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Citation: *J. Chem. Phys.* **5**, 252 (1937); doi: 10.1063/1.1750015

View online: <http://dx.doi.org/10.1063/1.1750015>

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The Primary Oxide Film on Iron

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(Received January 11, 1937)

The identity and structure of the invisible, air-formed oxide film on iron has never been determined although the practical importance of a knowledge of its properties in the study of corrosion has been demonstrated. Electron diffraction experiments are now reported which show this film to be structurally identical with Fe_3O_4 . In addition, it is found that the oxide has a definite orientation relationship with the underlying iron, viz., the $[\sqrt{2}10]$ directions in the oxide crystals are parallel to the $[111]$ directions in the iron. Freshly abraded surfaces of electro-

lytic and ingot iron were investigated. Evaporated films of electrolytic iron were prepared in the diffraction camera and pictures taken before and after exposure to air show that Fe_3O_4 forms rapidly in dry air at room temperature. An air pressure of 10^{-3} mm for a few minutes gave a measurable effect. Exposure to air at atmospheric pressure for periods longer than a few minutes does not greatly strengthen the oxide pattern. The factors affecting the sensitivity of this method of examining thin films on metals are discussed.

INTRODUCTION

THE existence of an air-formed oxide film on freshly cleaned iron surfaces has been suspected for a long time. Because a knowledge of the structure and properties of such a film is of practical as well as fundamental importance, a number of investigations have been undertaken during the last ten years. Vernon¹ demonstrated the practical effect of the primary oxide film in retarding the corrosion rate of iron. He found that clean iron exposed to filtered air acquired an invisible protective film which greatly diminished the rate of rusting when exposed to ordinary atmospheric air. Freundlich, Patscheke and Zocker² used optical methods to study the effect of air on iron mirrors prepared by the thermal decomposition of iron carbonyl. Mirrors prepared in a vacuum displayed considerable chemical activity but on exposure to air for less than 10 sec. they acquired a passivity which was not lost on reevacuation to pressures of 10^{-4} mm. They concluded that the passivity was the result of an oxide film about 10A thick. More recently Tronstad and Höverstad³ have made optical measurements on polished iron surfaces which they conclude are covered with a natural oxide film at least 20A thick. Using gravimetric methods, Vernon⁴ found that the oxide film formed by heating in air below 200°C is struc-

turally different from that formed at higher temperatures. Electron diffraction pictures substantiated this conclusion and gave Fe_2O_3 for the high temperature form and Fe_3O_4 for the oxide formed on heating at temperatures below 200°C .

No one has reported the application of electron diffraction to the study of natural oxide films on iron, but the method has been used successfully by Steinheil⁵ and Beeching⁶ to detect air-formed oxide films on evaporated aluminum, by Riedmiller⁷ on evaporated nickel, and by Finch and Quarrell on zinc.⁸ Since there is reason to believe that the natural oxide film is somewhat thicker on iron than on any of these metals, it seemed likely that the method might be successfully applied to iron. Moreover, electron diffraction pictures of freshly cleaned pieces of fairly pure iron exhibited extra bands which could not be attributed to impurities and which suggested the presence of an oxide film. The present work was undertaken, therefore, to study the structure of the primary oxide film formed on evaporated iron when exposed to dry air at room temperature, and to compare the results with the diffraction patterns observed on massive iron.⁹ Although some of the samples were heated in air to moderate temperatures, no attempt has been

¹ W. H. J. Vernon, *Trans. Faraday Soc.* **23**, 159 (1927).

² H. Freundlich, G. Patscheke and H. Zocker, *Zeits. f. physik. Chemie* **128**, 321 (1927); **130**, 289 (1927).

³ L. Tronstad and T. Höverstad, *Zeits. f. physik. Chemie* **170**, 172 (1934).

⁴ W. H. J. Vernon, *Trans. Faraday Soc.* **31**, 1670 (1935).

⁵ A. Steinheil, *Ann. d. Physik* **19**, 465 (1934).

⁶ R. Beeching, *Phil. Mag.* **22**, 938 (1936).

⁷ R. Riedmiller, *Zeits. f. Physik* **102**, 408 (1936).

⁸ G. I. Finch and A. G. Quarrell, *Proc. Phys. Soc.* **46**, 148 (1934).

⁹ A preliminary announcement of some of these results has appeared in *Nature* **139**, 30 (1937).

made to follow structural changes as a function of time and temperature. Heating was used simply as an auxiliary process to aid in the analysis of films formed at room temperature.

This investigation is a part of a general program designed to discover and develop useful metallurgical applications of the electron diffraction technique. Since the primary oxide film is the real starting point in studies of the corrosion and oxidation of ferrous materials, the present work forms an important part of such a program. The thinness of the films affords a sensitivity test of the method, and the factors which affect this sensitivity are discussed in some detail.

EXPERIMENTAL

The diffraction camera is similar to that described by Thomson and Fraser¹⁰ with a hot cathode substituted for the discharge tube. Rectified and filtered a.c. provides a constant accelerating potential. Voltages of 30 to 40 kv were used with a sample-to-plate distance of 40 cm. The grazing incidence or "reflection" method was used.

The evaporated films were prepared by evaporating pieces of electrolytic iron from a small electrically heated tungsten helix placed about 8 cm from the receiving surface in the specimen chamber of the camera. Although the vacuum system was not provided with a vacuum gauge, the pressure during evaporation was 10^{-4} mm or less as estimated from a test discharge tube attached to the system. The evaporation time ranged from a few seconds to a minute or more depending on the rate and the thickness of the desired deposit. Immediately after evaporation the freshly formed film could be moved into position to take a picture after which it was necessary to open the camera in order to change plates. From 4 to 7 min. were required to raise the system to atmospheric pressure, change plates and pump down to working pressure again. The samples were at atmospheric pressure only one to two minutes, the remainder of the time being required to raise and lower the pressure. Air and other gases were always admitted to the camera through a calcium chloride

drying tube. The evaporated iron was deposited on glass, quartz, iron and platinum surfaces. Various cleaning methods were used in preparing the glass and quartz plates. The simple technique of washing with soap and water, rinsing in distilled water and drying on a clean cloth seemed to be quite as effective as the more elaborate cleaning methods which were tried. No diffraction effects were detected which could be attributed to differences in the cleaning process.

Most of the massive iron samples were in the form of small rectangular blocks cut from ingot iron (Armco) of the following analysis:

	Percent
Carbon	0.02
Manganese	0.03
Phosphorus	0.019
Sulphur	0.026
Copper	0.05

A few samples were cut from annealed sheets of electrolytic iron. The specimens were cleaned by grinding all six surfaces before the final abrading process which is described in another section. Care was taken not to contaminate the surfaces with grease from the hands or other sources.

RESULTS

Evaporated iron—random orientation

Fig. 1 is the pattern obtained from a thin iron film evaporated under conditions which give nearly random orientation of the crystallites. The trace of this plate made on a Moll recording microphotometer is reproduced in Fig. 4A. Immediately after this picture was taken air at room temperature was admitted to the camera through the drying tube, and plates were changed. The picture taken directly thereafter is shown in Fig. 2, and Fig. 4B is the corresponding microphotometer curve. Fig. 4C is the curve obtained after the film had been exposed to air for several hours. It is apparent that exposure to air produces two obvious changes in the diffraction pattern. In the first place the background scattering is increased causing the iron rings to appear fainter, and, secondly, new rings appear in the form of two broad bands. One of these falls well within the (110) iron ring while the other is just inside the (200) ring and is usually

¹⁰ G. P. Thomson and C. G. Fraser, Proc. Roy. Soc. **A128**, 641 (1930).

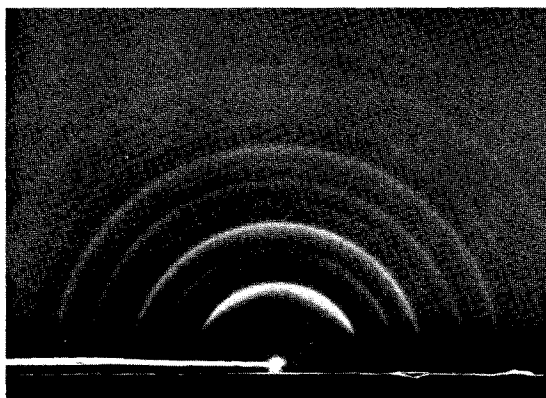


FIG. 1. Freshly evaporated film; random orientation; not exposed to air.

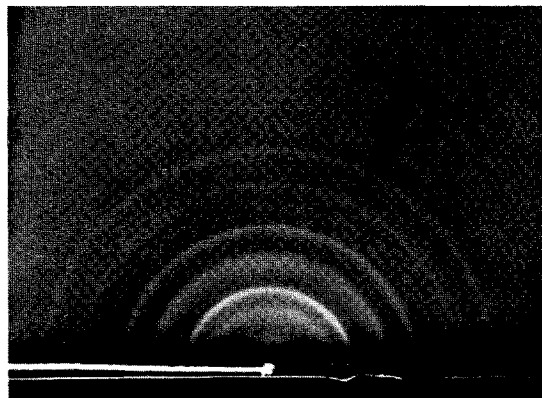


FIG. 2. Same film as Fig. 1 after exposure to air for several minutes.

not resolved therefrom. The pattern changes very little after the first few minutes of exposure to air. Over a period of a few hours there is a slight increase in the background scattering accompanied by a very slight increase in the intensity of the bands relative to the iron rings. Additional exposure to dry air up to 3 months produces no significant change.

Massive iron

If a flat iron surface is ground on successively finer grades of emery paper ending with No. 4/0, two types of surface can be obtained depending on the treatment given during the final stage. One type which we shall call an *abraded* surface is produced if the final stage consists of exerting light pressure on the sample as it is moved over unused areas of the emery paper. A different type which, for present purposes, is called a *burnished* surface is obtained if the final rubbing is carried out with greater pressure on the specimen, or if it is rubbed over used portions of the abrasive surface. Both of these processes break the surface up into successively smaller crystal fragments. The final step in the preparation of an abraded surface, however, is designed to leave the tops of ridges very thin and sharp, whereas in a burnished surface they are broad and rounded.

It is necessary, as first pointed out by Thomson,¹¹ that in the "reflection" type of diffraction the electrons must enter and leave the surface at the sides of ridges or projections. We would

expect, therefore, that a finely abraded surface with its sharp, jagged ridges composed of fine crystal fragments will yield a better reflection pattern than will a burnished surface. This expectation has been confirmed in a large number of plates taken during the course of the present work. Severely burnished surfaces give the well-known diffuse ring pattern which has been attributed by some investigators to a surface layer of amorphous metal.¹² Less severe burnishing gives a faint iron ring pattern superimposed on an intense background. Finely abraded surfaces, however, yield fairly sharp iron rings on a relatively weak background. In addition, the patterns from finely abraded surfaces contain two diffuse rings or bands in exactly the same positions as those which appear when evaporated

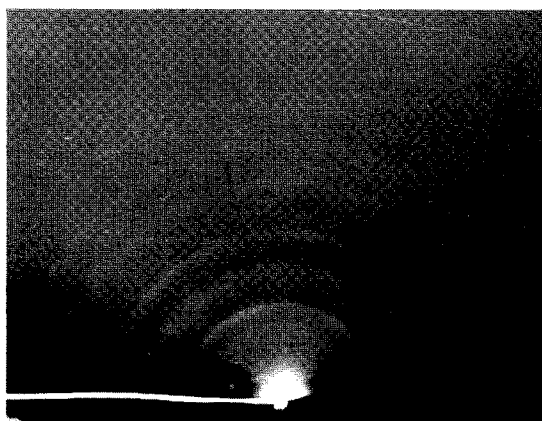


FIG. 3. Abraded ingot iron.

¹¹ G. P. Thomson, Proc. Roy. Soc. A128, 750 (1930).

¹² G. I. Finch and A. G. Quarrell, Nature, 137, 516 (1936).

films are exposed to air (see Figs. 2, 3, and 4). The microphotometer record of such a pattern from an abraded piece of ingot iron is shown in Fig. 4D. The similarity between this curve and those from air-exposed evaporated films is apparent.

A number of control experiments were performed to eliminate the possibility that the bands might be due to particles of abrasive left imbedded in the surface. Some abrasive deliberately left on one sample gave a very faint, spotted ring pattern whose maxima did not coincide with the bands. No trace of this abrasive pattern has been observed on lightly abraded samples.

Interpretation of the bands

Fig. 5 is a graphical representation of iron and iron oxide diffraction patterns plotted against spacings which were calculated from accepted crystal structure data. The averages of visual measurements on a number of plates from air-exposed evaporated films are given in Fig. 4D while plot E is a similar representation of patterns obtained from abraded iron. It is apparent that the observed patterns cannot be attributed to $\alpha\text{-Fe}_2\text{O}_3$ but are in good agreement with Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ superimposed on the normal iron pattern.¹³ The very small crystal size indicated by the lack of resolution of the strong oxide rings is discussed in a later section.

In an attempt to strengthen the oxide pattern, a number of samples were heated in air at 200°C and the changes in the film were followed by taking pictures at frequent intervals. In general when an abraded sample is heated, the iron rings fade out quickly and the bands become stronger without resolution into their component rings. The surface film first becomes visible after about 2 hrs. at 200°C and simultaneously traces of $\alpha\text{-Fe}_2\text{O}_3$ appear. Evaporated films behave similarly when heated except that usually there is a tendency for the bands to be resolved into the separate Fe_3O_4 rings before giving way to other oxide patterns.

Oriented evaporated films

During the course of this investigation, a marked tendency toward preferred orientation

¹³ Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have unit cells which are identical in size, and they are virtually indistinguishable by diffraction methods.

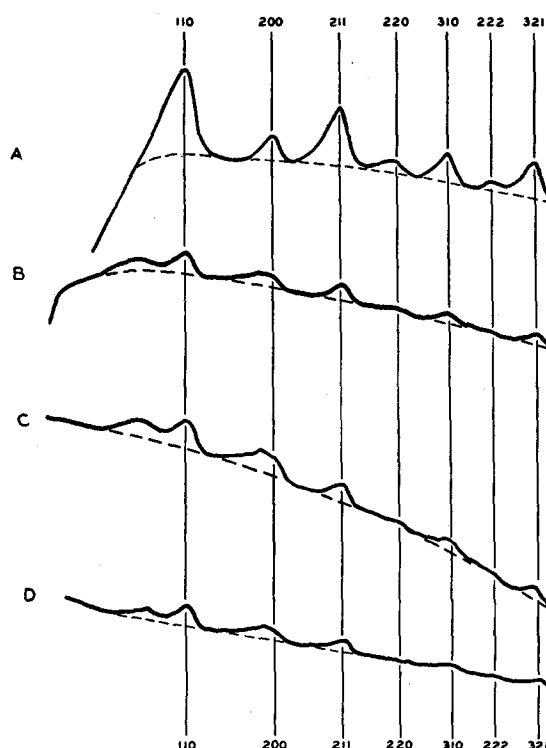


FIG. 4. Microphotometer curves. A, freshly evaporated film; B, same film after exposure to air for several minutes; C, after exposure for a few hours; D, abraded ingot iron surface.

of the evaporated films was observed. Neither the explanation of this effect nor the conditions which produce it are well understood and further work on that problem is under way.¹⁴ For present purposes, however, it is sufficient to say that the individual iron crystals tend to orient themselves with their [111] directions parallel to the direction along which the approaching iron atoms travel. In other words the [111] directions point toward the tungsten helix from which the iron came. It has been possible, therefore, to study the air-formed oxide layer on evaporated films whose [111] directions made nearly any desired angle with the surface. We shall limit our discussion to the orientation which is simplest to interpret, *viz.*, that in which the fiber axis, [111], is perpendicular to the electron beam and to the surface of the sample. In such a case the (111) planes will be parallel to the surface, and the rings corresponding to various orders of (111) reflections will show maxima in a direction

¹⁴ Beeching has recently found a somewhat similar effect in evaporated aluminum films. See reference 6.

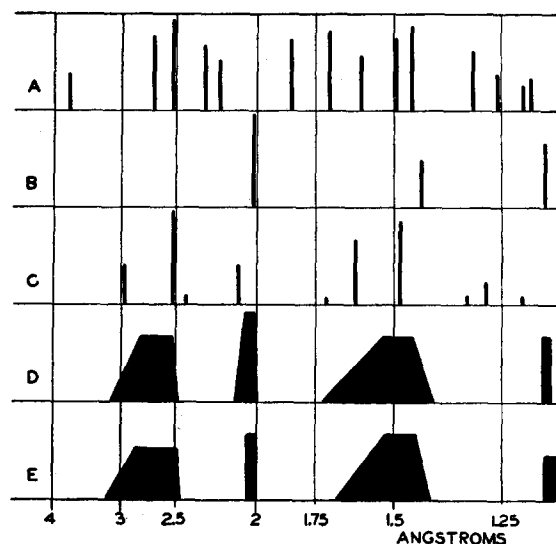


FIG. 5. Calculated and observed iron and iron oxide patterns. Calculated patterns: A, α - Fe_2O_3 ; B, α -iron; C, Fe_3O_4 . Observed patterns: D, air-exposed evaporated film; E, abraded iron. Heights of lines indicate relative intensities.

normal to the plane of the sample. Since the Bragg angles are small ($\theta < 3^\circ$), the normal to any plane which is in a position to reflect must be very nearly perpendicular to the incident beam. It follows, therefore, that the angle ϕ measured on the plate between radii from the central spot to the maximum corresponding to the oriented plane ($h_1k_1l_1$) and the maximum due to another plane ($h_2k_2l_2$) is equal to the angle between these two planes in the crystal. Thus we have

$$\cos \phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{[(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)]^{1/2}}$$

Since we are dealing with cubic crystals, the indices in this equation may be considered as Miller indices of planes or as directional indices of the normals to the corresponding planes.

A pattern from an iron film oriented with $[111]$ directions nearly perpendicular to the surface is shown in Fig. 6. All the maxima due to iron fall on well-defined layer lines which measure the distance between atoms in $[111]$ rows. Data from the iron pattern on this plate are given in Table I. The radius, r , of the plate is given in the first column while the next two columns give a comparison between values of ϕ calculated for $[111]$ orientation and the observed values. The agree-

ment is well within the error of measurement. This particular picture also contains maxima which do not fall on the layer lines, in particular an intense, elongated spot between the first and second layer lines at $\phi=0$ and others inside the first layer line. These are due to air-oxidation which took place when a slight leak developed immediately after evaporation. The pressure in the camera rose to a value which probably did not exceed 10^{-3} mm for a period of not over 5 min. Immediately thereafter plate 835 was taken. The history of this particular sample is given in Table II, and numerical data from the resulting pictures are presented in Table III.

Even before heating an oriented film, the various reflections are resolved because of the different angular positions of the maxima. Consequently the two diffuse bands observed on randomly oriented films can now be separated into their component reflections, as is indicated in the first three columns of Table III. Since, however, there was no observable change in the position and relative intensities of the oxide maxima as a result of heating, it follows that the primary oxide film is identical, as regards crystalline form and orientation, with the oxide film after heating. Therefore the complete analysis of the oxide pattern as given in Table III is made from the heated film with the assurance that the results apply to the primary film.

The observed reflections and their relative intensities are in good agreement with the pattern to be expected from Fe_3O_4 or γ - Fe_2O_3 . The observed value of a_0 is 8.38 Å as compared with the x-ray value of 8.374 Å.

Examination of a large number of oriented films leads to the conclusion that the oxide crystals are always oriented with the same crystallographic direction parallel to the Fe $[111]$ direction and that this relationship is independent of the angle the Fe $[111]$ direction makes with the surface. Inspection of the plates and an approximate calculation indicated that this direction in the oxide has the form $[hkl]$ where $h/k \approx 1.4$ and $l \ll h$ or $l=0$. If $l \neq 0$, reflections from the form (hhh) would in general have 4 maxima in a quadrant instead of 2 as observed, the form $(hh0)$ would show 6 maxima instead of 4, etc. Measurements on the plate cannot be made precisely enough to exclude the possibility

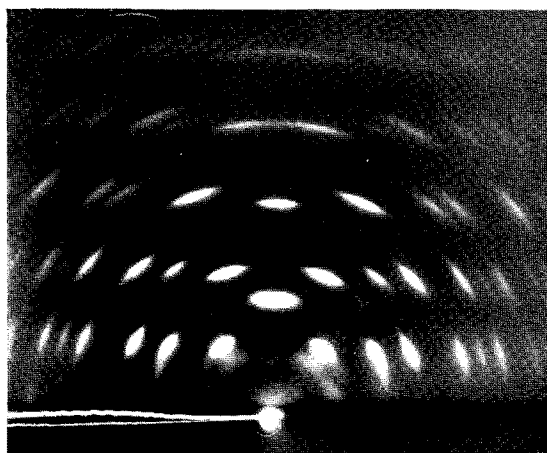


FIG. 6. Plate 835. Oriented film slightly exposed to air.

that l is small compared with h and k as, for example $[21, 15, 1]$. Since, however, there is no reason for believing the orientation relationship to be complex rather than simple, we conclude that $l=0$. Careful measurements on several plates give $h/k=1.40\pm0.05$. This includes the possibility of $[\sqrt{2}10]$ for which the values of ϕ , calculated to the nearest degree, are given in the last column of Table III. In comparing the observed and calculated values, it must be remembered that the shadow of the sample obscures maxima at large values of ϕ . The innermost reflections are cut off at about 55° while maxima on the outer rings cannot be measured accurately above 75° . If we start with a film in which the Fe $[111]$ direction is inclined to the surface but is set perpendicular to the beam, larger values of ϕ can be measured on one side of the line of symmetry on the plate. On such plates satisfactory agreement between observed and calculated values of ϕ has been found over a complete quadrant.

Miscellaneous experiments

In order to determine the complete spacial orientation relationship by this method it would be necessary to make a film in which the iron crystals are oriented about some axis other than $[111]$. Attempts to obtain such a film have failed. One method which was tried consisted of electroplating a thin layer of iron onto a piece of ingot iron. The plated film was indeed highly oriented but again with $[111]$ directions perpendicular

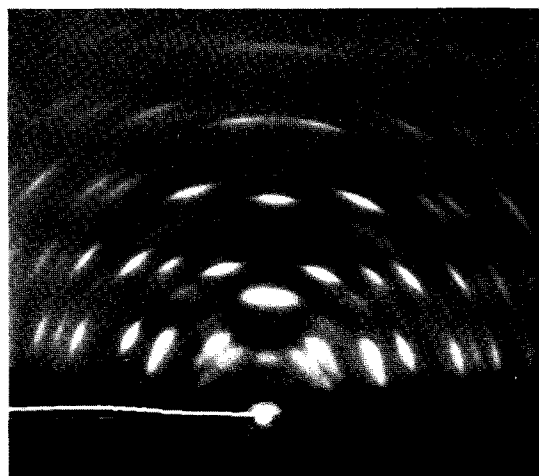


FIG. 7. Plate 836. Oriented film air-exposed for 2 min.

FIG. 8. Plate 839. Oriented film heated in air at 200°C for 15 min.

to the surface. In every respect the oxide patterns observed on this specimen, before and after heating, were like those on the evaporated films. In this case, however, there is some doubt as to how much of the initial oxidation took place before it was dry and how much was truly air-formed.

Most of the evaporated films were formed on glass, but some were deposited on quartz, platinum or iron surfaces. As might be expected the base has no apparent effect on the primary oxide film.

Some of the evaporated films were exposed to gases other than air. Ordinary commercial tank

hydrogen, oxygen, and carbon dioxide were used without purification. Brief exposure to any one of the three gave strong oxide patterns and no differences which could be considered significant were observed. Since oxygen is present as an impurity in both the hydrogen and carbon dioxide, it is probable that the oxygen partial pressure was appreciable during the exposure.

One transmission sample of evaporated iron, randomly oriented and 400 to 600 Å thick was tried. Even after exposure to air for several days there was only a faint trace of the inner oxide band.

Attempts to obtain abraded iron surfaces free from oxide films have not been successful. A sample abraded under benzene showed oxide bands exactly like dry abraded surfaces. The oxidation may have taken place during the abrading process or after the benzene evaporated. A scheme for abrading samples in the camera under a good vacuum is needed to test this point.

DISCUSSION

Using x-rays, Mehl, McCandless and Rhines¹⁵ have found a definite orientation relationship between crystals of FeO and the single crystal of iron on which they were grown by high temperature oxidation. Fe₃O₄ crystals which formed on partial decomposition of the FeO phase were found to be identically oriented with the FeO. The resulting orientation relationship between iron and Fe₃O₄ is therefore exactly that existing between iron and FeO which is described as follows: the cube or (100) plane in the oxide is

parallel to the (100) plane in the iron; the [110] direction in the (100) plane of the oxide is parallel to the [100] direction in the (100) plane of the iron.

When any two cubic crystals have this orientation relationship, the [111] directions in one are parallel to $[\sqrt{2}10]$ directions in the other. It is apparent, therefore, that the orientation relationship between iron and the air-formed oxide is the same as that which exists between iron and cubic iron oxides formed at high temperatures. Mehl and McCandless¹⁵ have pointed out that this orientation is reasonable on the basis of matching atomic positions in the cube faces.

The determination of particle size from the breadth of the diffraction rings is subject to many errors which could not be readily controlled. The diffraction patterns indicate that a wide range of particle sizes is involved. Neglecting geometrical and other factors which contribute to ring width, a rough calculation indicates that most of the crystals are larger than 15 Å. This figure is probably too small and in any case it gives no clue to the thickness of the oxide films. Finer particle sizes probably favor greater oxide penetration due to attack along grain boundaries.

The sensitivity of the electron diffraction method in detecting and examining thin films, such as these oxide films, merits consideration. The relatively low background intensity which is observed on patterns from evaporated films indicates that the surfaces must be exceedingly rough on an atomic scale with many small crystals projecting above the mean surface level in positions to yield a relatively high fraction of coherently scattered electrons. On exposure to

TABLE I. *Oriented iron pattern. Plate 835.*

r (CM)	ϕ OBSERVED (DEGREES)	ϕ CALCULATED [111] ORIENTATION	hkl	$h^2 + k^2 + l^2$	r $(h^2 + k^2 + l^2)^{1/2}$
1.29	34	35 90	110	2	0.912
1.82	56	55	200	4	.910
2.22	19 62	19 62 90	211	6	.907
2.55	34	35 90	220	8	.902
2.86	43 68	43 69	310	10	.905
3.13	0 70	0 70	222	12	.904
3.38	21 52 72	22 52 72 90	321	14	.904
3.62	56	55	400	16	.905
3.84	35 57 75	{ 57 74 35 90 330 }	{ 411 330 }	18	.905
4.05	39 75	39 75	420	20	.905
4.24	7 60 76	10 60 76	332	22	.904

$\lambda = 0.0649 \text{ Å}$; $L = 40.0 \text{ cm}$; $a_0 = (\lambda L/r)(h^2 + k^2 + l^2)^{1/2} = 2.87 \text{ Å}$; Accepted x-ray value: 2.8607 Å.

¹⁵ R. F. Mehl, E. L. McCandless and F. N. Rhines, *Nature* **134**, 1009 (1934); Mehl and McCandless, *Nature*, **137**, 702 (1936).

TABLE II. *History of an oriented evaporated film.*

TREATMENT	PLATE NO.	RESULTS
Evaporated film exposed to air pressure of 10^{-3} for 5 min.	835	Strong iron pattern, highly oriented Faint oxide pattern, highly oriented
Film exposed to dry air at atmospheric pressure for 2 min.	836	Iron pattern slightly fainter. Oxide pattern much stronger. Orientation the same.
Further exposure to dry atmospheric air for 14 hrs.	837	Very little change.
Sample in air at 200° for 15 min.	839	Iron pattern completely gone. Oxide maxima stronger and sharper with orientation unchanged.

TABLE III. *Diffraction data, oriented oxide film. Relative intensities: sss, very, very strong; ss, very strong; s, strong; m, medium; f, faint; ff, very faint; fff, very very faint.*

PLATE NO. 835	836	837	839						
d/n	d/n	d/n	d/n	Rel. Int.	a_0	ϕ Observed	$h^2+k^2+l^2$	hkl	ϕ Calculated [$\sqrt{2}10$] Orientation
3.05	3.01	2.95	2.98	<i>s</i>	8.42	6 53—*	8	220	10 55 66 80
2.51	2.56	2.52	2.52	<i>ss</i>	8.35	24 38 53—	11	113	24 40 56 65 74 86
2.16	2.14	2.13	2.11	<i>m</i>	8.44	36 55	16	400	35 55 90
			1.72	<i>f</i>	8.42	27 35 57 62—	24	224	25 36 55 64 82 84
1.62	1.64	1.61	1.60	<i>m</i>	8.32	27 36 46 70—	27	{333 115	36 82 26 45 48 68 74 87
1.49	1.49	1.47	1.475	<i>sss</i>	8.34	6 57 66	32	440	10 55 66 80
	1.30	1.29	1.275	<i>f</i>	8.36	27 35 52 65—	43	335	28 36 50 69 84 86
1.22	1.21	1.21	1.21	<i>m</i>	8.38	36 80—	48	444	36 82
	1.10	1.09	1.10	<i>m</i> , diffuse		Not resolved	{56 59	{642 731	12 maxima 12 maxima
		1.04	1.045	<i>f</i>	8.35	36 54	64	800	6 maxima
	0.99	0.97	0.97	<i>m</i>	8.39	6 19 36 42 (and more)	75	{555 157	35 55 90 36 82
			0.934	<i>ff</i>	8.36	8 27 45 60—	80	480	6 20 43 (and 9 more)
			0.884	<i>fff</i>	8.43		91	139	9 28 43 65 69 81
	0.86	0.86	0.855	<i>m</i>	8.37	26 36 56 65 80—	96	448	12 maxima
			Mean a_0 =		8.38Å				25 36 55 64 82 84

* A value of ϕ followed by a dash indicates that the maximum is cut off by the shadow of the sample.

air, this rough surface becomes coated with a thin film of oxide. At the peaks of projections, where the oxygen can attack from all sides, very small iron crystals, 50Å or less in diameter let us say, are probably completely oxidized. Since the peaks of projections are most likely to be hit by grazing incidence electrons, the oxide scatters with a high degree of efficiency. Lower down, where the projections are thicker in a direction parallel to the surface, the electrons must traverse a thin film of oxide followed by a core of iron, which may be ten or more times as thick, before again emerging through a thin film of oxide. Most of the electrons singly scattered in such a path will be scattered by the iron. An air-exposed evaporated film, therefore, should be expected to give strong oxide reflections superimposed on an iron pattern which has been considerably weakened by the exposure to air.

A finely abraded iron surface approaches the condition described above, but it is undoubtedly much coarser with broader peaks and consequently less opportunity for electrons to traverse

oxide alone. On burnished surfaces the ridges are even more flattened and there is still less chance that an electron will be scattered by the oxide film alone. It is also possible that some of the electrons strike the flattened tops of ridges at such small glancing angles as to suffer appreciable refraction.¹⁶

These considerations lead to the conclusion that thin films on polished or burnished metal surfaces cannot be detected or examined by reflection methods as readily as can the same films on surfaces which are rough on a sub-microscopic scale. Any method by which the roughnesses can be made finer will enhance the possibility of detecting a film. The sensitivity of the transmission method, on the other hand, is limited by the difficulty of preparing sufficiently thin metal films. It is difficult to mount films less than a few hundred angstroms thick. An oxide layer 30Å thick covering the surfaces of such a film would give a relatively weak pattern.

¹⁶ G. P. Thomson, *Phil. Mag.* **18**, 640 (1934).