in column 2 but it is easy to show that under the limitations imposed upon β and θ the corresponding reflection cannot occur.

TABLE II

Reflecting planes $n(HKL)$	α(obs.)	α[for $(hkl) = (211)$]
(111)	61°, 90°	19°28′, 61°52′, 90°
2(100)	36°, 66°	35°16′, 65°54′
2(110)	30°, 55°, 73°, 90°	30°, 54°44′, 73°13′, 90°

A second method of determining the plane (hkl) which coincides with the foil surface, was used in a few cases. This consisted in mounting the foil on a photographic spectrometer of the Bragg type, with the foil surface in place of the usual single crystal face. The foil was rotated with uniform angular velocity, and a screen containing an aperture, corresponding to the ionization chamber slit in the Bragg spectrometer but 10° in width, was rotated with just twice this angular velocity. With this arrangement no planes can reflect x-rays on to the photographic plate except those lying very nearly in the plane of the foil. The photographs taken in this manner resemble closely those

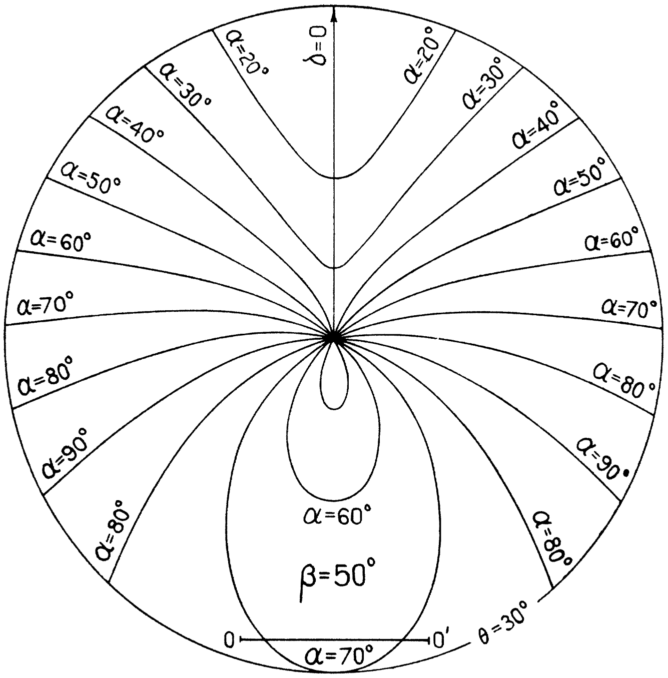

Fig. 3. Chart showing lines of constant α for $\beta = 50°$.

taken with a single crystal. This method gave results confirming in every case those of the first method described. The second metnod, while it has certain advantages, is open to the objection that it does not permit a satisfactory estimate of the degree of special orientation, such as can readily be derived from the appearance of the diffraction patterns obtained in the first method.

3. EXPERIMENTAL RESULTS

Electrolytic films of Fe, Co, Ni, Cu, Zn, Ag and Cd, deposited under various conditions, were examined with x-rays in the ways described above. Table III gives a summary of the results obtained. All deposits, unless otherwise stated were made on copper at room temperature with a current density of 0.005 amp./cm^2, and were 0.003 cm thick.

TABLE III

Metal	*Solution*	*Special orientation*
Fe	$FeSO_4$, 0.7m; NH_4Cl, 0.8m; $P_h=5.0$; 50°C; current density 0.050 amp./cm^2	(111) strong
Co	$CoSO_4$, 1.0m; saturated with H_3BO_3	Not determined, medium weak
Ni	$NiCl_2$, 0.1m; $NiSO_4$ 0.9m; H_3BO_3 0.6m; acid with H_2SO_4, P_h varied from 3.5 to 6.1; 40°C	(100) strong
Ni	$NiCl_2$, 0.9m; $NiSO_4$ 0.1m; H_3BO_3 0.6m; acid with H_2SO_4, $P_h=3.0$	(211) strong
Ni	$NiCl_2$, 1.0m; $P_h=4.0$	None
Cu	$CuSO_4$, 1.0m; H_2SO_4, 0.7m	None
Zn	Alkaline cyanide, Zn 0.5m, 40°C	None
Ag	Alkaline cyanide, Ag 0.2m	None
Cd	Alkaline cyanide, Cd 0.1m, 40°C	None

The effects of some of the different factors involved in deposition were investigated for the case of nickel. An interesting effect was observed when different thicknesses of this metal were plated from the same bath with the current density and other factors as nearly as possible the same, i. e., varying only the time of deposit. Photographs were taken using foils of thicknesses 2, 12, 23, 55 and 130 $\times 10^{-4}$ cm. The third and the last of these are reproduced in Figs. 5B and 5C, respectively. The photograph (not reproduced) taken with the thinnest foil shows no appreciable degree of special orientation. Fig. 5B shows that in the middle foil of the series the special orientation is appreciable, while Fig. 5C shows that in the thickest foil the crystals exhibit a decided tendency to become oriented so that their (100) planes are parallel to the surface of the foil. The photographs show, besides orientation effects, an increasing amount of x-radiation reflected on to the plate inside of the first Debye-Scherrer circle. This is general radiation[4] of wave-lengths in the region 0.30 to 0.50A, and its increasing prominence is due[5] to the fact that in increasing proportion the thicker foils are composed of very minute crystals, with dimensions of the order of 10A. Fig. 5D shows the diffraction pattern obtained from the later-deposited half of the thickest foil, the first-deposited half having been etched away with nitric acid. This pattern compared with that for the entire foil (Fig. 7) shows weaker diffraction effects due to fine crystals, and shows a higher degree of special orientation than any of the other patterns.

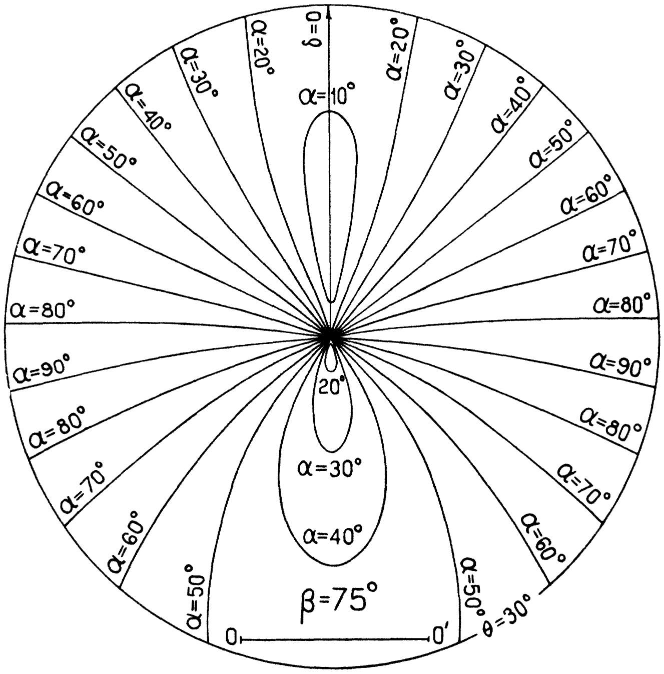

Fig. 4. Chart showing lines of constant α for $\beta = 75°$

Some experiments were performed in which Fe, Ni and Cu were deposited in magnetic fields having various strengths and various directions with respect to the surface of the cathode. Other experiments were made using an inert (Pt) anode. Although these modifications seemed at first to change the degree or kind of crystal orientation in Ni, the effects were later traced to changes taking place in the solutions.

---

[4] R. M. Bozorth, J.O.S.A. and R.S.I. **9**, 123-127 (1924).

[5] Zsigmondy, Kolloidchemie, 3d ed. (1920), pp. 394, 403-5.

4. Discussion of the Results

The experiments described above show that some metals, when deposited electrolytically from solution, tend to form crystals oriented in a definite way with respect to the cathode surface. This tendency is greater in iron and nickel than in any of the other metals investigated. It is evident, however, in cobalt and silver. Preliminary experiments show that the degree and kind of special orientations are influenced to some extent by the composition of the solutions from which the metals are deposited.[6] Results already obtained support the belief that the special orientations are intimately connected with the state of stress which exists in the deposited metal. Kohlschütter and Vuilleumier[7] have shown that deposits of Fe, Ni and Ag, as usually produced, are in a state of tension, and experiments performed in this laboratory yield quantitatively the values of these tensions for different thicknesses of iron deposit. Also, Polanyi[8] has shown that the tension produced in metals by working produces special orientations of their crystals, and he has given an explanation for the production of such orientations. A natural explanation for the observed orientations in electrolytic foils is, then, that the tension known to be present in such foils produces orientations of the crystal grains in a way similar to that in which orientations are produced in hard drawn wires or rolled sheets. In this connection it is significant that the metals Fe and Ni, which are deposited in a state of tension and with special orientations of their crystals, are much harder mechanically than Cu, Zn and Cd in which the crystals are orientated approximately at random.

The cause of the tension which exists in the metals Fe, Co and Ni, and the manner in which this tension produces the crystal orientations, have yet to be considered. Experiments with Ni, however, indicate that a necessary factor in producing the tension is the hydrogen which is deposited along with the metal; in fact Kohlschütter and Vuilleumier[7] have shown that hydrogen electro deposited upon a thin nickel deposit produces in it a marked expansion, which disappears when the circuit is broken. On this basis the following mechanism is suggested for the production of the stresses in the deposits. The hydrogen which is deposited with each "layer" of metal causes the metal atoms to be laid down somewhat farther apart than they normally

---

[6] This is also the conclusion of R. Glocker and E. Kaupp from their work described in Zeits. f. Phys. **24**, 121-139 (May 22, 1924).

[7] V. Kohlschütter and E. Vuilleumier, Zeit. f. Elektrochem. **24**, 300-321 (1918).

[8] M. Polanyi, Zeits f. Phys. **17**, 42-53 (1923).

are in crystals of the pure metal. As successive layers are added, however, the forces which held the hydrogen in the deeper layers while they were being deposited, no longer exist, and the hydrogen diffuses out of the metal leaving it in a state of tension. Since this process goes on continually during deposition the difference between the stresses in the innermost and outermost layers increases, and the compressive stress in the layer next to the cathode becomes greater and greater (but not, of course, in proportion to the thickness of the deposit.) The compressive stress in the layers first deposited may attain such a magnitude that some of the crystals are crushed, forming new crystals so fine that the reflection of x-rays by the metal is modified in a char-

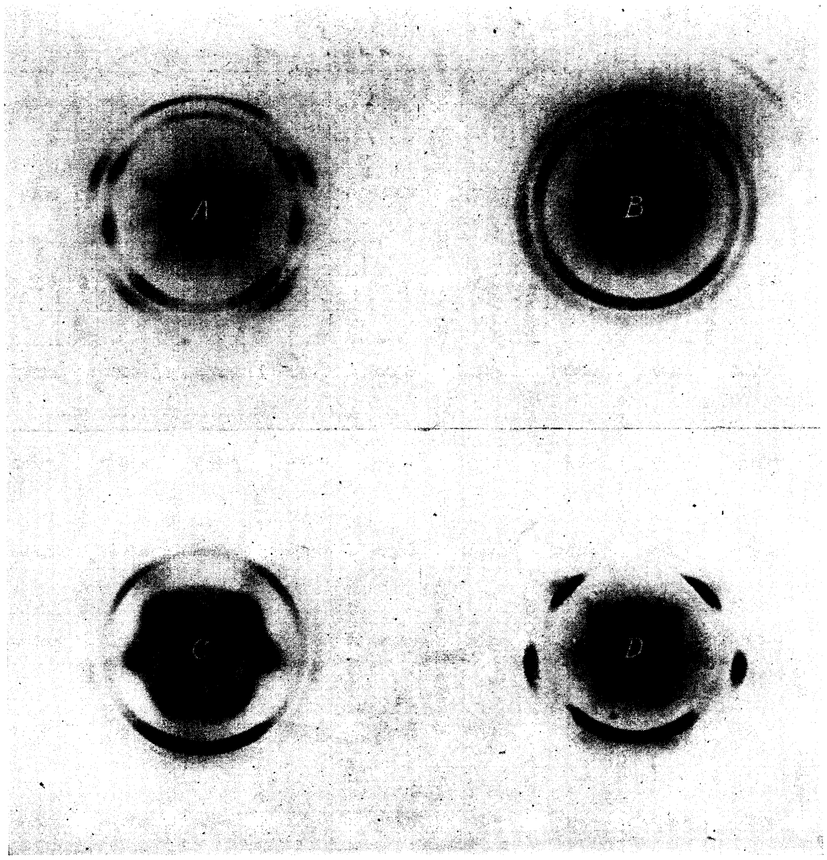

Fig. 5. X-ray photographs obtained with electrodeposited foils of nickel.
A. $\beta=50°$, $(hkl)=(211)$. B. Thickness 23×10^{-4}cm.
C. Thickness 130×10^{-4} cm. C. Thick foil, later deposited half.

acteristic way as seen in Fig. 5C and previously discussed. On the other hand, in the other layers where the crystals are formed under greater tension the orientations should be more marked, as was found to be the case.

It will be noted that the metals giving the most severely strained deposits are those of the iron group. Silver, which follows these in the intensity of strains and degree of special orientation is the next element following palladium. McKeehan has shown[9] that the space-lattice of palladium is expanded when it is made the cathode of an electrolytic cell producing hydrogen, and that the lattice again contracts upon the loss of hydrogen. The effects here discussed emphasize again the often-noted anomalies, magnetic and otherwise, associated with the eighth group elements and their neighbors in the periodic table.

In conclusion I wish to acknowledge my indebtedness to Dr. L. W. McKeehan and Dr. R. M. Burns for helpful discussions concerning the structure of electrodeposits, and to Mr. C. W. Warner for preparing some of the foils.

Bell Telephone Laboratories, Incorporated,
New York, N.Y.,
June 1, 1925.

---

[9] L. W. McKeehan. Phys. Rev. (2) **21**. 334-342 (1923).

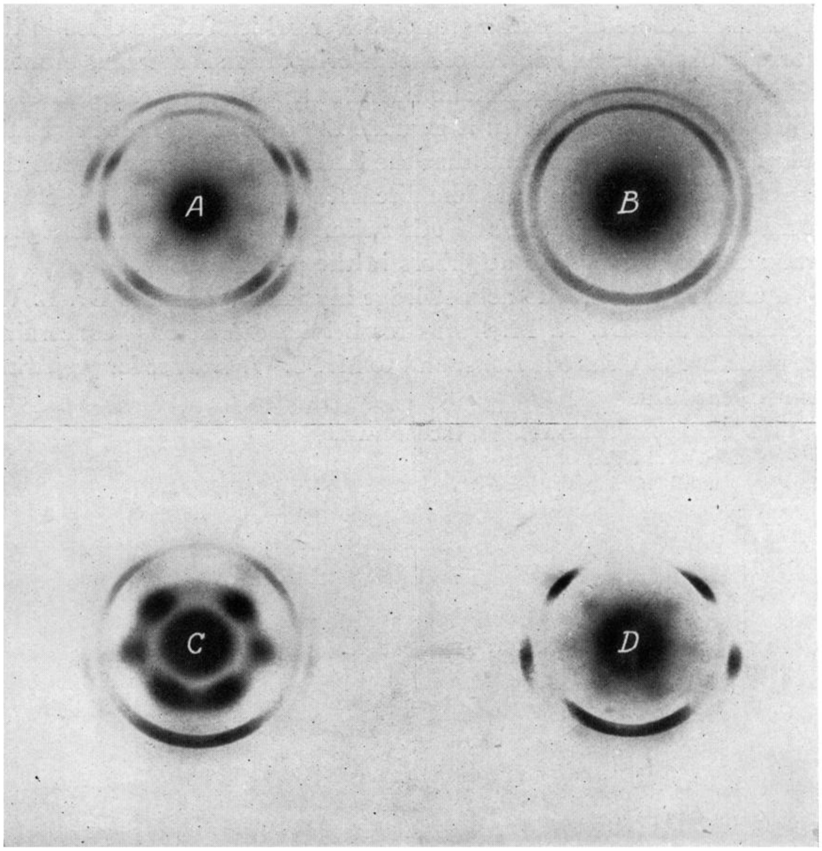

Fig. 5. X-ray photographs obtained with electrodeposited foils of nickel.
A. $\beta = 50°$, $(hkl) = (211)$.
B. Thickness 23×10^{-4}cm.
C. Thickness 130×10^{-4} cm.
C. Thick foil, later deposited half.