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A series of iron oxides with compositions between 76.08 and 76.72 percent Fe, all of them lying within the single phase solid solution area known as Wüstite has been prepared and the lattice constants and densities of the individual members determined. The NaCl structure found by earlier investigators and considered by them to be the structure of FeO has been found throughout this series. Contrary to the earlier results the size of the unit cell decreases as the iron content decreases. The solid solution is of a complex type; an oxygen ion replaces an FeO group with an accompanying increase in valence of 2 Fe^{++} to 2 Fe^{+++}. The results are discussed from the chemical and structural points of view.

INTRODUCTION

IN the binary system iron-oxygen there is a single phase solid solution area situated in the vicinity of the compound FeO. This phase is known, especially among the German metallurgists, as "Wüstite." Phase diagrams of the iron-oxygen system which include this area have been made on the basis of thermal analysis and microscopic examination by Pfeil,[1] Schenck and Hengler,[2] and Mathewson, Spire and Milligan,[3] to mention only three of the latest reports. In spite of much experimental work, it is still uncertain whether the Wüstite area actually includes the composition theoretically corresponding to FeO, reaches this composition as a limit at high temperatures, or has at all temperatures a minimum oxygen content significantly higher than the compound FeO. It may safely be inferred, that if either of the first two possibilities is correct, the minimum temperature will be above 1300°. The primary object in the present investigation was not to decide such questions but rather to study the crystal structure of the oxides lying entirely within this region. When it is recognized that from the chemical standpoint the oxygen content of such an oxide cannot be increased without at the same time changing the valence of its metallic constituent and further, that change of valence almost invariably involves a change of ionic size, such a series of single phase compositions as is possible within the Wüstite area is likely to involve solid solution phenomena of an unusual type. On account of the restricted scope of the present report and also because another investigation is in progress to determine, if possible, the limits of this area at various temperatures by x-ray methods, no attempt will be made here to discuss the relative merits of the several thermal diagrams which have been proposed.

PREVIOUS X-RAY INVESTIGATIONS

Two x-ray investigations have appeared dealing with compositions within the range of the present work, namely, by Wyckoff and Crittenden[4] and by Groebler.[5]

Wyckoff and Crittenden prepared the oxide by burning Armco iron in oxygen, resulting in a composition approximating Fe_3O_4, mixing four parts by weight of this with one part of iron and melting in an electric fusion pot. The resulting substance was ground up and remelted and the authors considered it to be a preparation saturated with iron. No other heat treatments are recorded. One of these preparations was subjected to magnetic purification and the final result was an oxide (No. 958 pur.) which analyzed 76.18 percent total iron and was considered as essentially ferrous oxide. Another oxide (No. 928) which ap-

[1] Pfeil, J. Iron and Steel Inst. (London) **123**, 237 (1931).
[2] Schenck and Hengler, Archiv. f. Eisenhüttenwesen **5**, 209 (1931).
[3] Mathewson, Spire and Milligan, Am. Soc. Steel Treat. **19**, 66 (1931).
[4] Wyckoff and Crittenden, J. Am. Chem. Soc. **47**, 2876 (1925); also Z. Krist. **63**, 144 (1926).
[5] Groebler, Physik. **48**, 567 (1928); this work is also reported with more detail as to preparation of the oxides in an article by Groebler and Oberhoffer, Stahl u. Eisen **47**, 1984 (1927).

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parently had not been magnetically purified gave
75.24 percent total iron. It is quite evident from
the complete analyses which the authors give,
that No. 928 was not in a state of equilibrium and
from a comparison with the results reported in
the present work this is probably also the case
with No. 958 pur. As the lattice constants, they
found for No. 958 pur. that $a_0 = 4.294$A and for
No. 928, $a_0 = 4.310$A, the latter showing many
lines from Fe_3O_4.

They conclude: "The length of the edge of the
unit cube of the ferrous oxide structure in No. 928
is consistently higher than a_0 for this substance in
No. 958 pur. The existing measurements do not
conclusively show that this difference in a_0 of
0.3–0.4 percent is outside the limit of experi-
mental 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."

Groebler prepared the entire series of oxides
between Fe_3O_4 and Fe by the reduction of Fe_2O_3
in various mixtures of CO and CO_2 at 800°C. Of
importance in the present connection is that for
five preparations with total iron contents be-
tween 75.95 percent and 77.10 percent, his x-ray
examination showed only the ferrous oxide lines
but without any change in the position of these
lines. The failure to observe any shift in these
lines would indicate that the lattice dimensions
remained constant throughout the range of solid
solution. Groebler, however, reported no quanti-
tative values for the lattice constants and merely
gave a diagrammatic survey of the observed dif-
fraction lines.

The results of the present investigation show
that as the iron content of the oxides in the
Wüstite area decreases there is an accompanying
decrease in the lattice dimensions. They dis-
agree, therefore, with the results of both the
previous investigations.

PREPARATION OF MATERIALS

The preparation of iron oxides with composi-
tions in the Wüstite area is very troublesome,
caused chiefly by the fact that no suitable sub-
stance exists which will hold the materials in-

volved at the required high temperatures. Any
metallic container will react with iron; any non-
metallic refractory reacts with the oxide. Pure
iron crucibles will serve for the iron saturated side
of the series but not for the magnetite side nor the
intermediate ranges. Platinum removes iron from
the oxides, especially above 1100°C but even at
950°, after prolonged contact with the oxides in
vacuo, there is an appreciable action. According
to the thermal diagrams of the system the dif-
ference in iron content of the two limits of the
solid solution at 1000° at the maximum is only
about 2 percent. For the x-ray examination it is
therefore necessary to have a series of oxides only
a few tenths of one percent apart in composition
while at the same time the individual samples
should be chemically homogeneous, without
physical strains due to grinding, etc., and of as
high a degree of purity as possible.

The scheme finally adopted was to prepare
large quantities of oxides with oxygen contents
higher than desired, grind this material to 200
mesh, and mix with pure iron powder to secure
the required composition. The thoroughly mixed
material was wrapped in thin platinum foil,
placed in an evacuated quartz tube and allowed
to sinter at approximately 1050° for 24 hours.
The tube was then rapidly cooled in water.

The large quantities of oxides were prepared
by two methods. The first is analogous to that
used by Pfeil.[1] Lumps of electrolytic iron were
placed in an Armco iron shell supported on an
aluminum boat. The whole was heated in air for
two days at about 1050°C. The portion in con-
tact with the iron shell was discarded. The in-
terior of the lumps consisted of unoxidized iron.
Two oxide specimens thus prepared analyzed
0.053 percent SiO_2 and approximately 74.3 per-
cent Fe. This was used in preparing oxides Nos. 1,
3, and 4.

The second method consisted of heating pure
Fe_2O_3 prepared from the oxalate and tightly
packed in a covered heavy walled crucible of
Armco iron in a high-frequency furnace. The
temperature was increased slowly until the oxide
skin which formed on the outside of the crucible
melted and ran down the sides. Different compo-
sitions could be secured by varying the rate of
heating, the temperature and the time at the
high temperature but the composition could not

be controlled in any satisfactory way. Hence a number of melts were made in this manner, analyzed and the desired compositions selected. One having 74.24 percent Fe and 0.030 percent SiO_2 was used in making oxide No. 6; another analyzing 76.15 percent Fe and 0.018 percent SiO_2 was used for No. 7 and 8.

The iron powder was made by heating pure Fe_2O_3 (from oxalate) in an alundum boat first in air to remove undecomposed oxalate, etc., and then in a stream of hydrogen at 658°C until reduction was complete. This iron analyzed 0.015 percent Si.

When the mixture of oxides and iron powder were sintered at 1050° as mentioned above, the product was a firm rod of material which was then ground up and analyzed. The platinum foil was generally quite brittle after this treatment indicating that it had taken up some iron. It was seldom that satisfactory films were obtained from these oxides without further annealing treatment of 1 to 5 hours. This was also performed in platinum foil but generally at lower temperatures, which as far as possible were selected below the point where sintering becomes troublesome. At the limiting compositions of the series, however, temperatures above 900° were required to ensure that the substance was kept within the Wüstite area. The proper conditions were determined by a large number of preliminary experiments. The iron content was determined after each annealing.

In spite of all efforts, however, x-ray examination revealed that complete chemical homogeneity had not been attained in any of the samples. The change of lattice dimensions with composition within this range is quite considerable so that the x-ray photograms give a very sensitive test on this point. A difference of 0.10 percent Fe causes a shift of 0.6 mm in the position of the outermost reflections which corresponds to a change of 0.003A in the lattice constant. For chemically homogeneous substances no difficulty is ordinarily experienced in determining the positions of these outermost reflections to within ±0.2 mm and generally the measurements may be checked to within ±0.1 mm. With the iron oxides, especially at the high iron end of the series, distinct sharp spots indicating particles of different compositions would sometimes be spread over 2 mm. Such results were discarded and the samples given further annealing treatments until the lines were more uniform and narrow. Even so the total range of composition on the high iron side was probably of the order of ±0.07 percent Fe, which is of the same order of accuracy as the chemical analysis; this difficulty, while entirely absent in only a few cases, was much less for oxides at the magnetite end or at intermediate compositions.

Attempts were also made to prepare pure FeO by decomposition of FeC_2O_4 under conditions closely similar to those described by Andrew, Maddocks and Howat.[6] Decomposition in vacuo at 680–700°C always resulted in a product which gave a distinct iron pattern on the x-ray photograms. Even after prolonged annealing under these conditions the iron lines appeared although samples were obtained which analyzed 77.69 percent Fe (FeO = 77.73 percent Fe). While our method was perhaps not absolutely the same as that of the above writers, our experience with it and the results of our x-ray analyses reported below give us no confidence that a substance analyzing 77.73 percent Fe and at the same time showing only lines from the NaCl type of structure can be prepared by such means. We have every reason to believe that if FeO as such exists at all it must be unstable at 700°C. An oxide containing 77.4 percent Fe annealed at 600°, 795°, 913° and 1035°C gave in each case iron lines on the x-ray photograms.

$FeCO_3$ precipitated, washed, dried and ignited without at any time coming into contact with air and with the ignition carried out in vacuo invariably gave nothing but magnetite.

ANALYTICAL METHODS

The total iron content was determined by titration with $K_2Cr_2O_7$ by using such concentration that approximately 80 cc of solution were required for a 0.3 g sample. The titrations were carried out with the utmost care with frequent standardizations of the solution as a check on the technique. As standards, Fe_2O_3 prepared by the decomposition of pure ferric nitrate, Fe_2O_3 from Kahlbaum ("zur analyse"), the Bureau of

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[6] Andrew, Maddocks and Howat, J. Iron and Steel Inst. (London) 24, 283 (1931).

Standards' Sibley iron ore and pure ferrous ammonium sulfate were used. For one solution, which at one time or another was standardized against all of these materials, the deviation was less than 0.1 percent.

The samples were dissolved in 10 cc of concentrated HCl to which a few drops of $SnCl_2$ solution had been added. The rate of solution of these oxides being very low even at boiling temperatures, the samples were dissolved at room temperature by allowing to stand over night. This avoided loss of iron by volatilization, spraying, etc. Diphenylamine was used as an internal indicator; the general technique followed was that recommended by Hillebrand and Lundell[7] except that back titration with ferrous sulfate solution seldom proved to be necessary.

The "free iron" content of these samples was not determined. Extensive investigations were made of the Sims and Larson[8] method of removing the metallic iron with copper sulfate and of the Wilner-Merck method as modified by Groebler and Oberhoffer[9] by using mercuric chloride. In agreement with the latter writers, it was found that the copper sulfate method gave high results. Our results indicated, however, that the accuracy of both methods seemed to be influenced by the physical character of the oxide, the degree of subdivision, etc., in an unpredictable way and for this reason attempts to determine the "free iron" were abandoned. Thus in the present work we rely entirely upon the homogenizing annealing treatment to remove any free iron which may have been present in oxides lying within the single phase solid solution area and upon x-ray measurements to determine whether the composition was within the limits of this area. The results of the investigation of the solid solution limits will be reported in another article.

There seemed to be no apparent advantage in separately determining ferrous and ferric iron. It may be remarked, however, that when samples known to contain free iron were dissolved in HCl under rigorously non-oxidizing conditions, the solutions showed by the characteristic yellow color that considerable ferric iron was present.

Silica was determined by solution in HCl followed by double dehydration. The general details followed were those recommended by Hillebrand and Lundell.[10] Four gram samples were used.

DENSITY MEASUREMENTS

The densities were determined from the loss of weight when the powder was immersed in carefully purified brom benzene. The density of the latter was obtained from the *International Critical Tables* (Vol. 3, page 29). Air was removed by boiling under reduced pressure. Correction was made for the temperature of the liquid.

X-RAY METHODS

The x-ray cameras used for making the measurements were of the Seeman-Bohlin type as designed by Phragmén.[11] These cameras were calibrated against carefully purified NaCl using radiations from both iron and copper targets. The value for the length of the cube edge of NaCl was taken as 5.6280A. Only the lines appearing in the camera covering the range where the most deviated reflections appeared ($\sin_2 \theta$ between 0.52 and 0.98 approximately) were used in calculating the lattice parameters of the oxides. Some indication of the sensitivity of these cameras in the present problem has already been given above.

In order to secure a comparison of the intensities of the reflections over the entire range of angles from $\theta = 0$ to $\theta = 90°$ several photograms were taken in a round Debye camera of 105 mm diameter. The radiation used in all cases was from an iron target in a Siegbahn-Hadding tube with a current of 12–15 m.a. at 45 to 50 kilovolts r.m.s. The current source is a high tension transformer with full wave mechanical rectification. Exposures of about 5 hours duration were required for the outermost reflections.

RESULTS

The experimental determinations of the lattice constants and densities are recorded in Table I together with a number of calculated quantities which will be discussed later. Due to the difficulty of attaining complete equilibrium on the

[7] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, p. 306, et seq.

[8] Sims and Larson, Ind. Eng. Chem. **17**, 86 (1925).

[9] Reference 5, p. 1986.

[10] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, p. 540, et seq.

[11] The cameras are described in detail by Westgren, Am. Inst. Min. and Met. Eng., Inst. Mets. Div., 1931, p. 13.

high iron side of the series the results on oxides numbered 6, 7 and 8 are averages of several analyses and lattice constant measurements. The letters a, b, c denote different final annealing treatments.

The sodium chloride structure reported by the earlier investigators is confirmed. The pronounced decrease in the lattice constant as the iron content decreases has not been previously recorded. The shift in the outermost reflections (331 planes) at the two limits of the series is approximately 5 mm. The variation of lattice constant with composition is linear within the limits of experimental error, although a slight downward sag yields the "best fit" (Fig. 1). Because of the short range of composition involved, the use of atomic percent instead of weight percent makes no observable difference. In describing the preparation of these oxides, small amounts of silica were noted. Results on another series of oxides containing approximately 0.9 percent SiO_2 when combined with the present series indicate that the values of a_0 in Table I are subject to corrections due to the presence of SiO_2 which would diminish the values of a_0 by 0.0002A to 0.0008A. Since these corrections lie within the reproducibility limits of the parameter determinations, they will not be further considered.

DISCUSSION

The observed change of the lattice constant with composition is clearly due to some form of solid solution. The next question is what type of solid solution will satisfy the observed data.
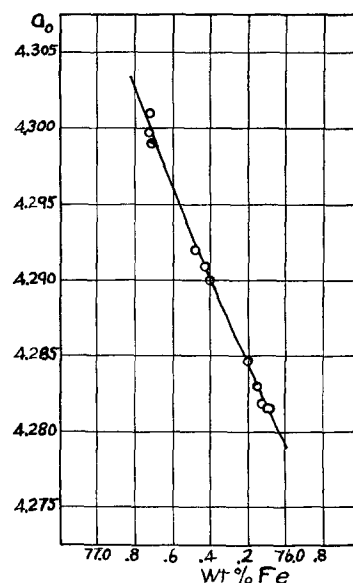

FIG. 1.

Four types of solid solutions are to be recognized as possibilities: (1) The ordinary substitu-

TABLE I.

Oxide #	1 Weight % Fe	2 Atomic % Fe	3 a_0 in A	4 Density obs.	5 $n_{Fe}+n_0$	6 n_t $(N=8)$	7 Weight % FeO	8 $n_{FeO}+n_0$	9 n_t $(N=4)$	10 N	11 Density calc.	12 $r_{Fe^{++}}$ in A
4 a	76.08	47.68	4.2816	5.613	9.72×10^{22}	10.19×10^{22}	97.88	5.09×10^{22}	5.10×10^{22}	3.99	5.622	0.744
4 b	76.07		4.2816									
4 c	76.12		4.2819									
1 a	76.15		4.2831									
1 b	76.20	47.85	4.2847	5.624	9.72	10.17	98.03	5.07	5.08	3.99	5.639	0.777
3 a	76.40		4.2900									
3 b	76.42	48.15	4.2909	5.643	9.72	10.13	98.31	5.04	5.06	3.98	5.667	0.783
3 c	76.48	48.23	4.2920	5.658	9.74	10.12	98.39	5.04	5.06	3.99	5.678	0.784
7 ave.	76.71		4.2990									
8 ave.	76.72	48.56	4.2997	5.725	9.81	10.06	98.70	5.05	5.03	4.01	5.706	0.791
6 ave.	76.72	48.56	4.3010	5.728	9.82	10.02	98.70	5.05	5.03	4.02	5.701	0.791
FeO	77.73	50.00	(4.332	—extrapolated—			100			4.00	5.883	0.816)

tional type in which an atom of one element simply replaces an atom of another in the latter's characteristic structure; (2) the interstitial type in which the foreign atom enters into the interstices of the base lattice; (3) a much rarer form of complex substitution which may take various forms but in any case the number of atoms per unit cell is different from that of the basic lattice; (4) also a rare form in which the lattice of the base substance is changed by the addition of foreign atoms in a more radical way, e.g., from cubic to tetragonal as in the case of the formation of tetragonal martensite.

The fourth possibility may be eliminated at once since it involves the appearance of new lines which have not been observed in the present investigation. To distinguish between the other three, the method of calculating the number of atoms of each kind per unit volume from the density and composition and comparing the sum of these with the number obtained from the structure data seems to be the most convenient. In applying this method[12] we shall first calculate the total number of Fe and O atoms per unit volume and compare this with the number of atoms or lattice points per unit volume of the NaCl lattice. The number of Fe atoms per unit volume is obtained by the relation

$$n_{Fe} = \frac{d x_{Fe}}{55.84 \times 1.65 \times 10^{-24}},$$

where d is the density, x_{Fe} the weight fraction of Fe, and 1.65×10^{-24} is the weight of a single atom of unit atomic weight. The value of n_0 is obtained in a similar way. The total number per unit volume from the structure data is simply $n_t =$ atoms per unit cell/volume of unit cell $= N/a_0{}^3$. If $n_{Fe} + n_0 = n_t$ within the limits of experimental error, we have a simple substitution type of solid solution. If $n_{Fe} + n_0 > n_t$ we would assume that the solution was of the interstitial type, while if the sum were less than n_t we should search for some complex form of substitution.

Columns 5 and 6 give the values of $n_{Fe} + n_0$ and n_t the latter being based on $N = 8$, the number of atoms in a unit NaCl cell. It is seen that the actual number of atoms present in a unit

volume is from 2.0 to 4.5 percent less than that corresponding to the full number of the NaCl structure. This is considerably beyond the experimental error which is of the order of 0.5 percent and which is due chiefly to the density measurements. Further it may be noted that the sum $n_{Fe} + n_0$ increases while n_t decreases. The preceding calculation thus eliminates the first two types of solid solution. That something unusual occurs in the solid solution in this particular case was inferred at an early stage of the investigation since either the simple substitution of oxygen for iron or the insertion of oxygen into the interstices of the FeO lattice should lead to an increase in the lattice constant and a decrease was observed. According to Wyckoff and Crittenden[4] the best agreement between the measured and calculated intensities of the diffraction lines is secured when it is assumed that the structure is built up of Fe^{++} and $O^{=}$ ions. The same conclusion may be arrived at from considerations of the radii of the cell constituents. It will be shown later that the lattice dimensions are consistent with those calculated from the ionic radii. The atomic radii lead to very much lower values. We shall, therefore, assume that the lattice is ionic.

As each oxygen is added we must have 2 Fe^{++} $+ O \rightarrow 2 Fe^{+++} + O^{=}$ which is accompanied by a decrease in the ionic radius of the iron ion. Taking the ionic radii as given by Wyckoff[13] $Fe^{++} = 0.80$, $Fe^{+++} = 0.67$ and $O^{=} = 1.35A$, we find that the substitution of an $O^{=}$ for a Fe^{++} would give a net increase of 0.29A and thus cause an expansion of the lattice. For the insertion of an $O^{=}$ in the interstices there would be a much larger expansion, the amount depending upon the position taken in the lattice. While the deformability of the ions has not been taken into consideration this factor alone could scarcely account for the actual decrease observed.

The correct form of substitution seems to be an oxygen for an FeO group.[14] The Fe content is computed over to FeO (Table I), column 7, and the calculation of the number of atoms or, in this

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[12] See H. Ott, Wien-Harms Handb. d. Exp. Physik, vol. VII, part 2, p. 283.

[13] Wyckoff, *The Structure of Crystals*, McGraw-Hill, 2d Edition, p. 192.

[14] These FeO groups are merely convenient structural units and have no chemical significance. The iron may actually be in the ferric state.

case, of FeO groups and extra oxygens is made in the same way as before; N in this case is four since there are four FeO groups in the ideal unit cell. The results of these calculations are given in columns 8 and 9. It may be seen that the agreement between the sum $n_{\text{FeO}}+n_0$ and n_t is excellent, the maximum difference being less than 0.5 percent. This is further confirmed by the value of N, the number of unit groups in the unit cell, obtained from the equation commonly used for this purpose.

$$N=\frac{a_0{}^3 d}{(71.84A+16.00B)\times 1.65\times 10^{-24}}$$

in which A and B are the molecular and atomic fractions respectively of FeO and O. Column 11 contains the densities calculated on the basis of $N=4$ which may be compared with the measured values.

The agreement between measured and computed quantities leads the writers to accept the substitution of an oxygen for an FeO group as the correct form of substitution throughout the range of this solid solution. There seems to be no reason for introducing Hüttig's conception of "vagabond oxygen atoms" in this lattice as suggested by Groebler and Oberhoffer.[5]

According to the ordinary interpretation of the thermal diagram, we would regard Wüstite as a solid solution of Fe_3O_4 in FeO, but from the structural standpoint, this interpretation is of doubtful value. The ideal unit cell of FeO contains only 4 FeO groups. Thus to consider the Fe_3O_4 molecule as a substitution unit would be to introduce a molecule or group of practically the same size as the whole cell into which it is to be inserted. If, however, a superstructure of double the observed cube edge were to be found, this idea of molecular substitution might well prove useful. No lines corresponding to such a superstructure have so far been observed in our films. Just how and why it is possible in this special case of solid solution to change the number of atoms per unit cell in this complex way and yet to retain the original type of structure is still to be explained. It might be expected that this type of solid solution in Wüstite, especially since there is likewise a change in electron distribution, would be accompanied by changes in the relative

intensities of the lines. Debye photograms of oxides 4 and 6 were identical with respect to intensities as far as visual inspection could determine.

It is evident that the substitution of an oxygen for an FeO group is equivalent to removing one iron. Since the lattice is an ionic one, this means the elimination of an Fe^{++} and thus leaves the unit cell electrically unbalanced by two excess negative charges. This is compensated by the oxidation of 2 Fe^{++} ions to 2 Fe^{+++}. Thus in those unit cells from which an Fe^{++} ion has been removed, each cell will contain 1 $Fe^{++}+2\ Fe^{+++}+4O^=$ or the chemical equivalent of Fe_3O_4. From this point of view the chemical reaction taking place as the oxygen concentration of the phase increased may be formally represented by $4\ FeO\rightarrow Fe+Fe_3O_4$.

There is a general agreement among the various thermal diagrams which have been proposed for the iron-oxygen system, that the FeO-phase (Wüstite) reaches a low temperature stability limit at about 570°C. Below this temperature it decomposes into iron and magnetite. It seems, therefore, that the chemical reaction in the homogeneous solid solution phase as the oxygen content increases is at least formally the same as the decomposition of the FeO. The difference lies in the fact that in the decomposition the rejected iron atoms unite to form the characteristic iron lattice and the remainder the magnetite lattice while in the homogeneous phase the rejected iron appears together with the additional oxygen as new FeO lattices. This point of view is supported by the fact that while the iron content decreases the number of unit cells per gram of iron increases, e.g., for 76.72 percent Fe, the number of unit cells per gram iron is 1.684×10^{21} and for 76.08 percent Fe it is 1.726×10^{21}.

As has already been pointed out, the range of homogeneous solid solutions does not actually include the chemical compound FeO (77.73 percent Fe), but always contains too much oxygen. It is to be mentioned that the results reported in Table I do not necessarily preclude the possibility of actually preparing pure FeO. Preliminary results of an investigation of the homogeneity range at various temperatures, however, indicate that if the compound FeO can exist in the pure state at all, it must be at temperatures above 1300°C.

It is, however, interesting to extrapolate the present results to the theoretical composition of FeO. Various methods of extrapolation were tried but none were found to give particularly satisfactory results due to the fact that the extrapolation range is greater than that of the data. The several methods, logarithmic and others, all gave values of a_0 for FeO (77.73 percent Fe) between 4.329 and 4.334A with 4.332 as a reasonable mean.

In the NaCl structure the shortest distance between neighboring atoms is found along the cube edge. With the extrapolated value of 4.332A for the cube edge of FeO and Wyckoff's value of 1.35 for the radius of the $O^=$, the radius of the Fe^{++} ion comes out at 0.816A which compares favorably with Wyckoff's value 0.80. If the distribution of the extra oxygen ions is statistical with a consequently similar distribution of the Fe^{+++} ions we should obtain essentially the same radius for the Fe^{++} ion throughout the series of alloys. In making the calculation we shall assume Wyckoff's value of 0.67A for the radius of the Fe^{+++} ion and obtain the values of the atomic percentages of Fe^{++}, Fe^{+++} and $O^=$ from the analyses. The results are given in Table I, column 12.

Considering the general uncertainty in the values of the ionic radii and, indeed, of the concept of a definite ionic radius in the solid state, it would seem that the difference between 0.816 and 0.80A has no special significance. On the other hand, if we may accept Wyckoff's value for r_{Fe}^{++} and the assumptions used in calculating the values in column 12, it is possible to arrive at some understanding of the otherwise rather curious lack of stability of the simple compound FeO. On this basis, we would suppose that the simple compound is unstable because the Fe^{++} has too much space available and the characteristic NaCl structure can only exist after the lattice constant has been reduced by the removal of Fe^{++} and the consequent oxidation of other Fe^{++} ions to Fe^{+++} ions to the point where the space available to the remaining Fe^{++} ions corresponds to 0.80A as the limiting radius. It will be seen in column 12 that the oxide containing the highest iron content approximates this value of 0.80A probably within the limits of uncertainty. That the structure is stable at lower iron concentrations where the space available for the Fe^{++} ions corresponds to radii of less than 0.80 is probably to be explained by a small amount of deformation of the oxygen ion. However, the accuracy of the methods available for estimating radii in the solid state do not permit much reliance or emphasis to be laid on arguments of this sort. On the magnetite end, such a treatment is less suitable. Structurally, magnetite is to be considered as $Fe_2^{+++} Fe^{++}O_4^=$ and if the $O^=$ ion retains the radius of 1.35A and is not deformed, the Fe^{++} ion would have a radius of only 0.46A. It is evident that the NaCl structure would become unstable long before such a value could be reached.