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Electron Diffraction Studies of Thin Films

I. Structure of Very Thin Films

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Films of metals and inorganic compounds, deposited upon organic supporting foils by vaporization in high vacuum, have been investigated by electron diffraction by the transmission method. Mean thickness of each of these films has been calculated from the total amount of vaporized material, distance of the film from the source, and calibration of the apparatus based upon weighing the material making up a known area of film. Films of the following substances have been studied: Au, CsI, Sb_2O_3, Pd, Cu, CuCl, Ni, CaF_2, Al, Mg, NaF and Be. Most of these films have been extremely thin, two-thirds of them less than 30A and many less than a single layer of atoms or molecules. The masking effect of the superposed diffraction pattern from the supporting foil is so slight that satisfactory patterns can be obtained from films of mean thickness as small as one layer of atoms if their atomic number is as large or larger than that of copper (29); in the case of beryllium (4) films as thick as 50A are required. Diffraction patterns obtained are characteristic of three-dimensional crystals. The ionic compounds studied produce films made up of rather large crystals, 100A or more on a side, even in the very thinnest films. Metal films are, in general, made up of smaller crystals than films of ionic compounds. *The observations prove that atoms and molecules are able to move over the surface of the supporting foil, and that they are drawn together into crystals of considerable size.* Crystals in metal films have been randomly oriented, except for slight orientation in aluminum films; crystals of some ionic compounds have been found to possess a strong preference for some particular orientation, and others have been randomly oriented. No correlation has been observed between average shape of crystal and degree of orientation. Intensity anomalies have been observed in diffraction patterns from calcium fluoride and cuprous chloride. Applications of the method of this investigation to study of corrosion and chemical change are suggested.

ELECTRON diffraction patterns obtained by the transmission method are often more satisfactory than those obtained by reflection. This paper is devoted to the description of a procedure for preparing films for investigation by this method, to studies of some representative films, and to an indication of fields of usefulness of such studies.[1]

The experiments described here were undertaken for the purpose of determining the structure of extremely thin films, and of discovering the limit of sensitivity of the method. Diffraction patterns have been obtained from films of many different substances and many different thicknesses; each film has been deposited by vaporization upon a supporting foil of organic material. The lower limit upon the mean film thickness which can be investigated successfully is determined by the structure of the film and the scattering powers of its atoms, and by the thickness and composition of the supporting foil which gives a diffraction pattern of its own superposed upon that of the film being studied. The amorphous supporting foils which are used are so thin that many satisfactory diffraction patterns have been obtained from films of average thickness less than a single layer of atoms or molecules. In most of these cases and in many others the average dimensions of crystals, both in the plane of the supporting foil and normal to it, are much larger than the mean film thickness.

Preparation of Films

Each film was prepared by vaporization in high vacuum from a V-shaped tungsten ribbon upon a thin foil of organic material supported across a narrow slit. An enlarged photograph of this slit[2] is reproduced as Fig. 1.

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[1] Many experimental papers describing electron diffraction experiments by the transmission method have been published since the pioneer work of G. P. Thomson. The most notable of the comprehensive investigations seem to be those of F. Kirchner; Physik. Zeits. **30**, 1025–1028 (1930); Zeits. f. Physik **76**, 576–596 (1932).

[2] The material of this slit is a copper-beryllium alloy. Slits used in earlier experiments were made of a nickel alloy. With this earlier alloy it was discovered that the organic foil spread across the slit often had upon its surface

The supporting foil is prepared from a chloroform solution of the plastic known as Formvar No. 1595, manufactured by the Shawinigan Products Corporation.[3] A drop of this solution is first placed upon a slightly greasy microscope slide, then immediately spread over the surface of the slide by means of a razor blade. By maintaining a predetermined clearance between blade and surface of the slide the thickness of the resulting foil of Formvar can be made fairly uniform and have any desired value. Most of the foils have been about 200A thick although 100A foils have occasionally been used. These values of thickness were determined by optical measurement of representative foils (upon chromium) using polarized sodium light in the method devised by Blodgett.[4]

After a Formvar foil has been deposited upon a glass slide, the slide is lowered at an inclination of about 30° to the horizontal into a beaker of water. The Formvar foil floats off on the water, and is captured from the water surface across the slit of Fig. 1.

Vaporization upon this foil of the material to be studied is carried out in high vacuum by a convenient technique devised by Dr. W. H. Brattain of these Laboratories. A tungsten ribbon 4 mm wide and 125 mm long is bent lengthwise into a narrow V. This is cleaned by a preliminary heating in vacuum for 10 seconds at a current of 52 amp., corresponding to a temperature of slightly over 3000°K. The slit with its Formvar foil is supported horizontally at an appropriate distance, 14 to 35 cm, above this V-shaped ribbon, and material placed in the V of the ribbon is vaporized upon it by heating for 5 seconds at 40 amp., corresponding to about 2600°K. (Palladium was vaporized at 50 amp.)

Mean thickness t of a vaporized film prepared in this manner is calculated from the amount of material M, its density δ, and the distance l of the Formvar foil above the V-shaped ribbon, by means of the formula $t=kM/l^2\delta$. The value of the constant k was found to be 0.45 by direct calibration of the apparatus; this consisted of weighing the film deposited upon a horizontally placed glass slide of known area by evaporation of a known amount of material. The data of this calibration are written down in Table I. It is interesting to point out that the constant $k=0.45$ is about 50 percent greater than the value, $1/\pi$, which it would have if the Formvar foil were mounted parallel to a surface from which evaporation from a point source satisfied the cosine law.

TABLE I. *Calibration of vaporization apparatus.*

VAPORIZED MATERIAL	MASS M	DEPOSITED FILM AREA a	DIST. l	MASS m	$k=ml^2/Ma$
Gold	59.6 mg	6.4 cm²	7 cm	3.39 mg	0.435
Gold	59.6	6.4	14	0.89	0.457
Cs I	70.8	6.4	17.5	0.674	0.455

FILM THICKNESS AND MEAN CRYSTAL SIZE

Diffraction patterns have been obtained from more than 100 different films of 12 different substances. In Table II are given data relating to about half of these films; the elements or compounds are arranged from gold to beryllium in order of decreasing atomic numbers. For convenience of reference the various films are designated by numbers in column 2. Diffraction patterns from some of the films are reproduced in this paper; the figure numbers of these are given in column 3. In column 7 is the mean thickness of each film as calculated from the data of columns 4, 5 and 6 by means of the formula $t=0.45\times10^{-8}M/l^2\delta\,A$. For many of the films mean crystal sizes have been estimated from microphotometer curves of diffraction rings. Widths of rings at half-maximum are written down in column 9, and in column 11 corresponding estimates of crystal dimensions. Finally, in the last column are given the "*Strukturbericht*" designations of the types of crystal structure corresponding to diffraction patterns obtained from the various films.

Films of gold

Gold films of mean thickness 22A, 10A and 5.2A, described on the first three lines of Table II, gave diffraction patterns characteristic

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oriented crystals of $Ni(OH)_2$, which produced diffraction patterns that were very annoying. [L. H. Germer, Zeits. f. Krist. **100**, 277–284 (1938)].

[3] In a few cases foils of Resoglaz have been used. These are prepared from a benzene solution of Resoglaz in the same way Formvar foils are prepared from a chloroform solution of Formvar.

[4] K. B. Blodgett, J. Phys. Chem. **41**, 975–984 (1937).

TABLE II. *Films formed by vaporization.*

1	2	3	4	5	6	7	8	9	10	11	12
		FIGS.	M (MG)	l (CM)	δ (G/CC)	MEAN THICKNESS t (*A*)	MICROPHOTOMETER RING	MICROPHOTOMETER WIDTH (MM)	MEAN CRYSTAL DIMENSIONS (LOWER LIMIT) (*A*)	MEAN CRYSTAL DIMENSIONS (PROBABLE VALUE) (*A*)	STRUCTURE
Au (79)	1	2	1.88	14	19.3	22	422	0.70	33	50	*A*1
	2		1.88	21		10					*A*1
	3	3, 4	0.44	14		5.2	311	*1.3	—	30	*A*1
	4		0.30	14		3.6			Partly Amorphous		
	5		0.69 0.67	22 22		3.3 3.2			Partly Amorphous		
	6		0.44	21		2.3			Partly Amorphous		
	7	5	0.69 0.67	31 31		1.7 1.6			Partly Amorphous		
	8		0.30	21		1.6			Doubtful		
	9		0.36 0.35	24.5 24.5		1.4 1.4			Partly Amorphous		
	10		0.10	14		1.2			Doubtful		
	11		0.36 0.35	28.5 28.5		1.0 1.0			Partly Amorphous		
	12		0.10	21		0.5			No Gold		
CsI (55, 53)	13		7.06	25	4.51	113					*B*2
	14		7.06	35		57					*B*2
	15	6	1.87	25		30	510	0.27	87	200	*B*2
	16		1.87	35		15					*B*2
	17		0.28	19		7.7					*B*2
	18	7	0.28	27		3.8	310	0.38	62	150	*B*2
	19		0.15	24		2.6					*B*2
	20		0.15	29		1.8	211	*0.4	—	100	*B*2
Sb_2O_3 (51, 8)	21		4.0	16	5.67	124					
	22	9	0.4	14		16		0.35	67	150	
	23		0.45	25		5.7					
	24		0.45	35		2.9		*0.4	—	100	
Pd (46)	25		14	22.5	11.7	†53	220	0.66	35	50	*A*1
	26		3.5	22.5		†13	422	0.74	32	50	*A*1
	27		1.80	35		5.6					—
	28		0.70	30		3.0					—

* These values were estimated from visual comparisons with other patterns for which more satisfactory microphotometer curves were obtained.
† The palladium films 25 and 26 were formed upon Formvar foils inclined by 30° to the line of vaporization.

of face-centered cubic crystals, although the pattern from the thinnest of these is so diffuse that one could not identify it with certainty if it were not known to be due to gold. This pattern, and that from the film of 22A thickness, are reproduced as Figs. 3 and 2, respectively. These, and all other photographs of diffraction patterns, including Fig. 4, are reproduced here slightly larger than three-fourths full size.) From relative widths of diffraction rings in these figures it is clear that the mean crystal size was much smaller in the thinner film. (In these patterns the innermost diffuse rings are due to the supporting foil. These rings are more prominent in Fig. 3 than in Fig. 2 because of the longer exposure required to produce the pattern of the thinner gold film.) Diffraction patterns from even more tenuous gold films, numbers 4 to 12, are made up of rings which are still more poorly defined than those of Fig. 3.

In the case of four films, numbers 5, 7, 9 and 11, an artifice was used to strengthen the pattern from the gold relative to that from the Formvar supporting foil; gold was vaporized upon both sides of the Formvar so that the foil formed the center of a sandwich between layers of gold of equal mean thickness. In this way the intensity of the film pattern was sensibly doubled. The improvement is illustrated by the fact that patterns from films number 8 and 10, 1.6A and 1.2A thick, respectively, show only doubtful evidence of the presence of any gold at all and patterns from film number 12, 0.5A thick, are quite indistinguishable from those from Formvar

TABLE II.—*Continued.*

1	2	3 FIGS.	4 M (MG)	5 l (CM)	6 δ (G/CC)	7 MEAN THICKNESS t (A)	8 MICROPHOTOMETER RING	9 WIDTH (MM)	10 MEAN CRYSTAL DIMENSIONS (LOWER LIMIT) (A)	11 (PROBABLE VALUE) (A)	12 STRUCTURE
Cu (29)	29	16	7	16	8.92	138	200 220	0.56 0.52	42 45	100 100	*A*1 *C*3
	30	17	1.24	14		32					*C*3, *A*1
	31	18	1.24	21		14	220	1.2	19	25	*C*3
	32		0.36	14		9.3					*C*3
	33	19	0.36	21		4.1					*C*3
	34		0.39	29		2.3					*C*3
CuCl (29, 17)	35	10*A*	‡	17.5	3.53	180	422	0.22	107	250	*B*3
	36	10*B*	Same after 5 days				— 220	0.28 0.25	84 94	200 250	— *B*3
Ni (28)	37		3.38	25	8.90	27	311	1.0	24	30	*A*1
	38		3.38	35		14	—	1.5	15	20	—
CaF_2 (20, 9)	39	11	10	16	3.18	553	620	0.38	64	150	*C*1
	40		1.9	20		67					*C*1
	41		1.9	30		30	400	0.46	51	100	*C*1
Al (13)	42	20	1.27	14	2.70	108	422	0.40	59	100	*A*1
	43		1.27	21		48					*A*1
	44		0.33	14		28	220	0.44	53	100	*A*1
	45		0.33	21		12	Amorphous				—
Mg (12)	46		—	—	1.74	500	$21\bar{3}3$	0.35	67	150	*A*3
Na F (11, 9)	47	12	18	18	2.79	896	420	0.33	71	150	*B*1
	48	13*A*, *B*	3.0	20		121	420	0.33	71	150	*B*1
	49		3.0	30		54	420	0.34	69	150	*B*1
	50	14*A*, *B*	0.6	20		25	400	0.34	69	150	*B*1
	51	15	0.6	30		11					*B*1
	52		0.2	20		8	220	*0.5	39	100	*B*1
Be (4)	53		1.00	14	1.823	126	$10\bar{1}1$	0.55	43	100	*A*3
	54		1.00	21		56	$10\bar{1}1$	0.53	44	100	*A*3

* This value was obtained from visual comparison with other patterns for which more satisfactory microphotometer curves were obtained.
‡ The film of CuCl, number 35, was prepared by vaporization of 7.5 mg of $CuCl_2 \cdot 2H_2O$, which decomposes on heating to produce CuCl.

alone; yet patterns from the double films 7, 9 and 11, of comparable mean thickness, are fairly clear.

Patterns from film number 5, 3.3A of gold on one side of the Formvar foil and 3.2A on the other side, resemble Fig. 3 rather closely. There is, however, a difference; on patterns from film number 5 the (111) Debye-Scherrer ring is relatively much too strong. This is more marked on the pattern from film 7, reproduced as Fig. 5, and still more marked on patterns from films 9 and 11. On the latter patterns no trace can be found of the (200) Debye-Scherrer ring, although there are clearly defined diffuse rings corresponding to the Miller indices (311) and (331)/(420) and weak indications of two other rings corresponding to (422)/(333)/(511) and to (531)/(600)/(442).

The films which produced patterns on which the ring at the (111) position is exceptionally strong are described in Table II as "partly amorphous." These films certainly contained some exceedingly small crystals, but they also contained gold atoms which produced a diffraction pattern consisting chiefly of a single diffuse ring corresponding by the Bragg formula to a spacing of 2.3A [the (111) ring of gold]. Although the mean size of the exceedingly small crystals has not been estimated, it was certainly very much less than 25A; this conclusion is based on the fact that rings of a face-centered cubic structure are fairly clear and prominent

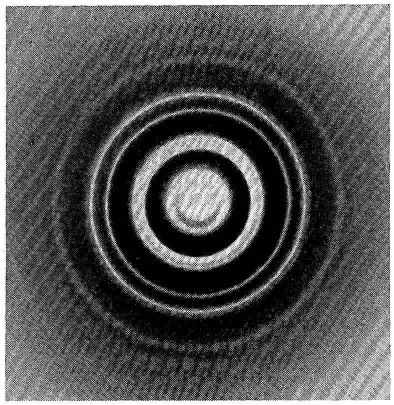


FIG. 2. Diffraction pattern from gold film of 22A mean thickness (number 1, Table II).

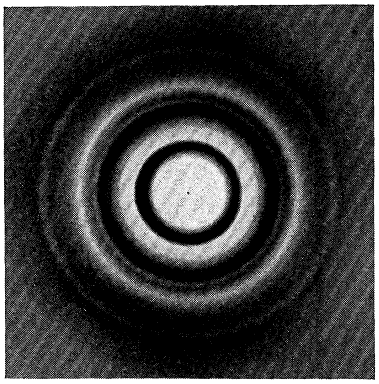


FIG. 3. Pattern from gold film of 5.2A mean thickness (number 3).

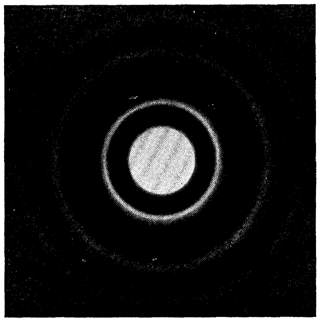


FIG. 5. Pattern from gold film number 7 (1.7A of gold on one side of Formvar foil and 1.6A of gold on the other side).

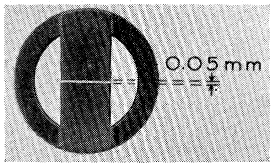


FIG. 1. Photograph of slit used as support.

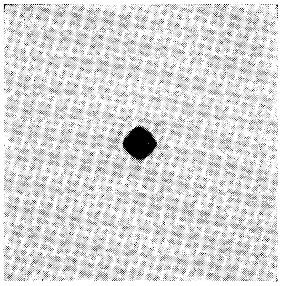


FIG. 4. Reproduction of the center of Fig. 3. enlarged 14.5 times, showing the shape of the primary electron beam.

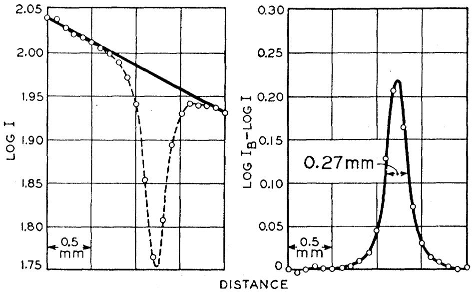


FIG. 8. Microphotometer curves of the (510) diffraction ring on the pattern from the caesium iodide film of mean thickness 30A (Fig. 6).

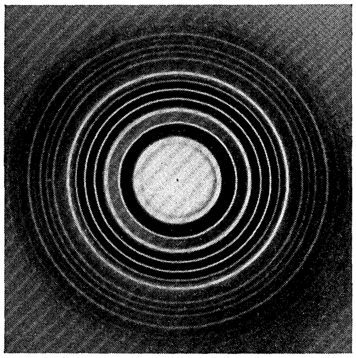


FIG. 6. Pattern at normal incidence from caesium iodide film of 30A mean thickness (number 15).

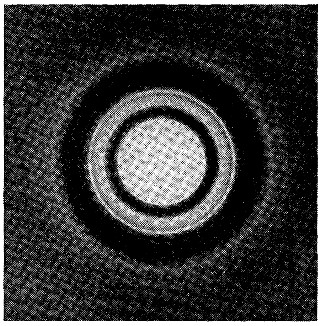


FIG. 7. Pattern at normal incidence from caesium iodide film of 3.8A mean thickness (number 18).

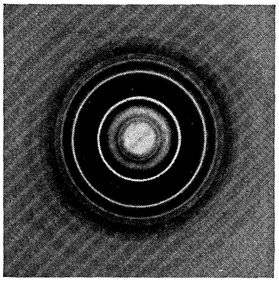
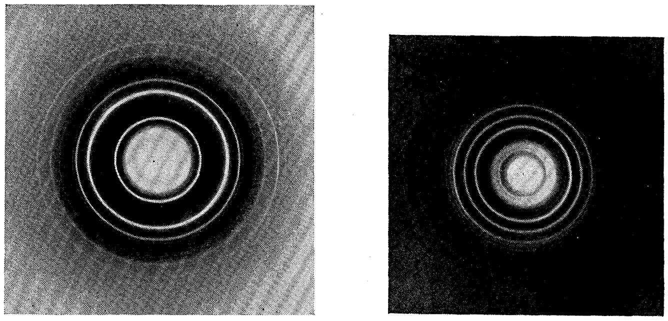


FIG. 9. Pattern at normal incidence from antimony oxide film of 16A mean thickness (number 22).



A B

FIG. 10. Patterns at normal incidence from cuprous chloride film of 180A mean thickness. A. Freshly prepared (number 35). B. After five days (number 36).

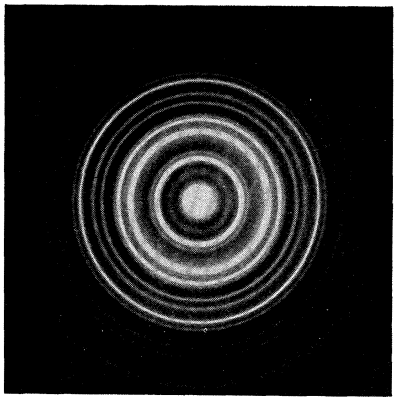


FIG. 11. Pattern at normal incidence from calcium fluoride film of 553A mean thickness (number 39).

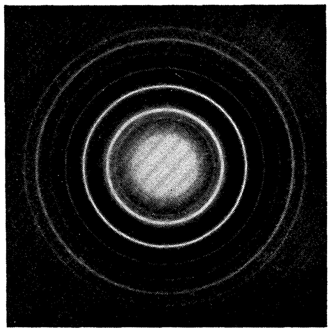
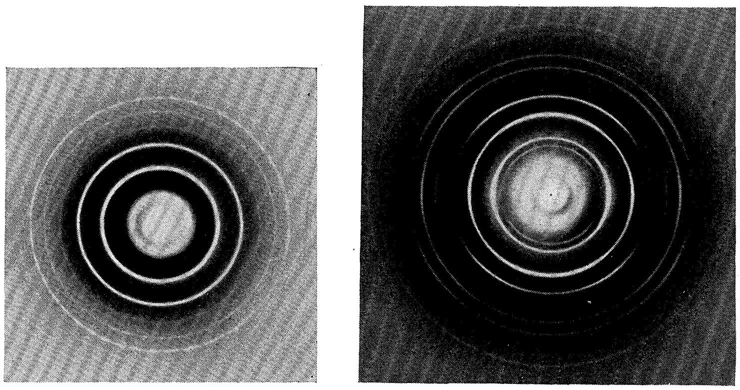
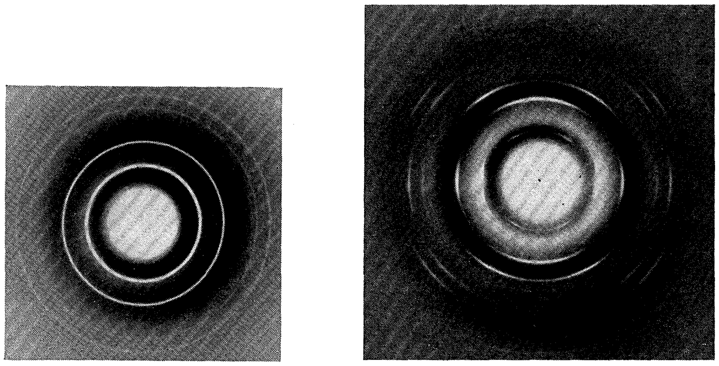


FIG. 12. Pattern at normal incidence from sodium fluoride film of 896A mean thickness (number 47).



A B

FIG. 13. Patterns from sodium fluoride film of 121A mean thickness (number 48). A. Normal incidence. B. 45° incidence (rotated about horizontal axis).



A B

FIG. 14. Patterns at normal incidence and at 45° incidence from sodium fluoride film of 25A mean thickness (number 50).

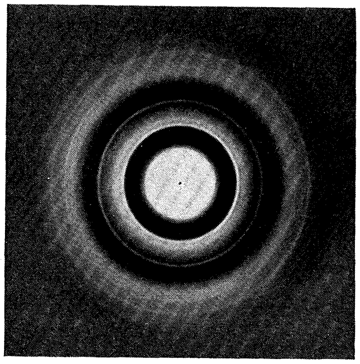


FIG. 15. Pattern at normal incidence from sodium fluoride film of 11A mean thickness (number 51).

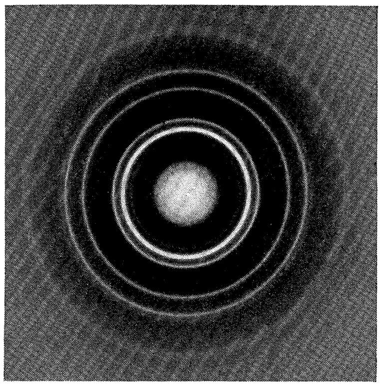


FIG. 16. Pattern from freshly prepared copper film of 138A mean thickness (number 29), showing the presence of some cuprous oxide.

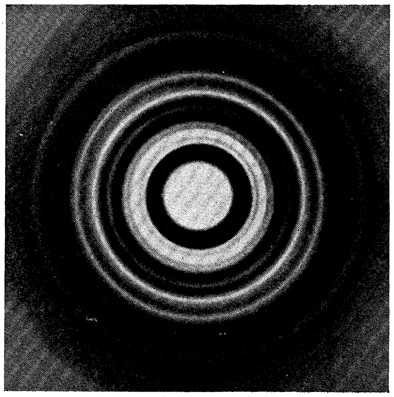


FIG. 17. Pattern from freshly prepared copper film of 32A mean thickness (number 30), showing rings due to oxide and rings due to copper of about equal strengths.

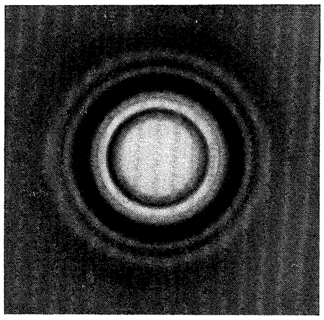


FIG. 18. Pattern from freshly prepared copper film of 14A calculated mean thickness (number 31), showing only rings due to oxide.

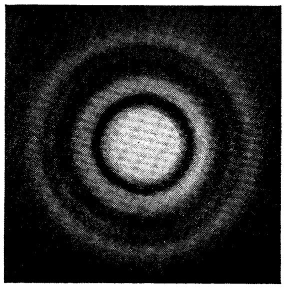


FIG. 19. Pattern from copper film of 4.1A mean thickness (number 33). Rings due to oxide can still be identified.

on a pattern from a film of cuprous oxide only 2.3A thick in which the mean crystal size was less than 25A (film number 34).

The average size of the crystals in directions normal to the primary beam is calculated from broadening of diffraction rings by means of the Scherrer formula. For fast electrons this formula can be written in the approximate form $C=L\lambda/\Delta R$, where C is the mean crystal size normal to the primary beam, $L\lambda=2.3\times10^{-6}$ mm^2 is the product of the specimen-plate distance and the electron wave-length, and ΔR is that part of the width of a diffraction ring at half-maximum attributable to finite size of crystals.

To determine mean crystal size one must measure widths of diffraction rings and must know the size of the primary electron beam at the photographic plate. The latter can be photographed directly, but this is often unnecessary; on a diffraction pattern obtained from a very thin film, which requires a relatively long exposure, the spot where the primary beam strikes the plate is reversed and the shape of the beam can sometimes be seen clearly at the center of the pattern. This spot appears at the center of Fig. 3, and in Fig. 4 the same spot is reproduced again after an enlargement of 14.5 times.

It is interesting to compare the spot of Fig. 4 with that to be expected from the electron optical system which produced the primary beam. Electrons from a tungsten filament were accelerated up to a square pinhole, which has vertical and horizontal edges 0.1 mm long, and beyond this they traveled for 84 cm in a space free from electric fields passing through a

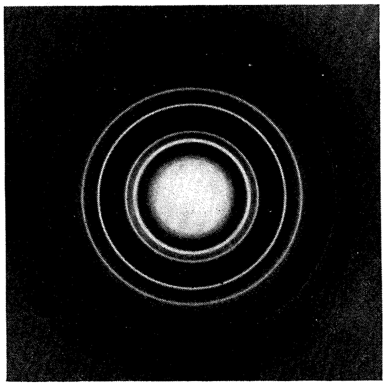


FIG. 20. Pattern from aluminum film of 108A mean thickness (number 42).

magnetic focusing coil located at a point one fourth the distance from pinhole to photographic plate.[5] If the optical system had been perfect the image of the pinhole on the plate would have been enlarged by a factor of approximately three and would have been somewhat rotated; thus the spot of Fig. 4 would have been a square with a side of $0.1 \times 3 \times 14.5 = 4.3$ mm, and diagonal of $4.3\sqrt{2} = 6.1$ mm. Measurement of the actual spot gives a diagonal of 6 mm, with the sides of the square bulged outward to make it somewhat barrel-shaped. This deformation was undoubtedly due to imperfection of the electron optical system.

The primary beam spot on the photographic plate is usually much smaller than that of Figs. 3 and 4, and is not approximately square. This would not be possible if the primary pinhole were a "diffuse" source of electrons. If, however, electrons came through the pinhole along parallel lines, as they do approximately, the hole would be analogous to an aperture illuminated by an infinitely distant source of light. It would then be possible for the magnetic electron lens to bring the electrons to a point focus. It is apparent from a number of observations of the primary electron beam that this condition was usually more nearly realized than was the formation of a true image of the pinhole. When the spot was extremely small it was always found to have a badly distorted shape which must have been due primarily to the fact that some electrons coming through the pinhole were moving in directions inclined to the line of motion of most of them.

Although size and shape of the primary beam were often noted no systematic observations were carried out. Thus estimates of mean crystal size from widths of diffraction rings are subject to this added uncertainty. In column 10 of Table II are given values of mean crystal size calculated directly by the Scherrer formula from widths of rings at half-maximum (column 9), and in column 11 values of crystal size calculated after the width at half-maximum has been reduced by the amount which is crudely guessed to be the size of the primary beam.

The gold films 1 and 3 are estimated in this manner to have been made up of crystals of mean size 50A and 30A, respectively. These crystals were randomly oriented, and the mean dimension normal to the film surface was in each case about the same as parallel to it. These conclusions were reached from comparisons of patterns obtained with the films inclined by 45° to the primary beam direction and normal to it; it was found that these patterns are identical.

Films of some inorganic compounds

Many films of inorganic compounds that have been examined have produced diffraction patterns made up of rings which are sharper than those from films of gold. Although this is not true of all compounds studied (for example, silicon dioxide, lead oxide and barium borate), it is true of those written down in Table II. Rings of the patterns of Figs. 6 and 7 from caesium iodide films are, for example, much sharper than those of any of the patterns from gold. The mean thicknesses of the films that produced these patterns were, respectively, 30A and 3.8A. A diffraction pattern was obtained from each film with the primary beam inclined by 45° to the surface normal as well as parallel to it. The patterns obtained at 45° are made up of rings along which intensities vary somewhat, indicating slight preferential orientation among the caesium iodide crystals. These rings are, however, as far as one can judge, of perfectly uniform width. This uniformity proves that the mean crystal size was in each case about the same in the plane of the film and in directions inclined to it by 45°. Thus in both of these films, and in all the other caesium iodide films as well, the crystals had about the same mean dimension in all directions.

Microphotometer curves were obtained from the (422), (510), (521), (440), (530) and (600)/(442) rings on the pattern of Fig. 6, and from the (211), (220) and (310) rings on the pattern of Fig. 7. One of these curves, from the (510) ring of the pattern of Fig. 6, is reproduced as Fig. 8. On the left are plotted as ordinates logarithms of the light intensity transmitted through the photographic plate, and at the right differences between these values and the background curve which is drawn in on the curve at

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[5] This is the diffraction camera which was described earlier [L. H. Germer, Rev. Sci. Inst. **6**, 138–142 (1935)], modified by the addition of the magnetic focusing arrangement and by some minor changes.

the left. The width at half-maximum is found to be 0.27 mm which agrees fairly well with values obtained from microphotometer curves of other rings of this pattern. The microphotometer curve of the (310) ring of the pattern of Fig. 7 has a width at half-maximum of 0.38 mm. These values, and ring widths of patterns from other films, are written down in column 9 of Table II, and the ring upon which each of the measurements was made is designated in column 8 by its Miller indices. In most cases the values obtained were checked by measurements upon other rings as well. In measurements upon very thin films it was necessary in each case to choose rings for which the diffuse rings due to Formvar do not introduce large errors into measured widths. Representative diffraction patterns were chosen for measurement; those which were not measured have rings of comparable widths.

The diffraction rings of Figs. 6 and 7, as well as those of patterns from other caesium iodide films, are somewhat narrower at half-maximum than the total width of the primary beam of Fig. 3. It seems clear that the beam must have been narrower when these patterns were obtained, and the estimated mean crystal dimensions of 200A and 150A given in column 11 take this into account. The diffraction pattern from the thinnest caesium iodide film, number 20 of mean thickness 1.8A, is not reproduced here because the diffraction rings from the Formvar supporting foil are relatively so very prominent that the rings from caesium iodide are unsuitable for exhibition purposes. These rings are, however, very sharp and correspond to crystals about 100A on a side both in the plane of the film and normal to it.

In Fig. 9 is reproduced a diffraction pattern obtained at normal incidence from a film of antimony oxide, film number 22 of mean thickness 16A. The rings of this pattern are extremely narrow and correspond to mean crystal dimensions of about 150A in the plane of the film. A pattern from the same film obtained with the primary beam inclined by 45° to the surface normal differs from that of Fig. 9 in two respects; the diffraction rings are no longer of uniform intensities around their circumferences, indicating a slight degree of preferential orientation among the crystals, and the widths also are not uniform. Along the diameter of the pattern that is parallel to the axis about which the film was rotated, the diffraction rings are as narrow as in Fig. 9, but along the diameter of the pattern at right angles to this the rings are definitely wider, although still rather sharp. From comparisons with other patterns it appears that these greater widths correspond to a mean crystal dimension of somewhat less than 100A in directions at 45° to the surface normal. Presumably the mean dimension normal to the film was still smaller by the factor, cos 45°, making this dimension equal to 50A or a little more. Thus the average dimensions of antimony oxide crystals in film number 22 were 150A in the plane of the film, and about 50A normal to it. Other antimony oxide films produced diffraction patterns which were not greatly different, indicating that crystals in all of them had slight preferential orientations and were, on the average, considerably thinner normal to the film surfaces than parallel to them.

Patterns from films of other compounds, cuprous chloride, calcium fluoride and sodium fluoride, appear in Figs. 10–15. These films and others formed from the same compounds are found to have been made up of large crystals, of the order of 100A or 200A on a side, even in those cases in which the average film thickness was very much less than 100A. Each of the cuprous chloride and sodium fluoride films was composed of crystals having nearly the same mean dimension normal to the film and parallel to it, although crystals are randomly oriented in one case and sharply oriented in the other. Some calcium fluoride films, on the other hand, produced diffraction rings at 45° incidence which, although apparently uniform in intensity, are not uniform in width. The patterns indicate that although these crystals were randomly oriented they were on the average lamellar in shape with the small dimension normal to the film.

The patterns from the thinnest films of caesium iodide and sodium fluoride are not exhibited here because these are less intense than the superposed patterns from the Formvar foils and would not show up well in reproduction. Because of the greater scattering power of caesium fluoride relative to sodium fluoride, patterns from thinner films of the former can be reproduced. Thus one sees that the rings produced by the caesium iodide film 3.8A thick (Fig. 7) have about the same intensity relative to the Formvar pattern as have the rings from the 11A film of sodium fluoride (Fig. 15). Assuming that the Formvar foils were of equal thickness, as they were approximately, one concludes that the caesium iodide and sodium fluoride films had equal scattering powers. This experimental observation can be checked. Consider rings of about the same diameters on the two patterns, corresponding to the same multiplicity of crystal planes, and for each of which the two sorts of atoms of its structure scatter in phase. If the crystal size in each film is assumed uniform the intensities of such rings will be proportional to $I=n^2Z^2/N$, where n is the number of atoms in a film, Z their atomic number and N the number of crystals in the film. For the caesium iodide film, $n=8.0\times10^{14}$ atoms per cm², $Z=54$ (the mean of 55 and 53) and N is proportional to the thickness, 3.8A; for the sodium fluoride film, $n=8.8\times10^{15}$ atoms per cm², $Z=10$ (the mean of 11 and 9) and N is proportional to the thickness, 11A (assuming that the crystal size is the same in the two films, as it is approximately). The ratio of intensities of the two rings is then

$$I_{\mathrm{CsI}}/I_{\mathrm{NaF}}=(8.0\times10^{14})^2(54)^2/3.8 \div(8.8\times10^{15})^2(10)^2/11=0.7,$$

which agrees well enough with the crudely estimated ratio of unity.

Films of metals

Many metal films have given diffraction patterns made up of rings much broader than those from any of the ionic compounds in Table II, and some very thin metal films have produced patterns which have not been interpreted.

The two thickest palladium films (numbers 25 and 26) produced rings characteristic of a face-centered cubic structure with ring widths about the same as those from gold films of comparable mean thickness. (See Fig. 2.) Patterns from the two thinnest palladium films (numbers 27 and 28) are made up of rather broad rings which have not yet been interpreted.

Interesting diffraction patterns were obtained from freshly formed copper films of various thicknesses. The pattern of Fig. 16, from film number 29 of 138A mean thickness, corresponds to two different sets of randomly oriented cubic crystals with spacings and intensities appropriate, respectively, to copper and to cuprous oxide. From relative intensities one estimates that about 15 percent of the film was oxide and the rest metallic copper. On the pattern from film number 30 of mean thickness 32A, Fig. 17, the rings due to copper and those due to oxide are of about equal intensity. Films number 31 and 33 of mean thickness, respectively, 14A and 4.1A gave diffraction patterns, Figs. 18 and 19, corresponding to cuprous oxide only. In the thicker of these films the average crystal size was about 25A, and in the thinner film considerably smaller. Rings corresponding to the structure of cuprous oxide can be seen clearly even in the pattern from film number 34 which was only 2.3A thick, although the pattern from the Formvar foil is in this case too prominent for good reproduction.

The thicker nickel film (number 37) produced diffraction rings agreeing with the face-centered cubic structure of metallic nickel, but the pattern from the thinner film (number 38) is not yet understood. Rings on both of these patterns are very broad and the nickel crystals in the thicker film were only slightly larger than those in the gold film which produced the pattern of Fig. 3.

Aluminum films gave diffraction rings, attributable to face-centered metallic aluminum, which are sharper than those produced by gold, palladium, copper or nickel. Rings from an aluminum film only 28A thick, number 44, seem to be just as sharp as those from a film 108A thick, which are reproduced in Fig. 20. A thinner film of aluminum only 12A thick (number 45) seemed to be entirely amorphous, due perhaps to the formation of amorphous Al_2O_3.

Excellent diffraction patterns were obtained from films of magnesium and beryllium. These patterns correspond to large randomly oriented crystals which have the hexagonal structures of the bulk metals. With even the thinnest Formvar foils, which can be handled at present, satisfactory patterns cannot be obtained from beryl-

TABLE III. *Orientation and crystal shape in various films.*

	Degree of Orientation	Variation of Degree of Orientation with Thickness	Crystal Shape
CsI	Slight	Same for all thicknesses	Equiaxed
Sb_2O_3	Slight	Same for all thicknesses	Lamellar
Cu_2O (formed from unoriented Cu crystals)	None	———	Equiaxed
CuCl	None	———	Equiaxed
Cu compound (formed from unoriented CuCl crystals)	Very marked	?	?
CaF_2	None	———	Sometimes Lamellar
NaF	Marked	Varying with thickness	Equiaxed

lium films much thinner than 50A because of the low scattering power of beryllium atoms.

CRYSTAL ORIENTATION

In some aluminum films there was a slight preference for orientation of crystals with a (111) plane parallel to the film. Except for this, no preferential orientation of crystals was found in any of the metal films studied. In films of inorganic compounds, crystals were entirely unoriented in some cases and sharply oriented in others.

Crystals were unoriented in films of cuprous oxide (numbers 31 to 34), cuprous chloride (number 35) and calcium fluoride (numbers 39 to 41). There was a slight preference for a particular orientation in caesium iodide films (numbers 13 to 18) and in antimony oxide films (numbers 21 to 23), and for both substances the degree of orientation did not vary perceptibly with thickness. Diffraction patterns from sodium fluoride indicate that crystals in many of these films were markedly oriented (with a (100) plane tending to lie parallel to the film surface). Orientation which seemed to be still sharper was discovered in an unidentified compound which was formed when cuprous chloride stood in air for several days. (Fig. 10B from film number 36 exhibits many diffraction rings of this compound in a pattern at normal incidence.)

Crystals in the thickest sodium fluoride film (number 47, 896A thick) were unoriented, as they were also in the thinnest films (numbers 51 and 52); the sharpest orientation occurred at a thickness of 25A, Figs. 14A and 14B. The variation of degree of orientation with thickness can be followed by observing relative intensities of various diffraction rings in patterns obtained at normal incidence; the (222) and (422) rings have normal intensities in Figs. 12 and 15, they are somewhat weaker in Fig. 13A, still weaker in a pattern at normal incidence from film number 49, and entirely missing in Fig. 14A. The degree of orientation is, however, more strikingly exhibited by patterns at 45° incidence, such as the patterns of Figs. 13B and 14B. A pattern at 45° incidence from the film of intermediate thickness, number 49, exhibits orientation of an intermediate degree of sharpness.

One might think that marked orientation would occur for crystals of lamellar shape, thinner normal to the film surface than parallel to it, and that randomly oriented crystals would tend to have the same mean dimension in different directions. From the collected data of Table III it appears, however, that there is no such correlation. Some lamellar crystals, thin normal to the film, were unoriented (CaF_2), and some crystals which had the same mean dimension in different directions, designated as "equiaxed," were oriented (CsI and NaF).

INTENSITY ANOMALIES

No abnormalities have been observed in *positions* of rings on any of the diffraction patterns which have been interpreted.[6] There is,

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[6] It has been stated that in some films made up of extremely small crystals the size of the unit cell does not have the normal x-ray value [G. I. Finch and S. Fordham, Proc. Phys. Soc. **48**, 85–94 (1936); E. Pickup, Nature **137**, 1072 (1936)]. Although I have observed no such anomaly, many of my measurements have not been of sufficient precision to detect the small variations which have been reported.

Quarrell has stated that films produced by vaporization of metals, which normally form face-centered cubic crystals, are sometimes rhombohedral and sometimes hexagonal however, a curious and unexplained anomaly in the *intensity* of a diffraction ring in patterns from films of cuprous chloride and similar anomalies have been found for a calcium fluoride film.

In patterns from other materials no anomalies are apparent. The diffraction rings obtained from caesium iodide at normal incidence seem, for example, to have normal relative intensities as was to be expected because of the slight degree of orientation of crystals in these films. This is illustrated by data relating to the pattern from caesium iodide film number 15, which are collected in Table IV.

In the first two columns of Table IV are written down measured diameters and estimated intensities of the 11 smallest rings on the pattern of Fig. 6. In the next three columns are given Miller indices of the first 20 rings to be expected from crystals of caesium iodide, values of $H=h^2+k^2+l^2$, and values of p the number of cooperating planes. In the sixth column are values of $S=[\mathrm{Cs}]+[\mathrm{I}]\cos\pi(h+k+l)$ characteristic of the caesium iodide structure; here $[\mathrm{Cs}]=(Z-F)_{\mathrm{Cs}}/H$ where Z is the atomic number of caesium and F represents values of the x-ray atomic structure factor taken from the tables of Pauling and Sherman,[7] and $[\mathrm{I}]=(Z-F)_{\mathrm{I}}/H$, the corresponding function for iodine. The calculated diameters are obtained from the relation $D=2L\lambda H^{\frac{1}{2}}/a$, where $a=4.56\times10^{-7}$ mm is the x-ray value for the edge of the unit cube of the caesium iodide structure[8] and $L\lambda=2.345\times10^{-6}$ mm^2 is the independently determined value of the product of the specimen-plate distance and the electron wave-length. Intensities in the last column of Table IV are values of S^2p multiplied by the arbitrary factor 3×10^{-2} so that they can be more conveniently compared with estimated intensities given in the second column. It is clear that positions and relative intensities of rings of the pattern of Fig. 6 agree well with the calculated values. (Nearly equally good agreements are obtained if one omits the F function and writes $[\mathrm{Cs}]=Z_{\mathrm{Cs}}$ in the expression for S and then uses, for the intensity, values of the function S^2p/H. This simple procedure was used in an earlier paper.[2])

TABLE IV. *Measured and calculated diameters and intensities for* CsI.

FIG. 6 MEASURED DIAMETERS (MM)	FIG. 6 ESTIMATED INTENSITIES (ARBITRARY SCALE)	*hkl*	*H*	*p*	*S*	CALCULATED DIAMETERS (MM)	CALCULATED INTENSITIES (ARBITRARY SCALE)
—	—	100	1	3	0.4		0.01
14.7	10	110	2	6	10.3	14.5	19.
—	—	111	3	4	0.3		0.01
20.5	5	200	4	3	7.4	20.6	4.9
—	—	210	5	12	0.2		0.01
25.3	9	211	6	12	5.7	25.2	11.7
29.0	5	220	8	6	4.8	29.1	4.1
—	—	300	9	3	0.07		0.0004
32.5	6	310	10	12	4.2	32.5	6.4
—	—	311	11	12	0.05		0.0009
35.6	3	222	12	4	3.9	35.6	1.8
—	—	320	13	12	0.03		0.0003
38.5	8	321	14	24	3.4	38.5	8.3
41.1	1	400	16	3	3.2	41.1	0.9
—	—	410	17	12	0.04		0.0006
43.7	4	330/411	18	18	3.0	43.6	4.9
—	—	331	19	12	0.04		0.0006
46.0	3	420	20	12	2.7	46.0	2.6
—	—	421	21	24	0.04		0.001
48.2	3	332	22	12	2.5	48.3	2.3

TABLE V. *Estimated and calculated intensities for* CuCl *and for* $\mathrm{CaF_2}$.

hkl	CUPROUS CHLORIDE INTENSITIES ESTIMATED (FIG. 10A)	CUPROUS CHLORIDE INTENSITIES CALCULATED	CALCIUM FLUORIDE INTENSITIES ESTIMATED (FIG. 11)	CALCIUM FLUORIDE INTENSITIES CALCULATED
111	9	6.3	8	7.8
200	—	0.02	*3	0.4
220	10	9.5	10	14.7
311	6	7.0	6	6.4
222	*2	0.03	*2	0.02
400	2	2.3	4	3.8
331	5	4.0	4	3.1
420	—	0.3	—	0.0002
422	5	5.6	6	10.9
511/333	2	3.4	3	2.3
440	1	1.9	1	2.9
531	2	3.8	3	2.3
600/442	—	0.4	—	0.02

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in structure—[A. G. Quarrell, Proc. Phys. Soc. **49**, 279–293 (1937)]. This I have not found. One observation regarding the Quarrell paper should be made. In this paper Fig. 4, a diffraction pattern from a film of copper produced by evaporation, is described as due to rhombohedral crystals and the ratios of the spacings corresponding to the second, third, fourth and fifth rings to the spacing corresponding to the smallest are given (Table II) as 0.855, 0.590, 0.499 and 0.476. I have measured diameters on the reproduction and obtained for the first five rings 17.8 mm, 20.7 mm, 29.2 mm, 34.2 mm and 35.8 mm. The ratios of the first of these to the others are 0.860, 0.610, 0.521 and 0.497. Corresponding ratios for face-centered cubic crystals are $(3/4)^{\frac{1}{2}}=0.866$, $(3/8)^{\frac{1}{2}}=0.612$, $(3/11)^{\frac{1}{2}}=0.522$ and $(3/12)^{\frac{1}{2}}=0.500$.

[7] L. Pauling and J. Sherman, Zeits. f. Krist. **81**, 1–29 (1932).

[8] W. P. Davey, Phys. Rev. **21**, 143–161 (1923); G. L. Clark and W. Duane, Phys. Rev. **21**, 380 (1923).

In the case of patterns from cuprous chloride and calcium fluoride measured and calculated values of ring diameters agree equally well, but for some rings measured and calculated intensities do not agree. Data illustrating these disagreements are given in Table V. For cuprous chloride $S^2 = X^2 + Y^2$, where $X = 4[\mathrm{Cu}] \cos \frac{1}{2}\pi(2h+k+l) \cos \frac{1}{2}\pi(h+2k+l) \cos \frac{1}{2}\pi(h+k+2l) + 4[\mathrm{Cl}] \cos \frac{1}{2}\pi h \cos \frac{1}{2}\pi k \cos \frac{1}{2}\pi l$, and $Y = -4[\mathrm{Cl}] \sin \frac{1}{2}\pi h \sin \frac{1}{2}\pi k \sin \frac{1}{2}\pi l$; for calcium fluoride $S = 4[\mathrm{Ca}] \cos \frac{1}{2}\pi(2h+k+l) \cos \frac{1}{2}\pi(h+2k+l) \cos \frac{1}{2}\pi(h+k+2l) + 8[\mathrm{F}] \cos \frac{1}{2}\pi h \cos \frac{1}{2}\pi k \times \cos \frac{1}{2}\pi l$. (In these expressions, as in the corresponding expression for caesium iodide, the symbols in the square brackets represent values of the function $(Z-F)/H$.) The calculated intensities written down in Table V are values of $S^2 p$ multiplied by the arbitrary factors, 3×10^{-2} for cuprous chloride, and 5×10^{-2} for calcium fluoride.

It is clear from Table V that the (222) diffraction rings from cuprous chloride and from calcium fluoride are about 100 times as strong as expected, and the (200) ring from calcium fluoride about 10 times as strong. (Asterisks are used in the table to call attention to these extraordinary intensities.) Anomalous strength of (222) reflections has been observed in patterns from a great many different cuprous chloride films, some of which were prepared by the direct reaction of copper and chlorine. Some calcium fluoride films have, however, given rings having more nearly normal intensities; the (440) ring is then stronger and appears normal. No explanation of these phenomena has yet been found.[9]

Some Applications

Crystal growth in thin films

It has been pointed out that in many of the thinner films the dimension of the average crystal in a direction normal to the film was much greater than the mean film thickness. Molecules of caesium iodide and antimony oxide, for example, formed relatively large three-dimensional crystals in films of mean thickness less than that of one molecular layer, and molecules of cuprous chloride, calcium fluoride and sodium fluoride formed large crystals in the thinnest films studied. These observations prove that atoms or molecules, deposited by vaporization, were able to move about on the surface of the Formvar foil and that they actually agglomerated into three-dimensional crystals, in many cases leaving a large fraction of the foil completely bare.

Diffusion of atoms upon surfaces has been deduced from measurements of resistance of extremely thin metal films,[10] from thermionic[11] and photoelectric measurement[12] upon composite surfaces, and from optical observations.[13] It is clear that electron diffraction offers an additional and rather direct method of investigating this type of diffusion.[14] The work reported here was, however, not undertaken with this in mind. Although the deductions which can be drawn from it are naturally extremely fragmentary, it is probably worth while to review some of them.

From Table II one sees that the ionic compounds studied (excepting only cuprous oxide produced from copper) form considerably larger crystals than the metals, and if one looks up melting points it appears that there is a tendency for low melting point substances to form larger crystals than those having high melting points. In films of ionic compounds mean crystal size varies only moderately with film thickness, whereas in gold films crystal size varies greatly with thickness. A test could not be carried out upon extremely thin films of palladium, copper, nickel or aluminum because all of these metals apparently formed chemical compounds, of which only cuprous oxide has been identified. In none of the experiments was there any control of the temperature of a film during vaporization, and

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[9] Intensity anomalies in electron diffraction patterns from zinc oxide have been observed and explained by H. J. Yearian, Phys. Rev. **48**, 631–639 (1935). It is not clear, however, that the abnormalities reported here can be interpreted in a similar way.

[10] E. T. S. Appleyard, Proc. Phys. Soc. **49**, Extra Part, 118–135, (Aug. 31, 1937).

[11] W. H. Brattain and J. A. Becker, Phys. Rev. **43**, 428–450 (1933).

[12] R. C. L. Bosworth, Proc. Roy. Soc. **A150**, 58–76 (1935).

[13] E. N. daC. Andrade and J. G. Martindale, Phil. Trans. Roy. Soc. **235**, 69–100 (1935).

[14] J. Krautkrämer [Ann. d. Physik **32**, 537–576 (1938)] has recently used electron diffraction to investigate films of metals deposited upon quartz by vaporization. He has concluded, in agreement with the observations of the present paper, that crystals of appreciable size occur even in the thinnest films.

those films which were only 14 cm from the V-shaped tungsten ribbon must have been much warmer than those at 35 cm. The only quantitative datum is furnished by knowledge of the softening point of Formvar supporting foils, about 250°C; it seems almost certain that this temperature was never exceeded.

The data seem to prove that molecules of the ionic compounds studied were able to move rather freely over Formvar surfaces, and that crystals of these compounds smaller than about 100A on a side were unstable, losing molecules to larger crystals by diffusion. It seems probable that for any compound upon any surface there is in general a critical temperature below which diffusion will not occur,[10] which may, of course, in some cases be above the melting point of the surface. Above this critical temperature there may be a minimum crystal size which is just stable, this size being probably a function of temperature.

The electron diffraction method seems well suited to investigation of the diffusion of molecules over surfaces, and to discovering the relation between temperature and minimum size of crystal. The first experiments might well be the condensation of extremely thin caesium iodide films upon Formvar held at various low temperatures, followed by investigation of crystal size in these films. These experiments might be followed by similar studies of caesium iodide upon beryllium surfaces. Some preliminary and as yet unsatisfactory studies of gold upon beryllium have already been made.

Corrosion and chemical change

Chemical change occurring in thin films can be followed by electron diffraction examination. The chemical and crystalline nature of new compounds formed can often be determined, and quantitative data obtained regarding rate of change.

A study of this sort has been made of a copper film, number 29, 138A thick. From a diffraction pattern produced by the freshly prepared film, Fig. 16, one concludes that about 15 percent of the film was cuprous oxide. After exposure to the air of an ordinary room for 12 days, another pattern was obtained which indicated that the film was then about 50 percent oxide. The oxidation of the copper has now been followed for nearly a year. The amount of oxide varied approximately as the square root of the time, until the film was completely oxidized.

Other studies of copper corrosion under carefully controlled conditions are in progress and under consideration. Corrosion of films of a number of other metals is also being investigated.

Electron diffraction methods can equally well be applied to the examination of chemical changes which cannot be classed as corrosion. In some cases more detailed information can be obtained than one can get in any other way. An example is furnished by the incompleted study of the change of cuprous chloride into some other compound on standing in air. (Films number 35 and 36, Figs. 10A and 10B.) The cuprous chloride crystals are large and completely unoriented. They change into other crystals which are equally large and very sharply oriented. It seems likely that the new compound will be identified in the near future, and that interesting and perhaps valuable information will be obtained regarding the mechanics of the chemical reaction involved.

I am indebted to Mr. W. E. Campbell and Dr. W. H. Brattain for valued advice and assistance. The corrosion studies were undertaken with Mr. Campbell's help and some of them are now being carried out under his direction. The first vaporized films were prepared for me by Dr. Brattain and his method has proved generally useful. I am also indebted to Drs. C. J. Davisson and W. Shockley for many instructive discussions, and to Mr. H. G. Wehe, Mr. K. H. Storks and Mr. A. J. Parsons for assistance with some of the experimental work.

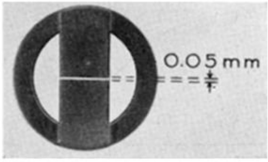
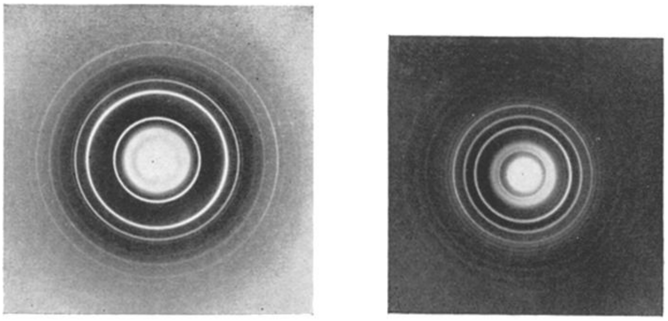


FIG. 1. Photograph of slit used as support.



A B

FIG. 10. Patterns at normal incidence from cuprous chloride film of 180A mean thickness. A. Freshly prepared (number 35). B. After five days (number 36).

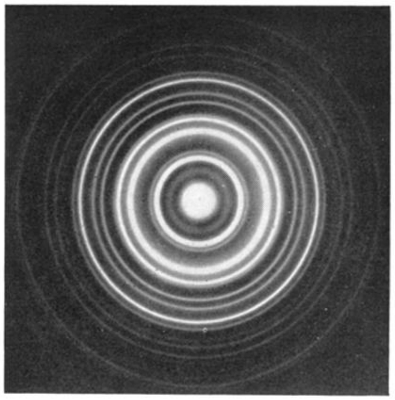


FIG. 11. Pattern at normal incidence from calcium fluoride film of 553A mean thickness (number 39).

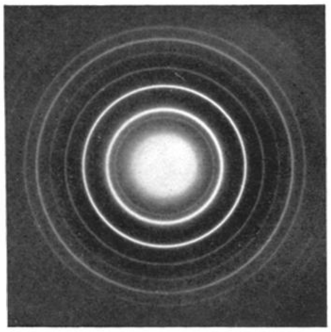
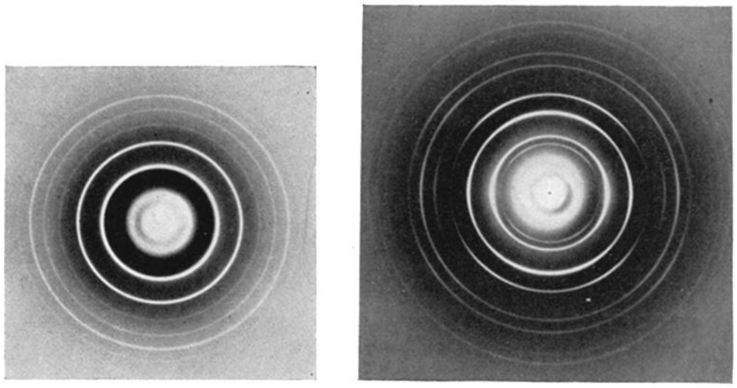


FIG. 12. Pattern at normal incidence from sodium fluoride film of 896A mean thickness (number 47).



A B

FIG. 13. Patterns from sodium fluoride film of 121A mean thickness (number 48). A. Normal incidence. B. 45° incidence (rotated about horizontal axis).

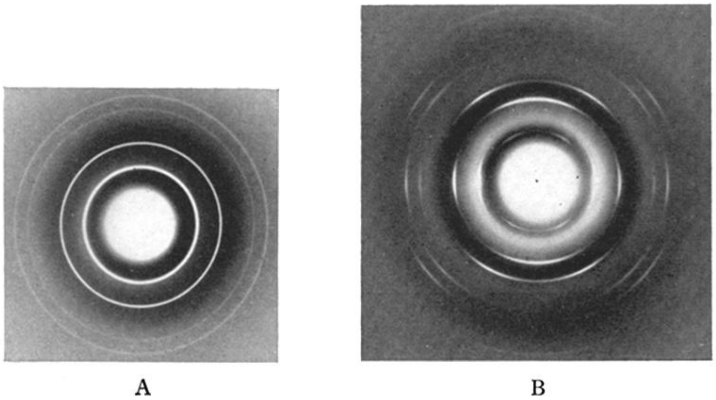


FIG. 14. Patterns at normal incidence and at 45° incidence from sodium fluoride film of 25A mean thickness (number 50).

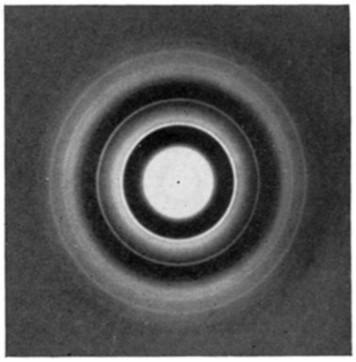


FIG. 15. Pattern at normal incidence from sodium fluoride film of 11A mean thickness (number 51).

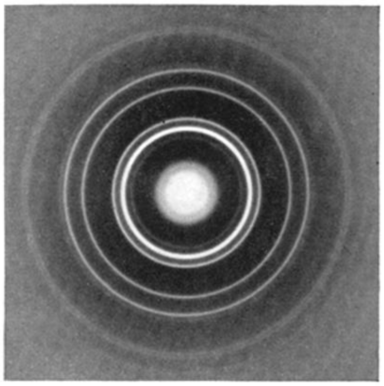


FIG. 16. Pattern from freshly prepared copper film of 138Å mean thickness (number 29), showing the presence of some cuprous oxide.

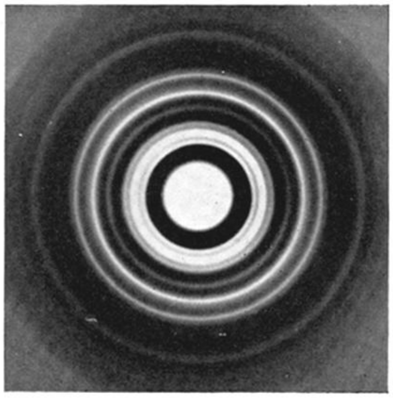


Fig. 17. Pattern from freshly prepared copper film of 32Å mean thickness (number 30), showing rings due to oxide and rings due to copper of about equal strengths.

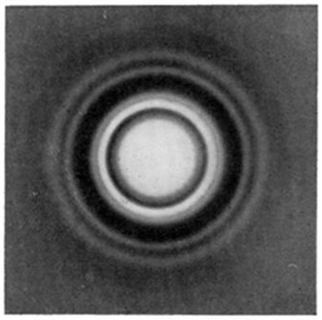


Fig. 18. Pattern from freshly prepared copper film of 14Å calculated mean thickness (number 31), showing only rings due to oxide.

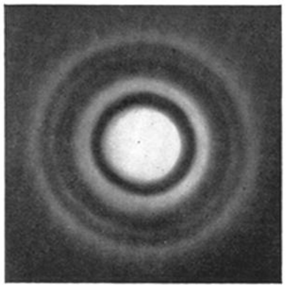


FIG. 19. Pattern from copper film of 4.1A mean thickness (number 33). Rings due to oxide can still be identified.

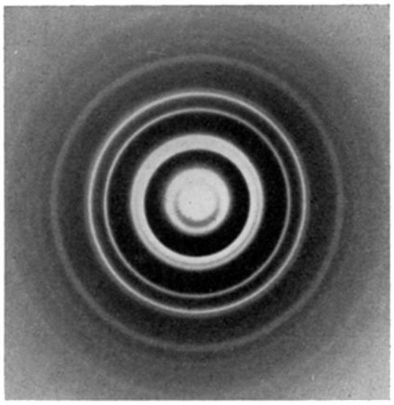


FIG. 2. Diffraction pattern from gold film of 22A mean thickness (number 1, Table II).

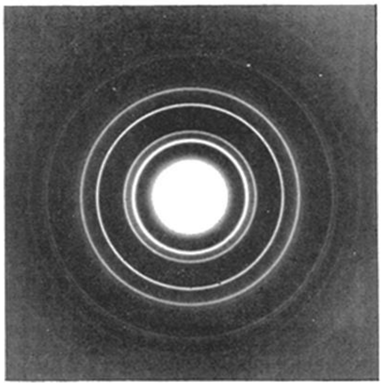


Fig. 20. Pattern from aluminum film of 108A mean thickness (number 42).

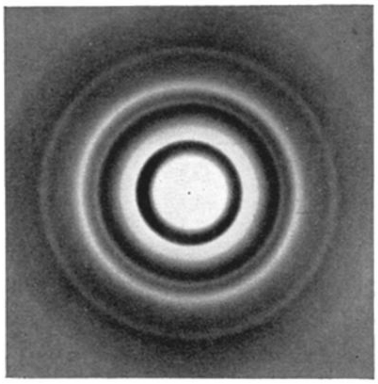


FIG. 3. Pattern from gold film of 5.2A mean thickness (number 3).

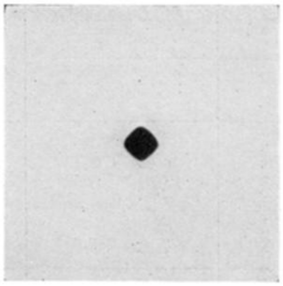


FIG. 4. Reproduction of the center of Fig. 3. enlarged 14.5 times, showing the shape of the primary electron beam.

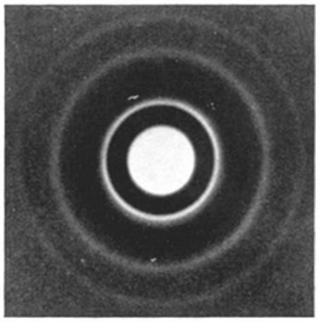


FIG. 5. Pattern from gold film number 7 (1.7A of gold on one side of Formvar foil and 1.6A of gold on the other side).

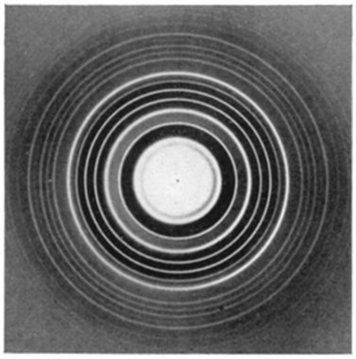


Fig. 6. Pattern at normal incidence from caesium iodide film of 30Å mean thickness (number 15).

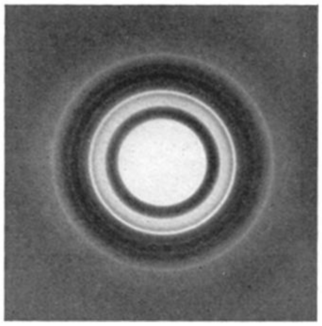


FIG. 7. Pattern at normal incidence from caesium iodide film of 3.8A mean thickness (number 18).

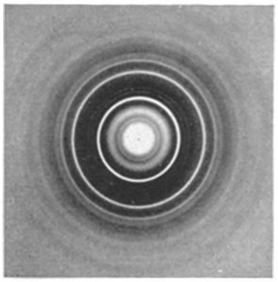


Fig. 9. Pattern at normal incidence from antimony oxide film of 16A mean thickness (number 22).