The length of the edge of the unit cube a_0, of the α-iron obtained by reduction of magnetite is 2.859 ± 0.004 Å. The size of the unit cell of iron in the reduced material containing the promoters differs from that of pure iron by less than 0.1%. The presence of the composite promoter potassium and aluminum oxides in the reduced catalysts has been found to maintain a large surface of iron by preventing the rapid growth of the iron crystals.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON AND THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE PREPARATION AND CRYSTAL STRUCTURE OF FERROUS OXIDE

BY RALPH W. G. WYCKOFF AND E. D. CRITTENDEN

RECEIVED JULY 23, 1925 PUBLISHED DECEMBER 12, 1925

Introduction

Numerous observations[1] on the existence of phases and phase equilibria in the system iron-oxygen are found in the literature. From them the lowest temperature at which ferrous oxide, FeO, is stable has been set at about 570°. As a result, products entirely free from ferric iron have never been prepared either by careful reduction[2] of a higher oxide or by precipitation[3] of ferrous hydroxide with subsequent removal of water. X-Ray diffraction data on oxides of iron exist only for pure ferric oxide[4] Fe_2O_3 and ferroferric oxide,[5] Fe_3O_4.

During the course of some X-ray measurements[6] on artificial magnetites, diffraction lines were found which were due to a phase richer in iron than magnetite but not due to iron itself. Efforts to establish the composition of this new phase have resulted in the preparation of a material which is essentially ferrous oxide.

The method of making this oxide and a determination of its crystal structure form the basis of this paper.

Preparation of Ferrous Oxide

An oxide of the average composition Fe_3O_4 was made by burning Armco iron in oxygen. Armco iron rods were added to this burned material in the proportion of one

---

[1] See Eastman, THIS JOURNAL, **44**, 975 (1922), for a review of the evidence; also Eastman and Evans, *ibid.*, **46**, 888 (1924).

[2] Hilpert and Beyer, *Ber.*, **44**, 1608 (1911).

[3] Friend, "Textbook of Inorganic Chemistry," Griffin and Co. (London), vol. IX, part 2, p. 109. Sosman, *J. Washington Acad. Sci.*, **7**, 55 (1917). Ferguson, *Can. Chem. Met.*, **7**, 175 (1923).

[4] Pauling and Hendricks, THIS JOURNAL, **47**, 781 (1925).

[5] W. H. Bragg, *Phil. Mag.*, **30**, 305 (1915).

[6] Wyckoff and Crittenden, THIS JOURNAL, **47**, 2866 (1925).

part by weight of iron to four of the oxide. This mixture was fused in an electric fusion-pot between water-cooled electrodes.[7] The resulting mass was broken up, crushed, and fused again. The molten mass was thoroughly stirred by magnetic convection and was *saturated* with iron. The melt was cooled to room temperature, broken up and uniform lumps from the center of the melt were chosen for subsequent use.

The iron oxide made in this way, in striking contrast to both magnetite and pure iron, is practically non-ferromagnetic. It is black and brittle and differs little in general appearance and hardness from fused magnetite. The oxide is practically insoluble in sulfuric acid and only slowly soluble in boiling hydrochloric acid. None of the usual etching reagents has an effect upon it. Optical examination[8] of polished sections of the selected oxide showed it to be homogeneous except for small inclusions of metallic iron.

In order to remove as much as possible of this free iron and any magnetite that might also be present, selected material was crushed to 40–200 mesh and subjected to a magnetic separation. This was made with a strong electromagnet having wedge-shaped poles 1 mm. apart. All material which was lifted from 12 mm. vertically below the poles[9] was rejected. The rest, all of which was lifted from distances greater than 9 mm., was retained for use (958 purified). The apparent specific magnetic susceptibility[10] of this preparation is about 0.00052 per g. as determined by the method of weighing the force exerted on the specimen by a non-uniform field of known intensity and gradient. This measurement sets an upper limit to the true susceptibility of ferrous oxide, since this specimen is known to contain some free iron, and shows that ferrous oxide must be classed with the non-magnetic oxides.

The results of chemical analysis[11] on this purified oxide for free, ferrous and ferric iron are shown in Table I. There is reason to believe, however, that the material contains much less ferric iron than these analyses indicate;[12] 8% of ferric oxide combined with ferrous oxide as magnetite would have made the preparation many times more magnetic than it was observed to be. Powder photographs gave only lines that can be ascribed to ferrous oxide, without any indication of lines of either free iron or magnetite. It thus seems clear that the purified material (958 pur.) has essentially the composition FeO.

TABLE I

CHEMICAL ANALYSIS OF FERROUS OXIDE

Material	Total iron, %	Free iron, %	Ferrous iron, %	Ferric iron, %
958 pur.	76.18	0.54	65.84[a]	9.80
...	...	..	68.33[b]	7.31
928	75.24	3.34	40.49[a]	31.41

[a] Method described by Sims and Larsen, *Ind. Eng. Chem.*, **17**, 86 (1925).

[b] Direct solution in HCl. Titration with $K_2Cr_2O_7$.

The Crystal Structure of Ferrous Oxide

Powder photographs of ferrous oxide (958 pur.) have been made in the usual manner, the oxide under investigation being formed into a

---

[7] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

[8] Optical examination and magnetic separations of these materials have been carried out by H. E. Merwin.

[9] At this distance magnetite lifts one hundred times its weight of non-magnetic material.

[10] The determination of the magnetic susceptibility was made by R. B. Sosman.

[11] These analyses were made by J. F. Shultz.

[12] Hillebrand, "Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey Bull.*, **422** (1916).

film using celluloid as a binder.[13] All of the observed diffraction lines are listed in Table II. Those nearest the central image are very intense; diffractions with large values of 2Θ are not to be expected because of absorption in the relatively dense celluloid film used as sample.

Table II

Typical Powder Data from FeO

Sin Θ	$\frac{0.710\ \text{Å.}}{2 \sin \Theta}$ Å.	Sin² Θ	Ratio of sin² Θ Observed	Ratio of sin² Θ "True"	Indices
0.14292	2.484	0.02043	2.99	3	111(1)
.16519	2.149	.02729	4.00	4	100(2)
.23373	1.519	.05463	8.00	8	110(2)
.27410	1.295	.07513	10.99	11	113(1)
.28680	1.238	.08225	12.04	12	111(2)
.33038	1.074	.10915	15.97	16	100(4)
.36068	0.984	.13009	19.04	19	133(1)
.37002	.959	.13691	20.04	20	120(2)
.40528	.876	.16425	24.04	24	112(2)
.42946	.826	.18443	27.00	27	111(3)
					115(1)

In a cubic crystal the ratios of the values of $\sin^2 \Theta_n$ for all reflections are the ratios of whole numbers. Reference to Col. 4 of Table II shows that this requirement is exactly met. The simplest set of integers proportional to the corresponding $\sin^2 \Theta_n$ are those of Col. 5. If these are correct, then since

$$\frac{\sin^2 \Theta_1}{\sin^2 \Theta_2} = \frac{(h_1^2 + k_1^2 + l_1^2)n_1^2}{(h_2^2 + k_2^2 + l_2^2)n_2^2}$$

the indices of observed reflections are those of Col. 6. Other series of "true" ratios of $\sin^2 \Theta_n$ would be obtained by multiplying the numbers

Table III

Further Typical Powder Data of FeO (See Table I)

d/n, Å.	a_0, Å.	Estimated intensity	Indices
2.484	4.302	8	111(1)
2.149	4.298	10	100(2)
1.519	4.296	9	110(2)
1.295	4.295	5	113(1)
1.238	4.289	4	111(2)
1.074	4.296	2	100(4)
0.984_5	4.291	1.5	133(1)
$.959_5$	4.291	3	120(2)
.876	4.291	3	112(2)
$.826_5$	4.295	1	111(3)
			115(1)
	4.294		

---

[13] Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, **1924**, Chap. VI.

of Col. 5 by an integer. Each of these new series would yield a new set of index assignments corresponding to larger unit cells. If the composition of 958 pur. could be proved by other methods to be that of pure ferrous oxide and if the density of this substance were accurately known, a selection could be made between these possible unit cells. They are, however, highly improbable because no arrangement, either a special or a general case of a cubic space group, is known which would yield the observed sequence of present and missing reflections.

The lengths, a_0, of the edge of the unit cube calculated from the spacings and indices of Table II are shown in Table III. Similar average values of a_0 from six comparison photographs made from a sample consisting of sodium chloride mixed directly with ferrous oxide are given in Table IV. The indices of Col. 6 of Table II are those of the reflections produced by either the "sodium chloride" (4b, 4c) or the "zinc sulfide" (4b, 4d) arrangement.[14] Four molecules are contained within the unit cell of each of these structures. If four molecules of ferrous oxide are associated with the unit cell of edge length, $a_0 = 4.29_4$ Å., its density is $\rho = 5.99$. An approximate determination of the density of No. 958 which had not been mechanically fractionated, gave $\rho = 5.7$. The probable presence of gaseous inclusions in this material makes the agreement as good as could be expected. Calculation of density for three and five molecules in the unit cell gave values very far from that observed: $\rho = 4.49$ (3 mol.) and $\rho = 7.48$ (5 mol.).

TABLE IV

AVERAGE VALUES OF a_0 FROM PHOTOGRAPHS OF FeO

Photograph	1	2	3	4	5	6	
a_0, in Å.	4.291	4.298	4.291	4.297	4.290	4.297	Av. 4.294_4

A distinction between the "sodium chloride" and "zinc sulfide" arrangements can be made by calculating the relative intensities of the first few lines produced by the two structures. The results of such a calculation using the customary expression[15] $I \alpha j \times (A^2 + B^2) \times (d/n)^{2.35}$ are compared with the observed intensities in Table V. The sequence of observed intensities is that to be expected from the "sodium chloride" arrangement; it differs so profoundly from that given by the "zinc sulfide" structure that the latter can be excluded from further consideration. More extended calculation shows that this conclusion is valid whether it is assumed that the atoms in ferrous oxide are charged or neutral, or whether intensity is proportional to the first[16] or the second power of the structure amplitude.

[14] Ref. 13, p. 270.

[15] Ref. 13, p. 201.

[16] W. H. Bragg, *Phil. Trans. Roy. Soc.*, **215,** 253 (1915). W. L. Bragg, *Proc. Roy. Soc.* (London), **105A,** 16 (1924); etc.

Table V

A Comparison between Observed Intensities of Powder Lines of FeO and Intensities Calculated for (4b, 4c) and (4b, 4d)

Indices	Observed	Intensities Calcd. for (4b, 4c)	Calcd. for (4b, 4d)
111(1)	8	3.2	10
100(2)	10	10	1.5
110(2)	9	8.8	8.1
113(1)	5	2.1	6.5

In Fig. 1, the observed estimated intensities of powder reflections from ferrous oxide are plotted against intensities calculated for the "sodium chloride" arrangement on these different assumptions. Best agreement is obtained in this particular case if it is assumed that ferrous oxide consists

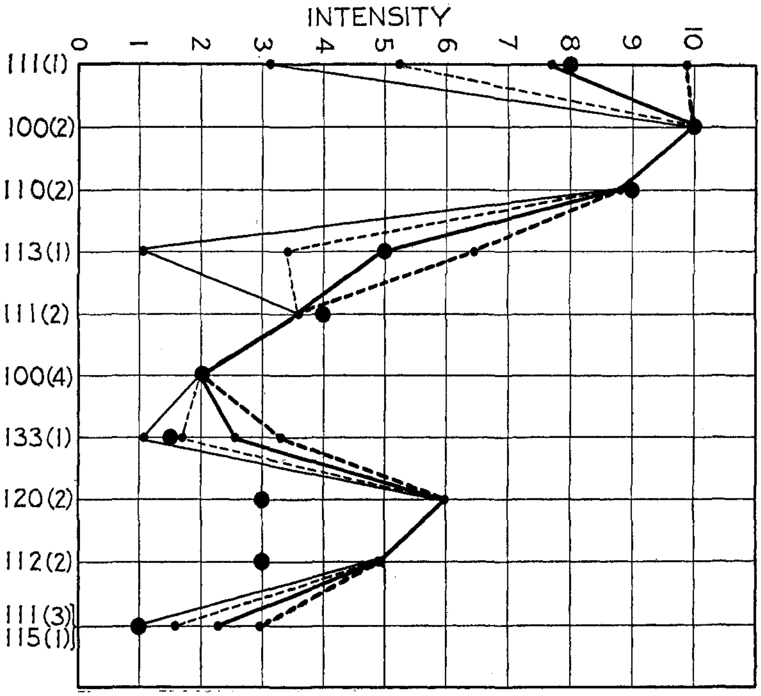

Fig. 1.—The relation between the observed intensities of the powder lines of FeO and intensities calculated upon several plausible hypotheses. Observed intensities are plotted as large black dots. Intensities calculated on the assumptions (1) that intensity is proportional to the first order of the structure amplitude and that the atoms are charged are connected by heavy full lines (2) that intensity is proportional to the second order of the amplitude and that the atoms are charged are connected by light full lines, (3) that the intensity is proportional to the first order of the amplitude and that the atoms are neutral are connected by heavy dotted lines and (4) that intensity is proportional to the second order of the amplitude and that the atoms are neutral are connected by light dotted lines, respectively.

of positive ferrous iron and negative oxygen ions and that intensity is proportional to the first power of the amplitude. How much significance can be attached to this agreement is not clear.

The preceding treatment shows that all the attainable X-ray diffraction data from Preparation 958 pur. are those to be expected from crystals of ferrous oxide having the "sodium chloride" arrangement (4b, 4c).

One further check on the correctness of this conclusion is furnished by comparisons of the relative sizes of the unit cells of magnesium oxide and of ferrous oxide. Determinations of structure and other X-ray measurements have shown that in the carbonates[17] and other compounds[18] ferrous iron replaces magnesium with very little change in shape or size of the unit cell. It might be expected, therefore, that if ferrous oxide and magnesium oxide were isomorphous, their unit cells would have nearly the same size. The present determination shows that the unit cells differ by only about 2%.

In order to determine whether there is any X-ray evidence of solid solution between ferrous and ferroferric (Fe_3O_4) oxides, comparison powder photographs (against sodium chloride as a standard) have been measured from 928. Chemical analysis of this material is given in Table I; its powder photographs show only the lines of ferroferric and ferrous oxides. Microscopic examination[19] shows that it consists of large crystals of ferroferric oxide embedded in a fine-grained eutectic mixture of magnetite and another phase which presumably is ferrous oxide. If magnetite can dissolve ferrous oxide and if the latter can dissolve magnetite

TABLE VI

DATA FROM A TYPICAL POWDER PHOTOGRAPH OF 928

		Ratios of $\sin^2 \theta$		Indices for		Spacings for		a_0 for	
Sin θ	$\text{Sin}^2 \theta$	FeO	Fe_3O_4	FeO	Fe_3O_4	FeO Å.	Fe_3O_4 Å.	FeO Å.	Fe_3O_4 Å.
0.32612	0.10635		59.25		137(1)		1.089		8.361
.27396	.07505	11.06		113(1)		1.296		4.298	
.23966	.05744		32		110(4)		1.481		8.380
.23302	.05430	8		110(2)		1.523_5		4.309	
.20763	.04311		24.02		112(2)		1.710		8.377
.16978	.02882		16.05		100(4)		2.091		8.364
.16405	.02691	3.96		100(2)		2.164		4.328	
.14033	.01969		10.97		113(1)		2.530		8.390
.11913	.01419		7.90		110(2)		2.980		8.429
							Average a_0 =	4.31_2	8.38_3

---

[17] Wyckoff, *Am. J. Sci.*, **50,** 317 (1920). Levi and Ferrari, *Rend. Accad. Naz. Lincei*, **33,** 516 (1924). Wyckoff and Merwin, *Am. J. Sci.*, **8,** 447 (1924).

[18] Wyckoff, Merwin and Washington, *Am. J. Sci.*, **10,** 383 (1925).

[19] This examination (by H. E. Merwin) was made on a polished section heated to dull redness. Magnetite is unchanged by this treatment but the surface of the FeO grains becomes matte.

at ordinary temperatures, a shift would be expected in the lines of one or the other, or both, of the structures. Data from a typical photograph of 928 are recorded in Table VI. Since the ratios of the $\sin^2 \Theta_n$ of the various lines of ferroferric and ferrous oxides are the ratios of whole numbers the two structures remain cubic. The averaged values of a_0 for the structures of the two oxides from six photographs are given in Table VII.

TABLE VII

AVERAGED VALUES OF a_0 FOR THE FeO AND Fe_3O_4 STRUCTURES FROM PHOTOGRAPHS OF 928

Film	1	2	3	4	5	6	7	8	Av.
a_0 for FeO, Å.	4.308	4.308	4.309	4.308	4.313	4.305	4.312	4.314	4.31_0
for Fe_3O_4, Å.	8.357	8.370	8.374	8.383	8.383	8.370	8.383	8.373	8.37_4

Since a_0 for magnetite in 928 does not differ by more than the experimental error (± 0.15%) from the corresponding a_0 of practically pure ferroferric oxide, it must be concluded that there is no evidence from spacing measurements of solid solution at ordinary temperatures of ferrous oxide in ferroferric oxide. The length of the edge of the unit cube of the ferrous oxide structure in 928 is consistently higher than a_0 found for this substance in 958 pur. The existing measurements do not conclusively show that this difference in a_0 of 0.3–0.4% is outside the limit of experimental error because only three ferrous oxide lines could be measured in these photographs. These data, nevertheless, make it highly probable that this substance formed in the presence of much magnetite has a slightly larger unit cell than pure ferrous oxide.

Many of the calculations of this paper were made by Elizabeth B. Derby.

Summary

An oxide of iron, which is essentially ferrous oxide, has been made by saturating magnetite, melted in an electric fusion-pot, with iron. This oxide is practically non-ferromagnetic and gives an X-ray pattern showing no traces of either iron or magnetite. The observed diffraction lines are fully explained on the assumption that this oxide is ferrous oxide having the "sodium chloride" arrangement (4b, 4c). The length a_0 of the edge of the unit cube containing four molecules of FeO is 4.29_4 Å. The density of ferrous oxide calculated from this structure is 5.99. There is no evidence for solid solutions at ordinary temperatures of ferrous in ferroferric (Fe_3O_4) oxide; the unit cube of ferrous oxide in a material containing much magnetite appears to be slightly larger than the unit cube of the pure substance.

WASHINGTON, D. C.