

ABSTRACT

The preparation of magnesium ferrite from ferric oxide and magnesium oxide under various controlled conditions of temperature, oxygen pressure and composition is described.

The limits of solid solution of magnesium oxide and ferric oxide in magnesium ferrite in an atmosphere of oxygen at $1200^{\circ} \pm 10^{\circ}\text{C}$. have been determined from lattice constant measurements. The nature of the lattice defects occurring in the mixed crystals is discussed.

The techniques employed to obtain atmospheres with a partial pressure of oxygen of 10^{-7} to 10^{-15} mm. at 1200°C . are described. The isothermal reduction of magnesium ferrite of stoichiometric composition and also of initial composition $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$ in this oxygen pressure range has been studied and the phase changes involved in the reduction elucidated by chemical and X-ray analysis. The ferrite phase is the only one found to be present above an effective oxygen pressure of the order of 10^{-10} mm. Below this pressure there are two coexisting solid phases, which above 2×10^{-13} mm. are the mixed crystals $(\text{Mg},\text{Fe})\text{Fe}_2\text{O}_4$ and $(\text{Mg},\text{Fe})\text{O}$ and below 2×10^{-13} mm. are $(\text{Mg},\text{Fe})\text{O}$ and metallic iron. The change in composition and concentration of these phases with change in effective oxygen pressure has been followed.

The effect of firing in oxygen in the temperature range $1100^{\circ} - 1500^{\circ}\text{C}$. on the dissociation of magnesium ferrite

has been investigated.

Magnesium ferrite has also been prepared by a fusion method and the product examined.

The magnetic properties at various frequencies of all the samples, except those prepared in very reducing atmospheres to study the phase changes, have been examined and correlated as far as possible with the structural features of the material, such as the lattice defects and lattice parameter.

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STUDIES IN THE CHEMISTRY AND STRUCTURE

OF

MAGNESIUM FERRITE

A THESIS

presented for the degree of

DOCTOR OF PHILOSOPHY

in the

UNIVERSITY OF LONDON

by

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SEPTEMBER, 1950

STUDIES IN THE CHEMISTRY AND STRUCTURE OF MAGNESIUM FERRITE

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The limits of solid solution of magnesium oxide and ferric oxide in magnesium ferrite in an atmosphere of oxygen at $1200 \pm 10^\circ\text{C}$. have been determined from lattice constant measurements. The nature of the lattice defects occurring in the mixed crystals is discussed.

The techniques employed to obtain atmospheres with a partial pressure of oxygen of 10^{-7} to 10^{-15} mm. at 1200°C . are described. The isothermal reduction of magnesium ferrite of stoichiometric composition and also of initial composition $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$ in this oxygen pressure range has been studied and the phase changes involved in the reduction elucidated by chemical and X-ray analysis. The ferrite phase is the only one found to be present above an effective oxygen pressure of the order of 10^{-10} mm. Below this pressure there are two coexisting solid phases, which above 2×10^{-13} mm. are the mixed crystals $(\text{Mg}, \text{Fe})\text{Fe}_2\text{O}_4$ and $(\text{Mg}, \text{Fe})\text{O}$ and below 2×10^{-13} mm. are $(\text{Mg}, \text{Fe})\text{O}$ and metallic iron. The change in composition and concentration of these phases with change in effective oxygen pressure has been followed.

The effect of firing in oxygen in the temperature range 1100°-1500°C. on the dissociation of magnesium ferrite has been investigated.

Magnesium ferrite has also been prepared by a fusion method and the product examined.

The magnetic properties at various frequencies of all the samples, except those prepared in very reducing atmospheres to study the phase changes, have been examined and correlated as far as possible with the structural features of the material, such as the lattice defects and lattice parameter.

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SECTION I

INTRODUCTION

SECTION I: INTRODUCTION

(1) The Occurrence of Spinel

The compound magnesium ferrite, MgFe_2O_4 , is a member of the spinel group. This group consists of many naturally occurring minerals and also of compounds which have been prepared, but which have not yet been found in nature. These minerals and synthesised compounds have the same crystal structure, that is, the structure of the mineral Spinel, MgAl_2O_4 , from which the name of the group as a whole is taken. Some examples of naturally occurring minerals of the spinel group are:-

Spinel	MgAl_2O_4
Chlorospinel	$\text{Mg}(\text{Al}, \text{Fe})_2\text{O}_4$
Magnesioferrite	MgFe_2O_4
Ceylonite	$(\text{Mg}, \text{Fe})\text{Al}_2\text{O}_4$
Picotite	$(\text{Mg}, \text{Fe})(\text{Al}, \text{Fe}, \text{Cr})_2\text{O}_4$
Hercynite	FeAl_2O_4
Chromite	FeCr_2O_4
Picrochromite	MgCr_2O_4
Gahnite	ZnAl_2O_4
Dysluite	$(\text{Zn}, \text{Fe}, \text{Mn})(\text{Al}, \text{Fe})_2\text{O}_4$
Jacobsite	$(\text{Mn}, \text{Mg})(\text{Fe}, \text{Mn})_2\text{O}_4$
Magnetite	FeFe_2O_4

The naturally occurring magnesium ferrite, known as magnesioferrite, is found in association with magnetite, Fe_3O_4 , which is a primary constituent of most igneous rocks.

Examples of spinels which have been synthesised, but not yet found in nature, are:-

Zinc ferric oxide	ZnFe_2O_4
Calcium ferric oxide	CaFe_2O_4
Nickel ferric oxide	NiFe_2O_4
Cadmium ferric oxide	CdFe_2O_4
Cobalt chromic oxide	CoCr_2O_4
Cupric aluminium oxide	CuAl_2O_4

All the spinels mentioned above have the general formula $\text{M}^{\text{II}}\text{M}_2^{\text{III}}\text{O}_4$, that is, they consist of an oxygen-ion lattice containing one bivalent metal ion and two trivalent metal ions to four oxygen ions. This is known as the "2:3" type of spinel. The spinel structure may also be formed in another way. This type, known as the "4:2" type, has the general formula $\text{M}_2^{\text{II}}\text{M}^{\text{IV}}\text{O}_4$. Thus, in this case, the structure consists of an oxygen-ion lattice containing one quadrivalent metal ion and two bivalent metal ions to four oxygen ions.

Examples of the "4:2" type of spinel are:-

Ferrous titanium oxide TiFe_2O_4

Magnesium titanium oxide TiMg_2O_4

Zinc stannic oxide SnZn_2O_4

It has been reported by S. Holgersson¹ that compounds having the general formula $\text{M}^{\text{II}}\text{M}_2^{\text{III}}\text{S}_4$, where $\text{M}^{\text{II}} = \text{Co, Ni, Cu or Fe}$ and $\text{M}^{\text{III}} = \text{Co, Ni, Fe or Cr}$, also have the spinel structure.

(2) Structure.

The spinels are preferably regarded from the structure viewpoint as mixed oxides, that is, as a lattice of oxygen ions containing more than one type of cation.

In the list of naturally occurring spinels given at the beginning there are examples in which the oxygen lattice contains up to five different metal ions, e.g. Chlorospinel, $\text{Mg}(\text{Al,Fe})_2\text{O}_4$ and Picotite $(\text{Mg,Fe})(\text{Al,Fe,Cr})_2\text{O}_4$. It is clear that cations of one type may be replaced by those of another without altering the overall spinel structure. In point of fact, these mixed spinel minerals are not of fixed composition. This serves to emphasise the point that the spinel structure will be preserved when the necessary interstices in the oxygen lattice are occupied by cations

which satisfy the valency requirements, and, which have ionic radii similar to those of magnesium and aluminium, the components of spinel proper. The ionic radii of common spinel forming elements are given in Table II, which appears on page 13.

Although reference is made to ions it is not intended to imply that the bonds in the lattice are entirely ionic in character, as there will be resonance in the system between ionic and covalent structures.

The oxygen lattice of the spinel structure consists of cubic close-packed oxygen ions. This arrangement may be considered to arise from the placing, one upon another, of identical layers of closely packed oxygen ions, regarded as spheres, in such a way that they form the sequence of layers A B C A B C ..., etc. That is, the centres of the spheres in the B layers are not perpendicularly above those in the A layers, and similarly the centres of the spheres in the C layers are not above those in the A or B layers. The centres in any A layer are perpendicularly above the centres in all the lower A layers, and similarly with the B and C layers.

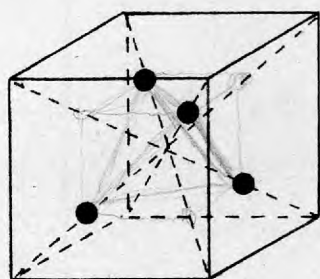
The elementary or unit cell of this system is a face-centred cube, which in the case of the spinel structure contains 32 oxygen ions, i.e., the unit cell contains the

equivalent of eight molecules of XY_2O_4 . From consideration of the oxygen ions alone, the unit cell may be divided into eight cubes, or octants, of identical size, each containing four oxygen ions. The oxygen ions in each octant lie one on each body diagonal at a distance from the nearest corner of the octant of approximately one quarter of the length of the diagonal, as shown in Figure Ia (Figure I is taken from a paper by E.J. Verwey, P.W. Haayman and E.L. Heilman²).

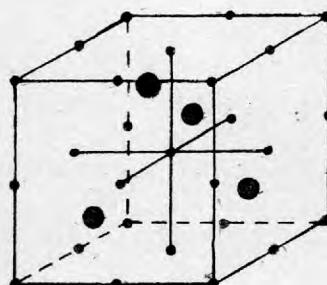
In this oxygen lattice there are two kinds of interstices, which the metal ions may occupy. Firstly, the interstices which are surrounded by four oxygen ions situated at the corners of a regular tetrahedron; these interstices are known as tetrahedral spaces. Secondly, the interstices which are surrounded by six oxygen ions situated at the corners of an octahedron; these interstices are the octahedral spaces.

The tetrahedral and octahedral spaces in the lattice are shown in Figures Ib and Ic by small black dots and circles respectively. The larger black dots represent the oxygen ions.

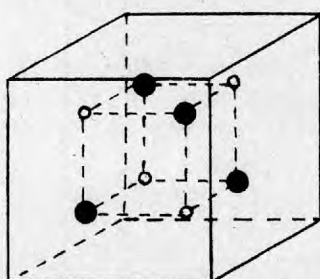
In each octant there are 4 octahedral spaces and 8 tetrahedral spaces. Thus, per unit cell there are 96 spaces available to 24 metal ions. The symmetry of the spinel



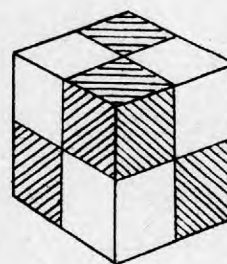
a



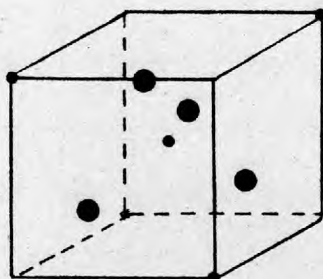
b



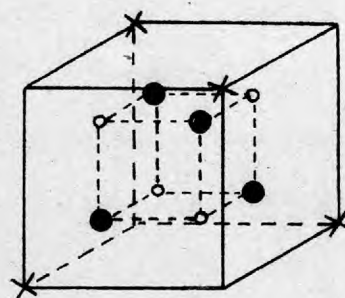
c



d



e



f

● REPRESENTS OXYGEN IONS
 • AND X REPRESENT TETRAHEDRAL SPACES
 ○ REPRESENTS OCTAHEDRAL SPACES

FIGURE I SPINEL LATTICE

structure, determined independently by W.H. Bragg³ and S. Nishikawa⁴, requires that the 24 metal ions shall occupy certain definite positions in the lattice.

It would be possible for these cations to occupy other positions, but only by a violation of the true symmetry of the spinel structure.

In this symmetrical structure of the spinels the metal ions are distributed in the oxygen lattice in such a way that there are two types of octant, which are arranged as shown in Figure Id. In the octants of one sort all the octahedral spaces are vacant and only two of the tetrahedral spaces, indicated in Figure Ie by small black dots, are occupied. If this type of octant is considered to be represented by the shaded areas in Figure Id, it will be seen that each corner at which an occupied tetrahedral space is situated is coincident with the corners of seven other octants. Three of these octants are of the same type as the first and the occupied tetrahedral space situated at the corner is considered to be shared between these four shaded octants, i.e., each shaded octant has a quarter share in this space. Such occupied tetrahedral spaces occur at four of the corners of each shaded octant, thus each of the octants of this type possesses four quarter spaces or one complete occupied tetrahedral space. This one

occupied space together with the other one situated at the centre of the octant, as shown in Figure 1e, make up the two tetrahedral spaces occupied in this type of octant.

In the octants of the other sort only the four octahedral spaces are occupied, as indicated by the circles in Figure 1f. Tetrahedral spaces, indicated by crosses are situated at four of the corners of this type of octant. These are considered to belong to the adjacent octants of the other type and they are, in fact, the occupied tetrahedral spaces situated at corners discussed above.

There are, thus, in a unit cell of a true spinel, 8 tetrahedral and 16 octahedral spaces available for occupation by the metal ions. The use of the remaining 72 spaces in the cell is not allowed by the observed symmetry of the spinel structure.

Considering first the "2:3" type of spinel, the most likely arrangement of the 24 metal ions would appear to be that in which the 8 bivalent metal ions occupy the 8 tetrahedral spaces and the 16 trivalent metal ions occupy the 16 octahedral spaces. This arrangement is the true one in many cases, e.g.,

Mixed oxides of aluminium and a bivalent metal	$M^{II}Al_2O_4$
Mixed oxides of chromium and a bivalent metal	$M^{II}Cr_2O_4$
Zinc ferric oxide	$ZnFe_2O_4$
Cadmium ferric oxide	$CdFe_2O_4$

In the case of the "4:2" type of spinel, a similar arrangement would appear to be the most probable. That is, one in which the 8 quadrivalent cations occupy the 8 tetrahedral spaces and the 16 bivalent cations occupy the 16 octahedral spaces.

However, in certain cases, e.g.,

Magnesium ferric oxide (i.e., Magnesium ferrite)	$MgFe_2O_4$
Magnesium gallium oxide	$MgGa_2O_4$
Magnesium indium oxide	$MgIn_2O_4$
Magnesium titanium oxide	$TiMg_2O_4$
Ferrous titanium oxide	$TiFe_2O_4$
Zinc stannic oxide	$SnZn_2O_4$,

although the compounds are undoubtedly spinels, the intensities of the lines of the X-ray diffraction patterns cannot be reconciled with the ionic arrangement of the spinel structure given above.

The most reasonable alternative distributions for the "2:3" type of spinel is the one in which the 8 bivalent cations occupy 8 of the 16 octahedral spaces and the 16

tervalent ions are divided equally between the remaining 8 available octahedral spaces and the 8 tetrahedral spaces. The 8 bivalent and the 8 tervalent ions are distributed at random among the 16 octahedral spaces. Thus, the octahedral spaces of a unit cell will contain equal numbers of bivalent and tervalent ions only on an average. In other words, as far as the metal ions are concerned, the concept of unit cell has here lost its usual significance.

The corresponding structure in the case of the "4:2" type of spinel is that in which the quadrivalent ions are situated only in the octahedral spaces and the bivalent cations are distributed equally between the octahedral and tetrahedral spaces.

This arrangement, known as the inversed spinel structure, may be represented by the general formula, $Y(XY)O_4$, instead of by XY_2O_4 , the general formula of the normal spinel structure.

The relative intensities of the lines on the X-ray powder photographs corresponding to these two ionic arrangements have been calculated for a number of spinels by T.F.W. Barth and E. Posnjak⁵. In Table I their calculated and observed values for the relative intensities of the lines in the pattern of magnesium ferrite are given. The figures in column I correspond to the normal spinel structure, XY_2O_4 ,

and those in column II to the inversed structure, $Y(XY)O_4$.

TABLE I
RELATIVE INTENSITIES IN THE MAGNESIUM FERRITE PATTERN

h,k,l	I	Observed	II
111	5.0	0.5	0.0
220	1.1	5	5.0
113	13.4	10	15.7
222	1.2	-	0.1
400	9.7	5	3.6
133	0.1	-	0.0
224	0.8	3	3.5
333) 115)	7.2	7	8.3
440	14.5	9	14.5
135	2.1	-	0.0
260	3.9	1	1.9
335	3.2	2	3.6
226	2.5	-	0.9
444	2.9	-	0.2
155) 117)	1.8	-	0.0
246	5.0	2	2.7
355) 137)	3.8	4	7.2
800	2.4	2	2.4
337	1.0	-	0.0
660) 228)	0.2	1	1.2
555) 157)	3.2	3	3.8
266	1.6	-	0.5
466	0.1	1	0.7
139	2.1	2	2.6

It is clear from Table I that the observed intensities are in far closer agreement with the values in column II, corresponding to $\text{Fe}(\text{MgFe})\text{O}_4$, than they are with those in column I, based on MgFe_2O_4 . These calculated values are based on the assumption of an atomic parameter value of $0.375a$, where " a " is the lattice constant of the unit cell. This parameter is the length of a side of one of the regular tetrahedra formed by the oxygen ions surrounding a tetrahedral space, shown in Figure Ia, given as a fraction of the length of a side of the whole unit cell, shown in Figure Id. It was found by T.F.W. Barth and E. Posnjak⁵ by plotting various parameter values against the relative intensities that the closest agreement with observed intensities is obtained by the use of a parameter of $0.390 \pm 0.006a$.

These investigators have thus shown that some spinels are of the inversed type, i.e., possess variate atom equipoints. This phenomenon is well-known in the case of mixed crystals, e.g., in $(\text{K},\text{Na})\text{Cl}$ the K^+ and Na^+ ions are distributed at random over the Na^+ positions in a rock-salt lattice. E. Posnjak and T.F.W. Barth⁶ have also shown that with regard to compounds those of the inversed spinel structure are not unique in exhibiting the variate atom equipoint

arrangement. The compound lithium ferrite, $\text{Li}_2\text{O}, \text{Fe}_2\text{O}_3$ or LiFeO_2 , has been found to crystallise in the rock-salt structure in such a way that the oxygen ions occupy the Cl^- positions and the Li^+ and the Fe^{3+} ions, of which there are an equal number, are distributed at random over the Na^+ positions.

The structure of certain spinels, however, cannot be determined in detail by X-ray diffraction methods, because of the similarity in X-ray scattering power of the different cations of these spinels.

E.J. Verwey, P.W. Haayman and E.L. Heilman² have concluded from a study of the lattice constants of many spinels that the compounds cobalt ferrite, CoFe_2O_4 , manganese ferrite, MnFe_2O_4 , and magnetite, FeFe_2O_4 or Fe_3O_4 , have the inversed structure. Their argument is given below.

TABLE II
LATTICE CONSTANTS OF SPINELS

	1	2	3	4	5	6
	IONIC RADII	Al ³⁺ (0.57A) LATTICE CONSTANTS	DIFFER- ENCE	Cr ³⁺ (0.64A) LATTICE CONSTANTS	DIFFER- ENCE	Fe ³⁺ (0.67A) LATTICE CONSTANTS
Ni ²⁺	0.78A	8.05A	0.25A	8.30A	0.06A	8.36A
Cu ²⁺	-	8.07A	-	-	-	8.37A
Mg ²⁺	0.78A	8.07A	0.24A	8.31A	0.05A	8.36A
Co ²⁺	0.82A	8.08A	0.24A	8.32A	0.04A	8.36A
Zn ²⁺	0.83A	8.07A	0.23A	8.30A	0.12A	8.42A
Fe ²⁺	0.83A	8.12A	0.22A	8.34A	0.05A	8.39A
Mn ²⁺	0.91A	8.26A	0.23A	8.49A	0.06A?	8.55A?
Cd ²⁺	0.97A	-	-	8.57A	0.12A	8.69A

From Table II it may be seen that on passing from an aluminate to the corresponding chromite that the lattice constant increases, as would be expected from the larger ionic radius of the trivalent chromium ion, by approximately 0.24A. Since the difference in radii between the Fe³⁺ and Cr³⁺ ions is about one half of that between the Cr³⁺ and Al³⁺ ions, it might be expected that the increase in lattice constant on passing from a chromite to the corresponding ferrite would be about $\frac{0.24A}{2} = 0.12A$. This is true for zinc and cadmium ferrites, i.e., for ferrites

known to have the normal spinel structure. However, for all other ferrites investigated, the increase in the lattice constant is much smaller, i.e., about 0.05Å. In this group are magnesium and copper ferrites, which are known to have the inversed structure. It is concluded from this that the ferrites of the other bivalent metals in Table II, except zinc and cadmium, i.e., cobalt, manganese and ferrous iron, also possess the inversed structure.

Another argument in support of this is the fact that the ferrites of magnesium, copper, cobalt, manganese and ferrous iron are all ferromagnetic, whereas those of cadmium and zinc are not.

Another case in which the structure must be deduced is that of Spinel itself, MgAl_2O_4 , as the scattering powers of the Mg^{2+} and Al^{3+} ions are practically identical.

A similar argument to that used above may be applied here. All the other aluminates are known to have the normal spinel structure. The difference in lattice constant between magnesium aluminate and chromite is in agreement with that between the aluminates and chromites of the other bivalent metals. Also, in common with the other aluminates, magnesium aluminate is not ferromagnetic.

Magnesium aluminate is thus considered to have the normal spinel structure.

The lattice energies of the alternative distributions of metal ions have been calculated², and consequently the electrostatically most stable forms are known. In the case of the "2:3" type of spinel, the most stable form is the normal structure. On the other hand, the stable form for the "4:2" type of spinel is the inversed structure. The ferromagnetic ferrites do not conform to this electrostatic theory.

The following generalisations concerning the distribution of cations in spinels may be made.

1. Tervalent and quadrivalent cations occupy the octahedral spaces in agreement with the electrostatic conception of the structure of spinels.
2. The exceptions to this are the trivalent ions of iron, indium and gallium, which have a preference for the tetrahedral spaces.
3. The bivalent ions of zinc and cadmium have a strong preference for the tetrahedral spaces, and are able to displace the trivalent ions of iron, indium and gallium from them.

These generalisations are valid also for the formation of mixed spinels.

(3) Lattice Constant of Magnesium Ferrite

The lattice constant of magnesium ferrite has been determined by a number of investigators. Their results are recorded below in Table III. In all cases where details of the method of preparation are given in the original paper, reference is made to the appropriate method in the sub-section on "Methods of Preparation", which follows.

It will be seen that the results of the various observers vary appreciably. Only in one case has a reason for this been suggested⁷. It is that the variations are due to impurities and the different temperatures of preparation.

The smallest value recorded is that of S. Holgersson¹, i.e., 8.342A. In this case the material examined was probably contaminated with potassium chloride, used in the preparation. The largest value, 8.377A, was reported by J. Bénard⁸, who prepared his sample of magnesium ferrite by heating the hydrated oxides in stoichiometric proportions at 800°C. under vacuum. It is probable that the method of preparation led to some decomposition.

TABLE III

RECORDED LATTICE CONSTANTS OF MAGNESIUM FERRITE

INVESTIGATOR	METHOD OF PREPARATION	LATTICE CONSTANT, a.
S. Holgersson ^{1, 9}	Naturally occurring mineral.	8.356 $\pm$ 0.004A
	Method 1, modified by the addition of an unspecified amount of KCl to the mixed oxides.	8.342 $\pm$ 0.005A
L. Passerini ^{10, 11}	Methods 7 and 10	8.360 $\pm$ 0.005A
E. Posnjak ¹²	Method 2	8.36 $\pm$ 0.01A
G.L. Clark, A. Ally and A.E. Badger ⁷	Method 8	8.366 $\pm$ 0.001A
T.F.W. Barth and E. Posnjak ⁵	No method given for MgFe ₂ O ₄ . Method 1 used for SnZn ₂ O ₄	8.36 $\pm$ 0.01A
O. Krause and W. Thiel ¹³	Method 1	8.35 $\pm$ 0.01A
E.J. Verwey, A.E. van Arkel and M.G. van Bruggen ¹⁴	Methods 1 and 4	8.37 ₀ $\pm$ 0.005A
J. Bénard ⁸	Method 4	8.377 $\pm$ 0.001A
E.J. Verwey, P.W. Haayman and E.L. Heilman ²	Method not given by investigators	8.36 $\pm$ 0.01A

(4) Methods of Preparation

From the foregoing discussion of the structure of magnesium ferrite it is clear that the compound may be considered as a mixed oxide. Of the many methods of preparation in the literature, a number are based on this conception, the simplest and probably the most satisfactory being Method 1 below.

The following methods of preparation have been reported in the literature.

1. In the method described by G.F. Hüttig and co-workers^{15, 16} magnesium oxide and ferric oxide were ground and mixed thoroughly in equimolecular proportions by being ground together in an agate mortar. The mixture was then heated at 1000°C., in one case for 36 hours, and in another for 72 hours.

The magnesium oxide was obtained by heating pure magnesium carbonate for two hours at 540°C. in an electric oven.

The ferric oxide was obtained by the ignition for two hours over the full blast of a Bunsen burner of hydrated ferric oxide, prepared by precipitation according to the method of G.F. Hüttig and H. Garside¹⁷, which is described fully in Section II: "Preparation of Materials", sub-section (2).

2. In the method of E. Posnjak¹², which is similar to the one above, an intimate mixture of finely divided magnesium carbonate and ferric oxide in equimolecular proportions was heated at 800°C. The material was then repeatedly ground and reheated at about 600°C. for several days.

3. K. List¹⁸ has described a method in which a paste of freshly ignited magnesium oxide and water was added to an acid free solution of ferric chloride until a bright brown flocculent precipitate resulted. A purer product is said to have been obtained if a dilute solution of magnesium sulphate or chloride was mixed with sodium or potassium hydroxide and then mixed with ferric chloride until the liquid was strongly alkaline. The precipitate, obtained in either way, was washed and roasted. The product was a sintered, cinnamon brown sample of magnesium ferrite.

4. H. Forestier¹⁹ repeated the work of K. List and decided that complete combination was not obtained by the latter's methods. H. Forestier simultaneously precipitated hydrated ferric and magnesium oxides from a solution containing equimolecular proportions of ferric and magnesium chlorides.

The precipitant used was either sodium or potassium hydroxide. The precipitate was dried at $150^{\circ}\text{C}.$, and finally, ignited at $900^{\circ}\text{C}.$ for 7 hours.

J. Bénard⁸ also used the simultaneous precipitation method. He heated the precipitate at $800^{\circ}\text{C}.$ under vacuum to obtain magnesium ferrite.

5. In the method of S. Hilpert and A. Wille²⁰ magnesium ferrite was obtained by heating sodium ferrite, $\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$, with magnesium chloride. The sodium ferrite was prepared by heating ferric oxide and sodium carbonate in the required proportions at a high temperature.

6. A fusion method has been used by K.A. Hofmann and K. Hörschele²¹, in which iron filings, ferric sulphate or ferric oxide were added to a melt of magnesium chloride and the mixture heated for several hours. When cold, the melt was found to possess a crust consisting of crystals of magnesium ferrite. This method is described more fully in a later section.

7. Some earlier work by F. Hundeshagen²² was carried out on similar lines. An iron rod was immersed in molten magnesium chloride under a pressure of 20 to 22 atmospheres of steam in a heated autoclave. This investigator claimed to have obtained dark glistening crystals, which could be easily disintegrated to an almost white, non-magnetic powder.

The composition of this material was given as 80.3% Fe_2O_3 and 19.7% MgO by weight. The stoichiometric compound MgFe_2O_4 contains 79.84% Fe_2O_3 and 20.16% MgO by weight.

The composition given for this material may be related to the unit cell of magnesium ferrite, which contains 32 oxygen atoms. On this basis, the stoichiometric compound is represented by $\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$ and the material obtained by F. Hundeshagen by $\text{Mg}_{7.85}\text{Fe}_{16.1}\text{O}_{32}$.

8. J.J. Ebelmen²³ has described another fusion method for the preparation of spinels, in which a mixture of the two oxides was heated with boric acid. The boric acid fused and dissolved the other oxides. The mixture was heated until all the boric acid had volatilised, leaving a crystalline spinel.

This method was used by G.L. Clark, A. Ally and A.E. Badger⁷ to prepare magnesium ferrite for X-ray examination. They purified the magnesium ferrite obtained by leaching it with dilute hydrochloric acid.

9. Magnesium ferrite of stoichiometric composition was prepared by E. Dufau²⁴ by heating a mixture of ferric and magnesium oxides in an electric arc of 300 amperes at 70 volts.

A fused, dark brown, very refractory product was obtained.

10. Crystalline magnesium ferrite has been obtained by St. C. Deville²⁵ in dark, glistening, regular octahedra. The method consisted in passing a stream of dry hydrochloric acid gas over a mixture of ferric and magnesium oxides at red heat.

11. K. Krant²⁶ has reported that a material of the approximate composition $6\text{MgO}, \text{Fe}_2\text{O}_3, 9\text{H}_2\text{O}$ was obtained by boiling a solution containing magnesium sulphate and ferric chloride.

If this material were to be considered, without the molecules of water, on the basis of the unit cell of magnesium ferrite, it would be represented as $\text{Mg}_{21.3}\text{Fe}_{7.1}\text{O}_{32}$.

(5) Properties of Magnesium Ferrite

In this section the various properties of magnesium ferrite are reviewed under separate headings.

Density

The density of magnesium ferrite has been determined, by means of a pycnometer, by a number of investigators.

L. Passerini¹¹ $\rho = 4.436$

E. Posnjak¹² $\rho = 4.481$

The density of the mineral magnesioferrite is given by J.D. Dana²⁷ as:-

$$\rho = 4.568 - 4.654$$

It is suggested that the higher value for the mineral arises from the isomorphous replacement of the magnesium by heavier atoms.

The density may be calculated from the formula:-

$$\rho = \frac{Mm}{a^3}$$

where M = Mass of a single molecule

m = Number of molecules per unit cell

a = Lattice constant

E. Posnjak¹² using his value for the lattice constant of 8.36Å found that:-

$$\rho = 4.518$$

Melting Point

The values for the melting point of magnesium ferrite which have been reported are given below.

H. Forestier ¹⁹	1650°-1700°C.
H.S. Roberts and H.E. Merwin ²⁸	1750°C.
A.E. van Arkel, E.J. Verwey and M.G. van Bruggen ²⁹	1760°C.

Solubility

Crystalline magnesium ferrite is insoluble in hot nitric acid, alkalis and dilute acids, but is soluble in concentrated hydrochloric acid. The material prepared in an electric arc²⁴ (Method 9) was reported to be decomposed by water and to be soluble in acids.

Decomposition

H.S. Roberts and H.E. Merwin²⁸ have prepared samples of magnesium ferrite, in stoichiometric and non-stoichiometric proportions, by the method of heating ferric and magnesium oxides. These investigators followed the course of the reaction by means of the change in refractive index of the product. A final mean value for the refractive index of 2.39 was obtained. The decomposition, in air at high temperatures (1000° - 1500° C.), of magnesium ferrite of four different compositions was investigated. One of the samples was of stoichiometric proportions and the remainder contained excess ferric oxide. The results are plotted in Figure II; the extent of decomposition is given by the percentage of ferrous oxide in the material.

From these results it appears that the stoichiometric compound is dissociated to a considerably less extent than the samples containing excess ferric oxide. Dissociation of the stoichiometric compound was detected at 1000° C. and was

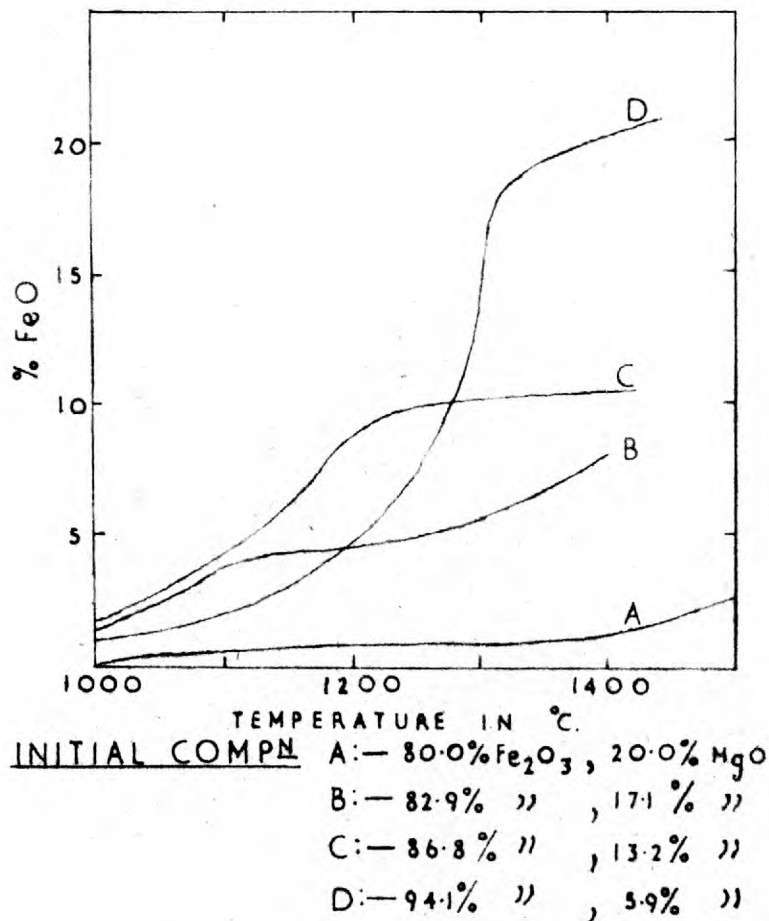


FIGURE II

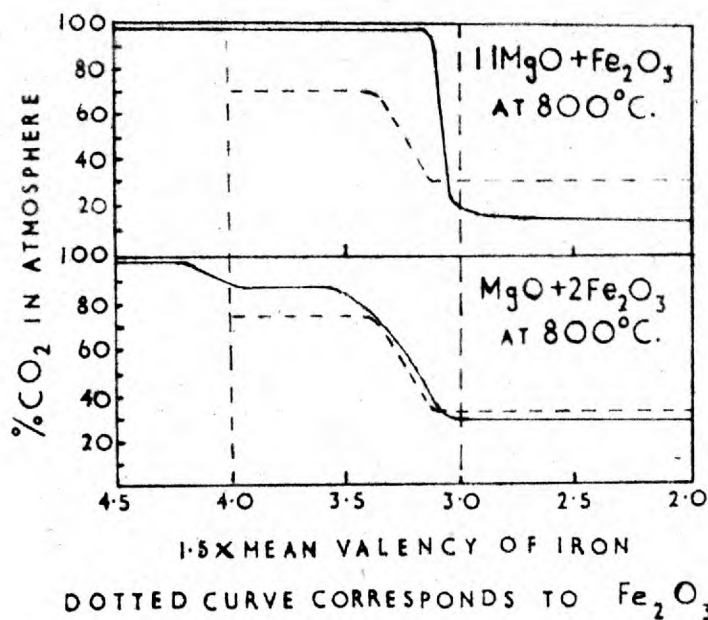


FIGURE III

found to be equivalent to 1.2% FeO at 1400°C. and 2% FeO at 1500°C. On the basis of the unit cell of 32 oxygen atoms, the dissociation corresponds to $\text{Mg}_{8.03}\text{Fe}_{16.06}\text{O}_{32}$ at 1400°C. and to $\text{Mg}_{8.06}\text{Fe}_{16.12}\text{O}_{32}$ at 1500°C.

R. Schenck and T. Dingmann³⁰ have studied the reduction of ferric oxide and also that of mixtures of ferric and magnesium oxides in the non-stoichiometric proportions $11\text{MgO}, \text{Fe}_2\text{O}_3$ and $\text{MgO}, 2\text{Fe}_2\text{O}_3$. The reduction was carried out in an atmosphere of carbon monoxide and carbon dioxide, the relative proportions of which were known. By varying the ratio of carbon monoxide to carbon dioxide the reduced states of the material in equilibrium with various mixtures of the gases were found. In the case of ferric oxide, reduction isotherms, i.e., the curves showing composition at equilibrium against atmosphere, were obtained for temperatures ranging from 600° to 1100°C. Reduction isotherms for the materials containing magnesium were obtained at 650°C. and 800°C., and are shown in Figure III.

In these experiments the relative pressures of carbon monoxide and carbon dioxide were known, thus the equivalent partial pressure of oxygen could be calculated from the equilibrium:-

$$2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$$

from which
$$P_{\text{O}_2} = \frac{D_{\text{CO}_2} \times P_{\text{CO}_2}^2}{P_{\text{CO}}^2}$$

Where, D_{CO_2} = Dissociation constant at the temperature of the reduction.

and P_{O_2} , P_{CO_2} , P_{CO} = The partial pressures of oxygen, carbon dioxide and carbon monoxide, respectively.

From the reduction isotherms the percentage of carbon monoxide in the gas, or the equivalent oxygen pressure, in equilibrium with material at the successive stages in the reduction could be found.

It has been stated also by H. Leibniz and E. Brandenburger³¹ that magnesium ferrite may be reduced to $(\text{Fe},\text{Mg})\text{O}$. This is equivalent to the reduction of all the ferric ions in the ferrite to the ferrous state. No details of the atmospheric conditions employed or of the temperature at which the reduction was carried out are given.

Solid Solutions

The phase diagram of the Mg - Fe - O system given by R. Hay and J. White³² shows $\text{MgO},\text{Fe}_2\text{O}_3$ to be the only compound between ferric and magnesium oxides. This is also stated by H.S. Roberts and H.E. Merwin²⁸.

It follows from this, if ferric and magnesium oxides are combined in other than the stoichiometric proportions of the compound $\text{MgO}, \text{Fe}_2\text{O}_3$ to form a single homogeneous phase, that a solid solution between the excess oxide and magnesium ferrite exists. The evidence in the literature on such solid solutions is conflicting.

H.S. Roberts and H.E. Merwin²⁸ examined quenched and rapidly cooled samples of magnesium ferrite microscopically. They did not detect a solid solution of ferric oxide in magnesium ferrite, but found approximately 1% of magnesium oxide in solution in magnesium ferrite in the temperature range 1000° to 1750°C .

H. Forestier¹⁹, on the other hand, has reported the existence of a solid solution of excess ferric oxide in magnesium ferrite, which is saturated at the composition $\text{MgO}, 1.13 \text{Fe}_2\text{O}_3$ in the temperature range 315° to 400°C . This corresponds to $\text{Mg}_{7.28}\text{Fe}_{16.46}\text{O}_{32}$. No solid solution of magnesium oxide in magnesium ferrite was detected by the method used, which was to observe the change in Curie point of the material with its change in composition.

A.E. van Arkel, E.J. Verwey and M.G. van Bruggen^{29,14} have investigated the solid solutions of excess ferric and magnesium oxides in the ferrite at 1300°C . by an X-ray method.

Their method depends upon the appearance of a second phase in the X-ray pattern of the material. The investigators draw attention to the fact that the method is not very accurate as the second phase must be present as a substantial percentage of the whole, perhaps 10%, before its presence will be detectable in the X-ray pattern. They found that the lines of excess ferric oxide first appeared in the X-ray pattern at the composition $4\text{Fe}_2\text{O}_3, 3\text{MgFe}_2\text{O}_4$, which corresponds to $\text{Mg}_{4.0}\text{Fe}_{18.67}\text{O}_{32}$. In the case of the solid solution of magnesium oxide in the ferrite, difficulty was experienced in detecting the appearance of the oxide phase owing to the similarity of the X-ray patterns. The relative intensities of the lines to be expected in the X-ray pattern of the material having the composition $14\text{MgO}, 3\text{MgFe}_2\text{O}_4$, i.e., $\text{Mg}_{20.93}\text{Fe}_{7.39}\text{O}_{32}$, were calculated on the basis of a solid solution and of a mixture. The calculated values were compared with those observed, see Table IV.

TABLE IV
OBSERVED AND CALCULATED INTENSITIES IN THE X-RAY PATTERN OF
 $\text{Mg}_{20.93} \text{Fe}_{7.39} \text{O}_{32}$

h,k,l	CALCULATED INTENSITIES		OBSERVED INTENSITIES		
	AS A MIXTURE	AS A SOLID SOLUTION	HEATED 6 HRS. AT 1300°C. + 2 HRS. AT 1400°C.	+ 100 hrs. at 1000°C.	+ 45 hrs. at 1200°C.
311	20	9	9.2	10.8	12.9
400	17	14.5	14.8	13.8	13.7
333;511	6.5	3	4.4	4.8	5.8
440	17	17	14.2	14.4	14.6

It was concluded from these results that the material of the composition $\text{Mg}_{20.93} \text{Fe}_{7.39} \text{O}_{32}$ exists as a solid solution at 1400°C., but at lower temperatures, e.g., 1200°C., not all the excess magnesium oxide is in solution.

The methods of preparation used in this work were Method 1, the heating of the oxides, and Method 4, co-precipitation of the hydrated oxides. It was found that after heating at 1200°-1300°C. for several hours samples obtained in either way showed no difference in their properties.

These investigators have produced evidence to show that phase changes in the case of copper ferrite proceed sufficiently slowly for the high temperature conditions to be studied by investigating samples quenched in air. Samples of copper ferrite of various compositions were examined by X-rays while heated electrically on platinum wire inside the camera. Patterns obtained in this way and from samples of the same composition, quenched from the same temperature, were identical. This was not the case with patterns obtained from slowly cooled or annealed specimens.

J. Bénard⁸ also reports the existence of a solid solution between magnesium oxide, magnesium ferrite and magnetite. His method was similar to that used earlier by H. Forestier¹⁹, i.e., the observation of change in Curie point with change in composition. J. Bénard reports that the limit of solubility in the temperature range 430°-450°C. is of the order of 40% MgO in $\text{MgO} + \text{Fe}_3\text{O}_4$. This corresponds to $\text{Mg}_{15.64}\text{Fe}_{12.24}\text{O}_{32}$.

He also deduced the existence of a complete solid solution range between magnetite and magnesium ferrite from the continuous curve of Curie point against composition. His results are given in Table V.

TABLE V
CURIE POINTS OF THE $\text{Fe}_3\text{O}_4/\text{MgFe}_2\text{O}_4$ SYSTEM

MOL PERCENT. OF MgFe_2O_4 IN $\text{Fe}_3\text{O}_4/\text{MgFe}_2\text{O}_4$	CURIE POINT	LATTICE CONSTANT
0	570°C.	8.38A
20	555°C.	
60	530°C.	8.37A
75	490°C.	
100	315°C.	8.37A

J. Bénard found the lattice constants of magnesium ferrite and magnetite to be too close to prove or disprove the continuity of the solid solution, by X-ray examination.

It has been shown in the section on the decomposition of magnesium ferrite that the reduction may be carried beyond the stage corresponding to the magnetite/magnesium ferrite solid solution discussed above. At the stage where all the ferric ions have been reduced to the ferrous state, the material consists entirely of ferrous and magnesium oxides, which form a solid solution. The existence of a complete solid solution range between these two oxides has been shown by A.H. Jay and K.W. Andrews³³,

These investigators have followed the continuous change in lattice constant of the solid solution with change in composition, see Figure IV. The samples for X-ray examination were prepared from Analar magnesium oxide, ignited at $850^{\circ}\text{C}.$, and ferrous oxide obtained by the ignition of ferrous oxalate in vacuo at $1050^{\circ}\text{C}.$ Mixtures (0.5 g.) were prepared by weighing out the required amounts of the oxides, followed by thorough mixing in an agate mortar. The powder was then rammed into a small cylinder, which was placed in an iron crucible supported inside a refractory tube. This tube was evacuated to a low pressure and inserted into a vertical electric furnace. The temperature readings were taken in the space between the furnace wall and the evacuated tube.

The heat treatment of the samples was as follows:-

Room temperature to $1350^{\circ}\text{C}.$ - $1370^{\circ}\text{C}.$ in 2 hours.

Maintained above $1350^{\circ}\text{C}.$ for 2 hours.

Cooled to $1150^{\circ}\text{C}.$ in 1 hour.

Maintained at $1150^{\circ}\text{C}.$ for 1 hour.

Cooled rapidly to room temperature by withdrawal of the evacuated tube from the furnace.

The results obtained from the X-ray examination of the samples in a 9 cm. camera are shown in Figure IV.

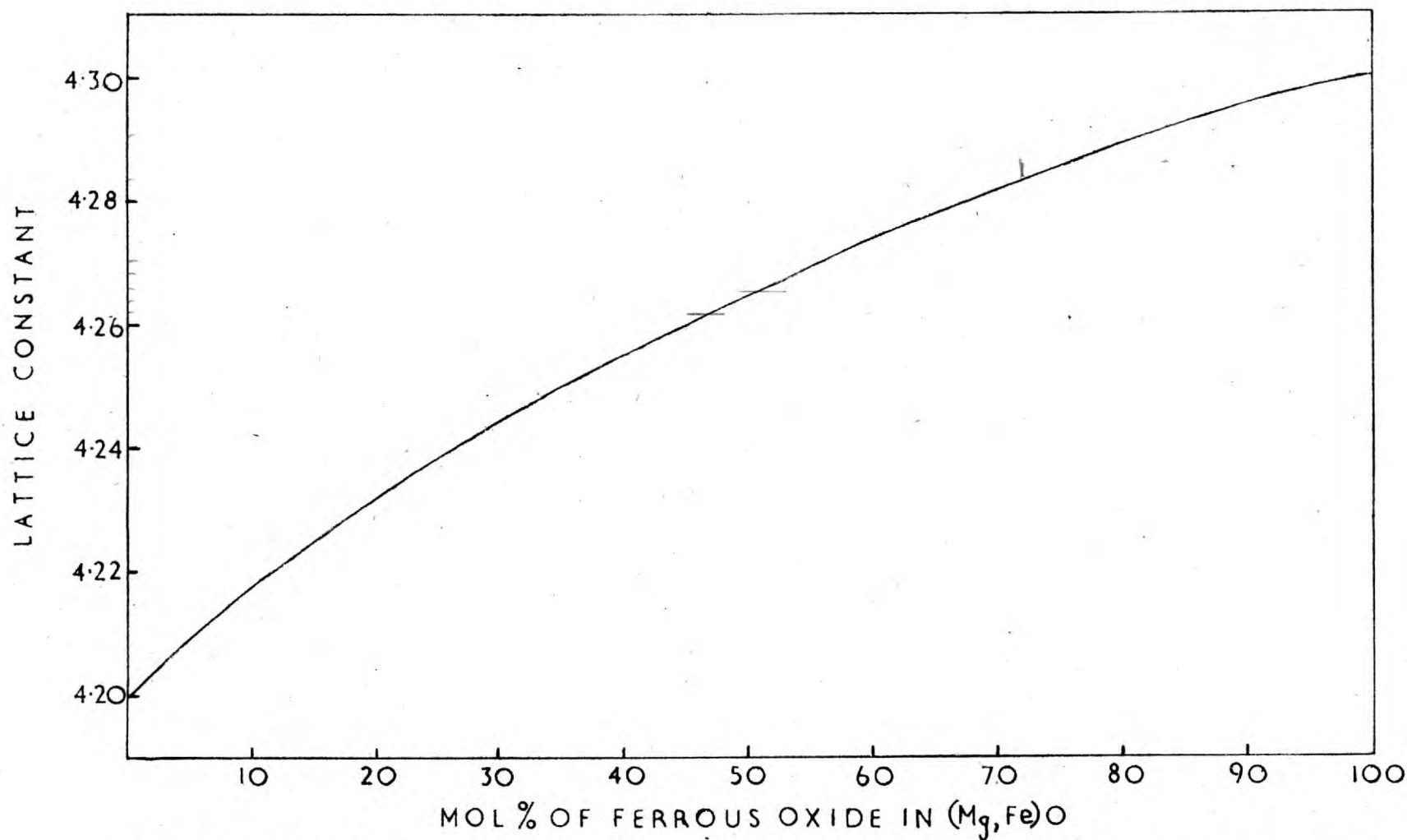


FIGURE IV

VARIATION IN LATTICE CONSTANT OF $(\text{Mg}, \text{Fe})\text{O}$ WITH COMPOSITION (A.H. JAY AND K.W. ANDREWS)

Magnetic Properties

In the section dealing with the structure of spinels, reference has been made to the fact that the ferrites having the inversed structure are ferromagnetic.

In reviewing this ferromagnetism, hysteresis will be considered first. The various factors concerned are related by equation:-

$$B = \mu_0 H + 4\pi I$$

Where B = Magnetic induction

μ_0 - Initial permeability

H = Magnetising force

I = Intensity of magnetisation

On division by H , the expression becomes:-

$$\mu = \mu_0 + 4\pi K$$

Where $\mu = \frac{B}{H}$ - Permeability

and $K = \frac{I}{H}$ - Susceptibility

On taking one cubic centimetre of a material through a cycle between $+H_{\max.}$ and $-H_{\max.}$, the energy dissipated as heat is the hysteresis loss. The induction remaining when H returns to zero is the remanance, B_r , and the negative magnetising force required to reduce B_r to zero is the coercive force, given the symbol H_c when the cycle has proceeded to saturation.

On heating a ferromagnetic material, a temperature, known as the Curie point, θ , is reached, at which the material ceases to be ferromagnetic and becomes paramagnetic. More exactly, the Curie point is T_0 in the Weiss Law:-

$$\chi (T - T_0) = \text{a constant}$$

Where T = Absolute temperature.

$$\chi = \frac{K}{\rho} = \text{Specific susceptibility}$$

ρ = Density of the material.

The magnetic properties of magnesium ferrite recorded in the literature are listed at the end of this section.

It has been pointed out by D.P. Raychaudhuri³⁴ that the magnetic properties of ferrites are dependent upon the method of preparation. However, the variations are probably due to impurities and the varying heat treatment of the specimens.

In their determination of the Curie point of magnesium ferrite, H. Forestier and R. Lille³⁵ did not use the direct method of observing the temperature at which the material ceases to be attracted by a magnet. Their method is based on the decomposition of acetic acid into acetone, carbon dioxide, carbon monoxide and hydrogen, which is catalysed by magnesium ferrite. The catalytic activity

increases sharply at the temperature corresponding to the Curie point. It was shown that the results obtained by this method agree with the results from thermomagnetic analysis in the case of the material having the composition 49.4 MgO, 50.6 Fe_2O_3 , for which the Curie point is 350°C .

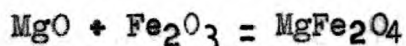
It has been shown by J.L. Snoek³⁶ that the addition of the non-magnetic zinc ferrite to the ferromagnetic ferrites lowers their Curie points. As the permeability of a substance is at a maximum at a temperature just below the Curie point, it follows that a material having its Curie point a little above room temperature will have maximum permeability at room temperature. In the case of $(\text{Mg},\text{Zn})\text{Fe}_2\text{O}_4$ the optimum proportions are $\text{MgO}, \text{ZnO}, 2\text{Fe}_2\text{O}_3$. The maximum initial permeability of this material is 700.

A number of phenomena associated with unignited magnesium ferrite have been examined by various investigators. Their observations are given below.

A Michel³⁷ has studied the magnetisation in weak fields of various ferrites, including that of magnesium, at various temperatures. It was found that the magnetisation reached a maximum between 300° and 500°C ., according to the field strength. This phenomenon disappeared with strong fields or with samples ignited at 1200°C .

H. Forestier and R. Lille³⁸ have heated samples of magnesium ferrite, prepared by the simultaneous precipitation of the hydrated oxides, for thirty minutes at various temperatures. The temperature of heating was plotted against the magnetisation of the sample. With the ferrites of nickel, barium, lead, copper and strontium, there was found to be a rise in the magnetisation at the temperature of heating corresponding to the Curie point of the ferrite. There was a further rise at the temperature of heating corresponding to the Curie point of ferric oxide. In the case of magnesium ferrite only the latter rise was observed.

It has been reported that active intermediates are produced during the course of the reaction:-



The catalytic effect of the active intermediates on the decomposition of nitrous oxide³⁹ and the oxidation of carbon monoxide⁴⁰ has been studied by G.F. Hüttig and co-workers and related to the magnetic susceptibility of the material at the temperature of the reaction. The temperature of maximum catalytic activity, 625°C. with carbon monoxide and somewhat lower with nitrous oxide, corresponds approximately to the temperature at which the susceptibility rises to ferromagnetic proportions.

On similar lines, measurements of magnetic susceptibility have been used by H. Kittel⁴¹ to show that the spinel structure is not formed from the oxides until a temperature of 600°C. is reached. This is the temperature at which the lines of the X-ray diffraction pattern of an equimolecular mixture of ferric and magnesium oxides were first observed to be displaced¹⁶.

However, J. Longuet and H. Forestier⁴² have detected reaction at lower temperatures. From magnetic measurements they have determined the rate of reaction between ferric and magnesium oxides at temperatures from 100° to 500°C. It was found that approximately 1% combined in 10 minutes at 450°C. After this time the reaction proceeded more slowly.

Recorded Magnetic Measurements of Magnesium Ferrite
Curie Point

H. Forestier and G. Chaudron⁴³

Composition.

From approximately $98\text{MgO}, 2\text{Fe}_2\text{O}_3$ (i.e., $\text{Mg}_{30.2}\text{Fe}_{1.2}\text{O}_{32}$)
to $\text{MgO}, \text{Fe}_2\text{O}_3$ (i.e., $\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$) 310°C.

From $\text{MgO}, \text{Fe}_2\text{O}_3$ to $44\text{MgO}, 56\text{Fe}_2\text{O}_3$
(i.e., from $\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$ to $\text{Mg}_{6.65}\text{Fe}_{16.91}\text{O}_{32}$) 310°-400°
(Above 56 mol percent. Fe_2O_3 400°C.)
(Curie point of excess Fe_2O_3 675°C.)

H. Forestier and R. Lille³⁵

MgO, Fe ₂ O ₃ (i.e., Mg ₈ Fe ₁₆ O ₃₂)	315°C.
49.4 MgO, 50.6 Fe ₂ O ₃ (i.e., Mg _{7.86} Fe _{16.10} O ₃₂)	350°C.
47.5 MgO, 52.5 Fe ₂ O ₃ (i.e., Mg _{7.41} Fe _{16.40} O ₃₂)	390°C.

J. Bénard⁸

MgO, Fe ₂ O ₃ (i.e., Mg ₈ Fe ₁₆ O ₃₂)	315°C.
60(MgO, Fe ₂ O ₃), 40Fe ₃ O ₄ (i.e., Mg _{4.80} Fe _{19.20} O ₃₂)	530°C.

Specific Susceptibility

E.F. Herroun and E. Wilson⁴⁴

Precipitated oxides dried at 90°C.	7.9 x 10 ⁻⁵	C.G.S.Units
After ignition	3.1 x 10 ⁻³	"

H. Forestier and G. Chaudron⁴⁵

In a magnetic field of 0-100 gauss	5.4 x 10 ⁻²	"
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Coercive Force

J.L. Snoek⁴⁶

Samples heated for 5 hours at 1250°C.

Maximum at 10MgO, 90Fe₂O₃ (i.e., Mg_{1.14}Fe_{20.57}O₃₂).. 60 gauss

Minimum at 65MgO, 35Fe₂O₃ 7 "

(i.e., Mg_{12.24}Fe_{13.18}O₃₂)

SECTION II

PREPARATION OF MATERIALS

SECTION II: PREPARATION OF MATERIALS.

In the present work, magnesium ferrite has been prepared from ferric and magnesium oxides, as described in the later sections. The sources of the oxides used are given below.

(1) Magnesium Oxide

Analar magnesium oxide has been used. The maximum iron content of this material is specified as 0.01%, and the moisture content as less than 5%. The actual moisture content varies. Results of 4.33% and 3.86% moisture have been obtained on different occasions.

(2) Ferric Oxide

The ferric oxide obtainable commercially is insufficiently pure for the present work, the chief impurity being manganese. Consequently, it was necessary to prepare the ferric oxide required; the methods employed are given below.

Precipitation

At first ferric oxide was prepared by the ignition of precipitated hydrated ferric oxide after the method of G.F. Hüttig and H. Garside¹⁷.

In this method the starting material was Analar crystallised ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The limits of impurity of this material are specified as:-

Free Chloride	0.001%
Sulphate	0.005%
Nitrate	0.002%
Ferrous Iron	0.03%
Copper	0.005%
Lead	0.0025%
Zinc	0.002%
Manganese	0.05%
Alkalis and other metals	0.01%
Arsenic (As_2O_3)	0.0025%

One gram-molecule of crystallised ferric chloride was dissolved in water, 100 ml. of concentrated hydrochloric acid were added and the solution diluted to one litre with water (Solution A). An aqueous solution containing one gram-molecule of ammonium chloride per litre (Solution B) and a third solution consisting of 5% aqueous ammonia (Solution C) were prepared.

50 ml. of Solution A were mixed with 50 ml. of Solution B and the resulting solution diluted to one litre with water. This solution was warmed to 70°C . and Solution C added drop-wise with constant stirring, until the solution contained a very slight excess of ammonia, as shown by a drop of the solution placed on a piece of filter paper moistened with methyl red solution. The clear supernatant liquid was

decanted and the residue agitated with about a half a litre of water at 50°C. and the wash liquid decanted. This washing by decantation was repeated two or three times. Finally, the precipitate was transferred to a Buchner filter funnel, sucked dry, removed from the filter with about half a litre of water at 50°C., agitated and filtered again. These agitations and filtrations were repeated five or six times. The washing was considered complete when the wash liquid gave not more than a very slight trace of turbidity with nitric acid and silver nitrate solution.

In order to reduce the amount of washing required, a centrifuge was later employed to remove the wash liquid more effectively.

The process was carried out later on a far larger scale in a glass tank of twenty litres capacity. The liquid was electrically heated and the supernatant liquid removed by means of a water pump. After the last decantation the hydrated ferric oxide was centrifuged.

It was found that the hydrated ferric oxide settled more quickly if a very dilute solution of ammonia was used as a wash liquid instead of distilled water.

The hydrated oxide was dried in a steam oven and subsequently ignited in platinum at 1000°C . in an electric muffle. The large scale process gave 40 g. of ignited ferric oxide per run.

This method was abandoned when a source of pure iron powder became available.

Ignition of Ferric Nitrate prepared from Pure Iron

About 400 ml. of 50% Analar nitric acid were heated on a steam bath or over a spirit lamp. To this hot acid 100 g. of pure iron powder were added in approximately 2 g. portions. The iron powder used was Mond Nickel Company carbonyl iron Grade MC containing less than 0.1% of carbon. The maximum impurities in the nitric acid were:-

Non-volatile matter	0.001%
Chloride	0.0001%
Iodate	0.0005%
Sulphate	0.0003%
Heavy metals (Pb)	0.0002%
Iron	0.0001%
Arsenic (As_2O_3)	0.000005%

It was necessary to use a large beaker, 2 or 3 litres capacity, to contain the acid, because the liquid frothed violently when the acid was fresh. Nitrogen

peroxide was evolved copiously and it was essential that the preparation should be carried out in a fume-cupboard or in the open air. The solution was kept covered with a clock glass and stirred periodically to prevent the iron forming a passive sludge on the bottom of the beaker. As the reaction became less vigorous further acid was added. About 600 ml. of concentrated acid were required in all for the dissolution.

When all the iron had been dissolved, the solution was transferred to a large porcelain evaporating basin. The contents of the basin were evaporated to a viscous state on the steam bath, and then taken to dryness on a sand-tray, and finally heated directly over a rose burner.

The hard, dry material was removed from the basin, broken up in a mortar, and ignited in a platinum dish at 1000°C . to decompose any remaining ferric nitrate. The resulting ferric oxide was then ground to a fine powder in a Wedgwood-end-runner mill.

Several kilograms of ferric oxide were prepared in this way.

(3) Preparation of Oxide Mixtures

Samples of homogeneous mixtures of magnesium oxide and ferric oxide were usually prepared in approximately 200 g. quantities at one time.

Approximately the required amount of magnesium oxide was ignited at 1000°C . in a platinum dish to constant weight. This usually required about five ignitions and weighings, owing to the fact that magnesium oxide is extremely hygroscopic. The magnesium oxide was then transferred to a ball-mill pot by means of a sheet of glazed paper. A camel hair brush was used to dust any oxide remaining on the paper into the pot. The platinum dish, together with any remaining magnesium oxide, was ignited to constant weight.

From the weight of magnesium oxide and the composition of the desired mixture, the amount of ferric oxide required was calculated.

The platinum dish was cleaned, ignited and reweighed. About 0.1 g. more than the required amount of ignited ferric oxide was weighed into the platinum dish on a rough balance. The dish and ferric oxide were ignited at a 1000°C . and weighed. Ferric oxide was removed from the dish until the correct weight was obtained. The dish and oxide were ignited and weighed once more after the last removal of oxide to ensure a true weight had been obtained for oxide free from moisture. It was found that it was necessary to allow the ferric oxide to cool for about one and a half hours in the desiccator before weighing.

The weighed ferric oxide was transferred to the same ball-mill pot as before. In this case the platinum dish was thoroughly dusted with a camel hair brush to ensure that all the oxide was transferred. This complete transference was possible in the case of the ferric oxide, as it does not adhere to the platinum dish.

The oxides were then ball-milled for 110-120 hours. Each day the caked powder was scraped away from the sides of the pot and broken up with a spatula. At the end of the period of milling the powder was removed from the pot, and finally, ground in an agate mortar. The powder was then ready for the subsequent stages of the preparation.

SECTION III

METHODS OF ANALYSIS

SECTION III: METHODS OF ANALYSIS

In the present investigations on magnesium ferrite, which are described in the later sections, it was necessary to know the exact chemical composition of the samples obtained. From the analyses, the valency state of the iron in the material and hence the extent of reduction, if any, could be determined. The methods of analysis employed are given fully below.

When the ratio of magnesium to iron in the sample was known from the original weights of the oxides taken, an analysis for iron was all that was required. However, when this ratio was not known, a complete analysis for magnesium and iron was necessary.

The iron was determined by the method of reduction with the silver reductor, described by G.H. Walden, L.P. Hammett and S.M. Edmonds⁴⁷, and titration of the reduced iron solution with a standard solution of potassium dichromate. The magnesium was precipitated with diammonium hydrogen phosphate and weighed as magnesium pyrophosphate.

Determination of Iron

The material was finely powdered in an agate mortar and dried in an electric oven at 110-120°C. in a weighing bottle. 1 to 1.5 g. of the sample were weighed out accurately into a 100 ml. beaker containing approximately 10 ml. of distilled water.

The beaker was covered with a watch glass and 15 to 20 ml. of Analar concentrated hydrochloric acid added to the contents of the beaker. The solution was digested on a steam bath or on an electric hot plate overnight. The solution was diluted with about 20 ml. of distilled water and allowed to cool.

The solution was then filtered through a 7 cm. No. 41 filter paper into a 250 ml. calibrated flask. The residue of difficultly soluble material was transferred to the filter paper and the beaker rinsed thoroughly with cold water several times and the washings poured through the funnel into the flask.

The residue and the filter paper were ignited in a platinum crucible until the paper had been burnt to ash completely. Approximately 0.5 to 1 g. of anhydrous sodium carbonate was added to the residue in the crucible. The sodium carbonate was fused over a full Bunsen burner flame for about thirty minutes.

The crucible was allowed to cool and placed in the 100 ml. beaker used previously, containing about 10 ml. of water. A further 10 ml. of water were placed inside the crucible and the beaker covered with a watch glass. The beaker was placed on a steam bath until the fused mass had disintegrated. Concentrated hydrochloric acid was then

added in small quantities until no more carbon dioxide was evolved. A further 5 to 10 ml. of acid were added in excess. The solution was again digested on the steam bath until it became quite clear. This solution was allowed to cool, and the crucible removed from the beaker with a glass stirring rod and rinsed. If the solution was clear, as was usually the case, it was added to the bulk of the solution in the 250 ml. flask. The beaker and stirring rod were rinsed five or six times, the washings being added to the flask. The solution in the flask was made up to the mark with distilled water and well shaken. If any insoluble matter still remained after the fusion with sodium carbonate, the solution was filtered through a 7 cm. No. 41 filter paper into the 250 ml. flask already used. The filter, beaker and stirring rod were rinsed five or six times, the washings being added to the flask. The solution was made up to the mark and well shaken.

The insoluble and the filter paper were ignited and weighed in a platinum crucible of known weight. An insoluble was found at this point in the analysis in only two or three cases. Its weight was insignificant, being of the order of 0.0002 g. to 0.0004 g.

In order to be certain that the silver reductor gave a satisfactory "blank", 150 ml. of 0.5 N. hydrochloric acid were passed through it at a rate of 30-40 ml. per minute. The acid was added in small portions, the silver being kept covered all the time with the acid. The acid was collected in a covered 400 ml. beaker. 4 ml. of syrupy phosphoric acid and six or seven drops (0.2 to 0.25 ml.) of N-methyl diphenylamine sulphonate indicator solution were added. The phosphoric acid was added to decolourise the ferric ions as they were formed during the titration.

The silver reductor was considered to be satisfactory when the addition of less than one drop of 0.1 N. potassium dichromate solution developed the colour of the oxidised form of the indicator (purplish-red) in the solution in the 400 ml. beaker.

50 ml. of the iron solution were pipetted into a 100 ml. beaker and passed through the reductor at a rate not exceeding 40 ml. per minute. The beaker and stirring rod were rinsed five or six times with N. Hydrochloric acid from a wash-bottle, the washings being added to the reductor. Finally, the reductor was rinsed through with 150 ml. of 0.5 N. hydrochloric acid. (The silver must be kept covered with acid all the time.) The reduced iron solution was

collected in a 400 ml. beaker; 4 ml. of syrupy phosphoric acid and six or seven drops of N-methyl diphenylamine sulphonate indicator solution were added. The solution was then titrated against standard deci-normal potassium dichromate solution, until the colour changed from green to purplish red.

Another "blank" was carried out on the reductor after the titration to test the completeness of washing.

The reduction and titration were repeated with a further 50 ml. portion of the iron solution. If the two titrations were not concordant, further titrations were carried out until concordant results were obtained.

All the volumetric apparatus used in the determinations had been calibrated previously.

The silver for the reductor was prepared as follows⁴⁷. 29 g. of silver nitrate were dissolved in 400 ml. of distilled water and 5 ml. of 2 N. nitric acid added. 5 g. of clean electrolytic copper foil were cut into pieces about one centimetre square, added to the silver nitrate solution and stirred vigorously by a mechanical stirrer until the exchange was complete (30 to 60 minutes). The supernatant liquid was decanted and washed with 2 N. sulphuric acid until free from copper ions. The silver was not allowed to become dry at any time. The yield was sufficient for one reductor.

Determination of Iron and Magnesium

The material for analysis was dried, weighed, and dissolved as before. The resulting solution was diluted to about 200 to 250 ml. with distilled water. The solution was brought to the boiling point and the iron precipitated with 1:1 aqueous ammonia, added until the solution was just alkaline to methyl red. The ammonium chloride, which must be present during the precipitation, was formed from the neutralisation by the aqueous ammonia of the excess acid left after the dissolution.

The solution was boiled gently for one minute, filtered through a 9 cm. No. 41 filter paper and the precipitate rinsed with 2% aqueous ammonium chloride. The original beaker was placed beneath the filter funnel and the precipitate dissolved in dilute (1:1) hydrochloric acid. The paper was washed thoroughly with hot water and then once with very dilute aqueous ammonia. The funnel was set aside for the next filtration. The last washing with aqueous ammonia was necessary in order to neutralise any hydrochloric acid remaining in the funnel. If this acid were allowed to remain it would dissolve a small amount of the

hydrated ferric oxide transferred to the funnel after the second precipitation.

The iron was reprecipitated from the solution at its boiling point, transferred to the filter paper used before, a feather being used to transfer the last traces. The precipitate was washed three or four times with hot 2% aqueous ammonium chloride and twice with 2% aqueous ammonium nitrate. This precipitate was dissolved completely in dilute (1:1) hydrochloric acid, the solution being added to a 250 ml. calibrated flask. The filter was washed with 2 N. hydrochloric acid from a wash-bottle, the washings being added to the 250 ml. flask. The solution in the flask was made up to the mark and the iron determined as before.

The united filtrates from the iron precipitations were made just acid by means of dilute (1:1) hydrochloric acid and evaporated to about 300 ml. in a porcelain evaporating basin. 2 g. of diammonium hydrogen phosphate plus 1 g. for each 100 ml. of solution were added. When the solution was cold, dilute (1:1) aqueous ammonia was added drop-wise with constant stirring of the solution until the magnesium ammonium phosphate was precipitated. 5-10 ml. of dilute (1:1) aqueous ammonia were added for each 100 ml. of solution. The solution was stirred well for ten minutes and set overnight in the refrigerator.

The precipitate was transferred to a 9 cm. No. 40 filter paper; the beaker and precipitate were washed two or three times with dilute (1:25) aqueous ammonia. The filtrate was discarded.

Any precipitate remaining in the beaker and on the stirrer was dissolved in 25 ml. of 2 N. hydrochloric acid, which was then poured through the paper to dissolve the bulk of the precipitate. The filtrate was collected in a 250 ml. beaker. The stirrer, beaker and filter paper were rinsed with hot dilute (1:100) hydrochloric acid until the volume of the filtrate reached 150 to 200 ml.

0.1 to 0.3 g. of diammonium hydrogen phosphate were added to the solution and the magnesium ammonium phosphate precipitated as before; the contents of the beaker were stirred well for ten minutes, and set aside overnight in the refrigerator. The precipitate was transferred to a 9 cm. No. 40 filter paper, a feather being used to transfer the last traces. The paper and precipitate were ignited in a weighed platinum crucible and weighed as magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.

Trial Analyses

The ignited ferric oxide which had been prepared gave on analysis the following results:-

99.85, 99.91,

99.87, 99.91% Fe_2O_3

Samples of carbonyl iron powder were found to give low analyses for iron owing to aerial oxidation of the very fine particles (5.3 to 5.7 microns in diameter). The results were lower the longer the iron had been removed from the air-tight container in which it was supplied.

Analyses of samples containing known amounts of magnesium oxide and iron were carried out. Separate solutions of magnesium and iron were made up in calibrated 250 ml. flasks. 50 ml. portions of these solutions were sufficient for one analysis.

In order to weigh out the magnesium oxide accurately, it was necessary to ignite it to constant weight in a platinum crucible. The magnesium oxide was dissolved out of the crucible in a covered beaker with hydrochloric acid. This solution was transferred to a 250 ml. calibrated flask, made up to the mark and well shaken.

The oven-dried iron powder was weighed out into a 150 ml. covered beaker containing about 10 ml. of distilled water and dissolved in 40 to 50 ml. of concentrated hydrochloric acid. This solution was transferred to another 250 ml. flask, made up to the mark and well shaken.

A 50 ml. portion was pipetted from each of these solutions into one 400 ml. beaker and a further 50 ml. portion from each solution pipetted into another 400 ml. beaker. The contents of these two beakers were analysed for iron and magnesium as previously described.

The results obtained are given below.

	Magnesium Oxide	Iron
Weight taken for analysis	0.1039 g.	0.7378 g.*
Weight determined	(a) 0.1037 g.	(a) 0.7365 g.
	(b) 0.1040 g.	(b) 0.7360 g.
Mean	0.1038 g.	0.7363 g.
Percentages of material taken for analysis	12.34%	87.66%
Mean percentages of the total as determined	12.33%	87.48%

* This weight was calculated from the percentage of iron in the iron sample as determined in a parallel analysis, in which the iron content of the material was found to be 98.9%.

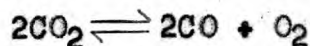
SECTION IV

METHODS OF OBTAINING LOW EFFECTIVE
OXYGEN PRESSURES

SECTION IV: METHODS OF OBTAINING LOW EFFECTIVE OXYGEN PRESSURES

The present investigations involved the preparation of magnesium ferrite from mixtures of ferric and magnesium oxides, under different effective oxygen pressures. In the cases where an oxygen pressure of one atmosphere was required in the reaction furnace, it could be readily obtained by the use of a cylinder of compressed oxygen. However, in the cases where the effective oxygen pressure required in the furnace at 1200°C. was in the range 10^{-7} to 10^{-15} mm. Hg, it was necessary to adopt a different method.

The method used by R. Schenck and T. Dingmann³⁰ to attain such low effective oxygen pressures has been described in the Introduction. It is based on the equilibrium:-



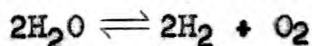
If the carbon monoxide and carbon dioxide are passed into the reaction furnace in known relative proportions, the partial pressure of oxygen may be calculated from the expression:-

$$P_{\text{O}_2} = \frac{D_{\text{CO}_2} \times P_{\text{CO}_2}^2}{P_{\text{CO}}^2}$$

Where D_{CO_2} = Dissociation constant of CO_2 at the temperature of the reaction furnace.

In order to maintain a constant partial pressure of oxygen, the relative proportions of carbon monoxide and dioxide must remain the same. In practice, this involves separate streams of the two gases flowing at constant relative rates into a mixing chamber prior to entering the furnace tube. This method, although sound, has the disadvantage that any change in the relative flow rates during the course of a run will alter the effective oxygen pressure in the furnace.

Another method depending on the equilibrium between two gases in order to attain the required partial pressure of oxygen in the furnace is based on the equilibrium:-



In this case, the partial pressure of oxygen is given by the expression:-

$$P_{\text{O}_2} = \frac{D_{\text{H}_2\text{O}} \times P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2}$$

Where $D_{\text{H}_2\text{O}}$ = Disassociation constant of H_2O at the temperature of the reaction furnace.

and P_{O_2} , $P_{\text{H}_2\text{O}}$ and P_{H_2} = Partial pressures of oxygen, water vapour and hydrogen, respectively.

As in the method above, it is necessary that the relative proportions of the gases passing into the furnace, in this case hydrogen and water vapour, should remain the same during the course of a run, in order that the effective pressure of oxygen should be constant. An apparatus in which this may be done is described in the following section. It is also necessary that the temperature of the furnace should be constant, as the dissociation constant of water vapour varies with temperature.

The theoretical limits to the oxygen pressures attainable in this way are the pressures corresponding to 100% water vapour and 100% hydrogen. Using water vapour and hydrogen, the range of oxygen pressure conveniently obtainable at 1200°C . with the apparatus used was:-

from 1.5×10^{-12} mm. Hg ($P_{\text{H}_2\text{O}} = 355$ mm. Hg; $P_{\text{H}_2} = 405$ mm. Hg)
to 10^{-15} mm. Hg ($P_{\text{H}_2\text{O}} = 17.5$ mm. Hg; $P_{\text{H}_2} = 742.5$ mm. Hg)

In order to extend the range above 1.5×10^{-12} mm. Hg, it is necessary to increase the ratio of water vapour to hydrogen. This may be accomplished by diluting the hydrogen with an inert carrier gas, e.g., nitrogen.

This dilution may be effected by the use of separate streams of hydrogen and nitrogen passing into a mixing chamber prior to the introduction of the water vapour into the gas.

Such a method has the same disadvantage as the carbon dioxide/carbon monoxide gas mixture method previously described, i.e., any change in the relative flow rates of the gases alters the effective oxygen pressure in the furnace.

A preferable method involves the use of a cylinder of compressed gas, containing known proportions of hydrogen and nitrogen, as a source of diluted hydrogen. In this case, the effective oxygen pressure in the furnace is given by the expression:-

$$P_{O_2} = \frac{D_{H_2O} \times P_{H_2O}^2}{\left(\frac{y(P_T - P_{H_2O})}{100} \right)^2}$$

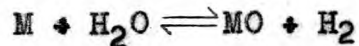
Where y = Percentage of hydrogen in the cylinder of compressed gases

and P_T = Total pressure in the system.

In this way the required range of effective oxygen pressures, i.e., 10^{-7} to 10^{-12} mm. Hg, could be covered.

The preparation of such cylinders of mixed gases is described in the following section.

An alternative method of obtaining the hydrogen/water vapour ratio required to cover this range of oxygen pressures is based on the equilibrium between a metal and water vapour, according to the general equation:-



If the activities of M and MO are taken to be unity,

$$\text{then } K_p = \frac{P_{H_2}}{P_{H_2O}}$$

Where K_p = Equilibrium constant at the temperature of the metal M.

As before, the effective oxygen pressure in the furnace in which the ferric and magnesium oxides are being reacted is:-

$$P_{O_2} = \frac{D_{H_2O} \times P_{H_2O}^2}{P_{H_2}^2}$$

Substituting K_p for $\frac{P_{H_2}}{P_{H_2O}}$,

$$P_{O_2} = \frac{D_{H_2O}}{K_p^2}$$

K_p may be found from the expression:-

$$\text{Log}_e K_p = \frac{-\Delta G}{RT}$$

Where ΔG = Change in free energy at the temperature of the metal M in the reaction:-



ΔG may be calculated from the specific heats of the substances concerned in the reaction and the heat of reaction.

It is clear that the effective oxygen pressure in the reaction furnace is independent of P_{H_2O} , provided that the latter remains constant.

The oxygen pressure in the furnace is dependent on K_p , which may be varied by altering the temperature of the metal M.

From consideration of the values for the change of free energy accompanying the oxidation of various elements, given by H.J.T. Ellingham⁴⁸, nickel and iron appear to be the most suitable metals for use in this method.

If nickel is used, the effective oxygen pressures attainable in the reaction furnace are in the range:-

$$P_{O_2} = 4.2 \times 10^{-9} \text{ mm. Hg (Ni at } 505^\circ\text{C.)}$$

$$\text{to } P_{O_2} = 2.0 \times 10^{-9} \text{ mm. Hg (Ni at } 285^\circ\text{C.)}$$

The results of experiments using nickel in this way are given in a later section.

If iron is used, the effective oxygen pressures attainable are of the order:-

$$P_{O_2} = 1.1 \times 10^{-12} \text{ (Fe at } 1100^\circ\text{C.)}$$

$$P_{O_2} = 8.6 \times 10^{-13} \text{ (Fe at } 1000^\circ\text{C.)}$$

SECTION V

DESCRIPTION OF APPARATUS

SECTION V: DESCRIPTION OF APPARATUS

(1) Apparatus for the Preparation of Magnesium Ferrite in Oxygen Atmospheres

The apparatus used at first to prepare samples of magnesium ferrite from the mixed oxides in oxygen at one atmosphere pressure was of simple construction. It consisted, as shown in Figure V, of a sulphuric acid bubbler and a U-tube, containing alkali (Sofnolite) and anhydrous magnesium perchlorate (Anhydron), through which oxygen was passed into a furnace tube, contained in an electric furnace. On leaving the furnace, the gas was led below water to prevent air diffusing into the furnace tube.

The furnace tubes used were mullite ($\Delta H5$) of $1\frac{3}{4}$ " external and $1\frac{1}{2}$ " internal diameter and 36" in length.

The electric furnace, which was made by Johnson Matthey and Co., Ltd., consisted of a sintered alumina tube wound with platinum plus ten per cent. rhodium wire. This furnace could be operated satisfactorily up to a temperature of 1500°C . The current was supplied to the furnace windings by means of a transformer contained in a control unit, which embodied a "Sunvic" energy regulator.

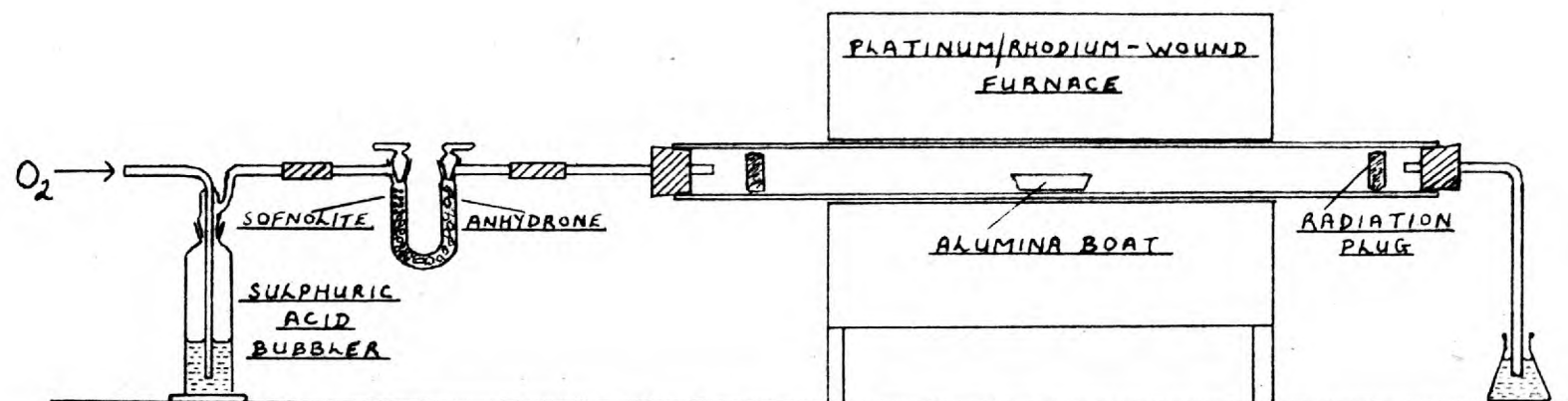


FIGURE V APPARATUS FOR THE PREPARATION OF MAGNESIUM
FERRITE IN AN ATMOSPHERE OF OXYGEN

The temperature of the furnace was measured by means of a platinum-platinum plus thirteen per cent. rhodium thermocouple, which ran the length of the furnace between the wound alumina tube and the mullite furnace tube. The thermojunction was situated in the central, i.e., the hottest, zone of the furnace. The ends of the thermocouple were connected by an auto-compensating lead to the galvanometer, calibrated to read directly in degrees Centigrade, contained in the control unit. The zero of this instrument was set by adjusting the reading to room temperature when the galvanometer was disconnected from the thermocouple.

Magnesia boats were used to contain the charge of approximately 100 g. of intimately mixed ferric and magnesium oxides in the preliminary runs. These boats were found to be unsatisfactory as they were too fragile and the contents adhered to the sides after reaction. Alumina boats were used subsequently as they were found to be far stronger and the contents contracted on reaction, so that they did not adhere to the boat.

(2) Apparatus for the Preparation of Magnesium Ferrite in either Oxygen or Controlled "Reducing" Atmospheres

The apparatus which was constructed subsequently in order to prepare samples of magnesium ferrite either in an atmosphere of pure oxygen or in a controlled reducing atmosphere of hydrogen and water vapour is shown diagrammatically in Figure VI, and in the photographs which form Figures VII and VIII.

In this apparatus the gas to be used was passed through a sulphuric acid bubbler and a U-tube packed as before. Immediately after the U-tube there was a side-arm dipping into mercury, which acted as an escape for gas should the pressure in the system have increased beyond a certain amount. From this point a by-pass tube led directly to the reaction furnace. In cases where the atmosphere required was oxygen at atmospheric pressure, the oxygen could be led through this by-pass to the furnace. The gas line from here included a flowmeter of the glass capillary type previously calibrated against a standard gas-meter, a manometer, both containing butyl phthalate as the manometric liquid and a nichrome-wound hard glass tube containing palladised asbestos at 350°C. The heated palladised asbestos

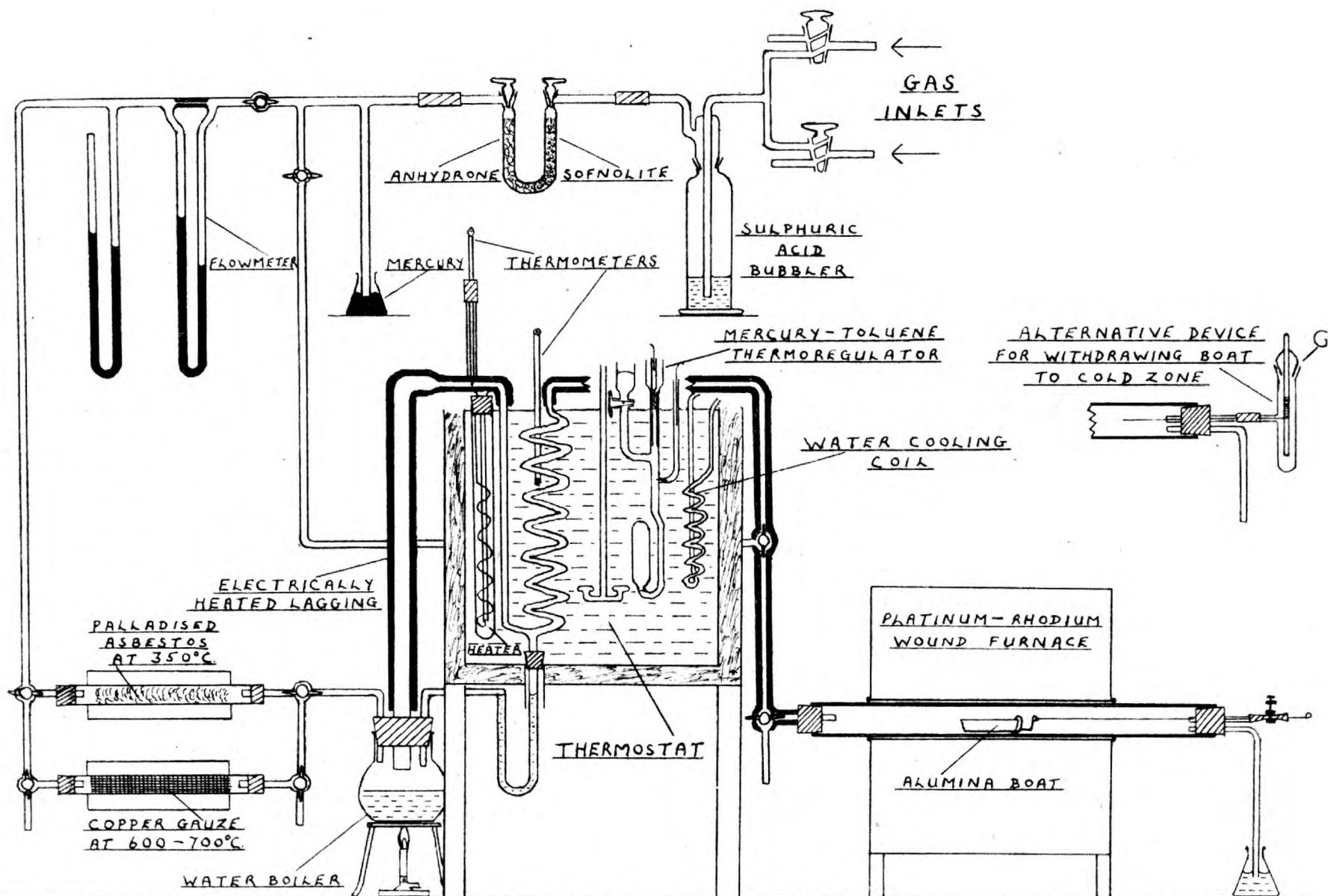


FIGURE VI APPARATUS FOR REACTING FERRIC AND MAGNESIUM OXIDES AT LOW EFFECTIVE OXYGEN PRESSURES



FIGURE VII APPARATUS FOR REACTING FERRIC AND
MAGNESIUM OXIDES AT LOW EFFECTIVE OXYGEN PRESSURES



FIGURE VII APPARATUS FOR REACTING FERRIC AND
MAGNESIUM OXIDES AT LOW EFFECTIVE OXYGEN PRESSURES

quantitatively removed traces of oxygen from the hydrogen by catalysing the reaction to water. In parallel with the palladised asbestos tube was a hard glass tube containing a tightly wound roll of copper gauze kept at a temperature of between 600° and 700°C. , by means of an electrically heated outer tube of alumina wound with nichrome wire. This heated copper was used to remove traces of oxygen from the nitrogen which was passed over samples whilst cooling in some cases.

The gas then passed into the water boiler and together with steam passed up an electrically heated lagged tube, past a thermometer introduced by means of a sealed side-arm, into the thermostat. In the thermostat the gas passed up a glass spiral in which water condensed and ran back into a U-tube. When the U-tube was full, the water overflowed back into the water boiler. The gas, saturated with water vapour at the temperature of the thermostat, passed out of the thermostat through electrically heated lagged tubing, maintained at a temperature above that of the thermostat, into the reaction tube in the furnace, which was as in the simpler apparatus previously described.

The thermostat consisted of one galvanised iron tank inside another, the space between them being packed with felt. The water in the thermostat was heated by means of an electric heater consisting of a spiral of nichrome wire wound round a thick walled pyrex glass tube, of external diameter approximately 1 cm., contained in a larger pyrex glass tube, of external diameter approximately 3 cms., having a closed end at the bottom. The temperature of the thermostat was kept constant to $\pm 0.05^{\circ}\text{C}$. by means of a mercury-toluene thermo-regulator and a "Sunvic" control unit. The mercury-toluene regulator was found to be superior to the bimetal spiral type. The thermostat also contained a water cooling coil of lead tubing, an electrically driven stirrer, a thermometer graduated in tenths of a degree and an extra heater, similar to the first, in order to be able to raise the temperature of the thermostat quickly.

It was found that when the thermostat was being run at temperatures above about 45°C . it was necessary to pour a small quantity of oil on the surface of the water and to fit a tin-plate lid in order to prevent excessive evaporation.

The hydrogen and nitrogen used were in all cases B.O.C. oxygen-free gases. By an arrangement of taps it was possible to change from one cylinder of gas to another without delay.

In place of the mullite tubes previously mentioned, an alumina tube of $1\frac{1}{2}$ " external and 1" internal diameter and 27" in length was used when preparing smaller samples of the order of 4 g., owing to its greater resistance to thermal shock.

In the case of the longer mullite tubes it was necessary to lag the ends of the tube, the entry end being electrically heated. With the shorter tube it was necessary to water cool the ends by means of partly flattened lead tubing. This, together with radiation plugs of refractory brick placed in the ends of the tube, largely prevented pyrolysis of the rubber bungs. Even so, the bungs were replaced periodically to ensure that the apparatus was gas-tight.

In the experiments in which the reducing atmosphere in the reaction furnace was obtained from the equilibrium between water vapour and nickel, as discussed in the previous section, the apparatus was modified as follows. An alumina

tube packed with nickel powder, contained in a small nichrome-wound furnace, was introduced into the gas line between the exit from the thermostat and the main reaction furnace. The temperature of the nickel powder was measured by means of a thermocouple passed between the packed alumina tube and the nichrome-wound furnace tube. Nitrogen was passed through the tube containing copper gauze heated at 600° to 700°C. to remove traces of oxygen before entering the water boiler. From the water boiler the nitrogen and steam passed through the thermostat, over the heated nickel and thence into the main reaction furnace.

(3) Preparation of Cylinders of Mixed Gases

In SECTION IV, methods of obtaining the required percentage of hydrogen in the furnace gas have been discussed. The method adopted here involved the use of cylinders of compressed hydrogen and nitrogen, the preparation of which is given below.

1. Mixture to contain a small percentage of hydrogen.

The apparatus shown in Figure IX was evacuated by means of a rotary oil pump, taps B and C and valve D being open, valve A being closed. Tap B was closed to the pump and B.O.C. oxygen-free hydrogen admitted to the cylinder M

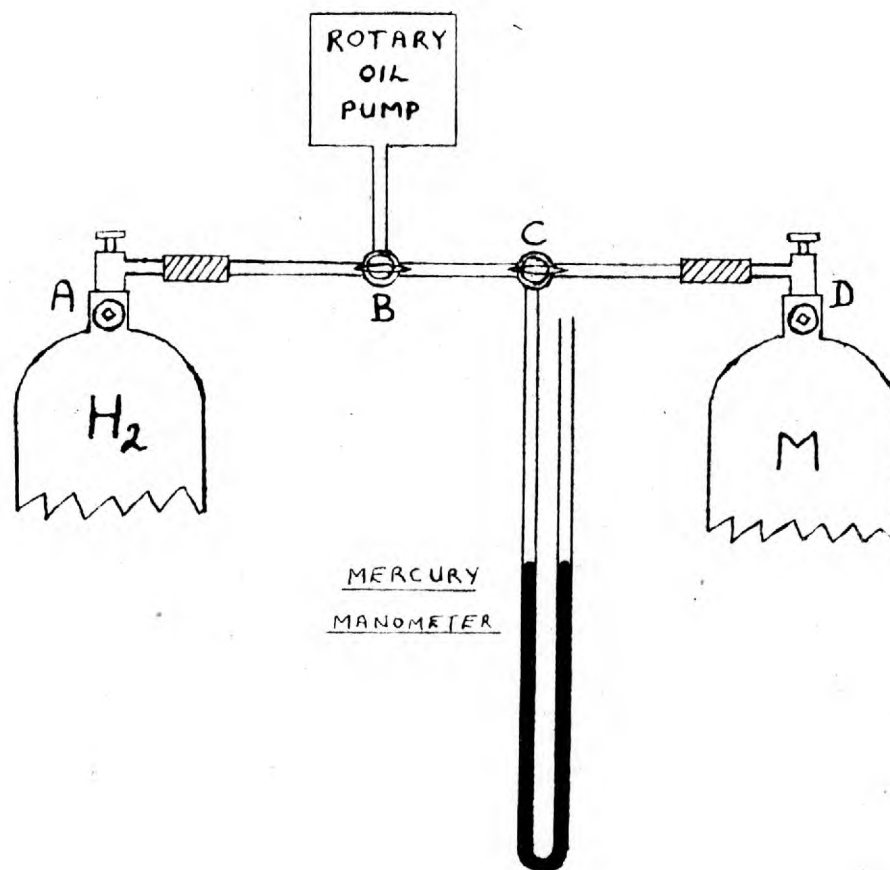


FIGURE IX APPARATUS FOR THE INTRODUCTION OF
HYDROGEN INTO A GAS CYLINDER

to the limit of the mercury manometer. Valve A was closed and the apparatus evacuated as before. The cylinder M was filled and evacuated once more. Hydrogen was admitted to the cylinder M until the required pressure, as read on the manometer, had been reached. Valve D was closed and the cylinder disconnected.

The B.O.C. oxygen-free nitrogen was introduced by means of a similar arrangement, using high-pressure copper capillary tubing and a steel three-way block in place of the glass apparatus used to admit the hydrogen. A 150 Atmosphere pressure gauge was used in place of the manometer. An oil pump was not included; consequently, the connecting tubes and the pressure gauge were flushed free from air by admitting nitrogen to them to a pressure of approximately 100 Atmospheres. The pressure in the tubes and the gauge was allowed to fall to about 10 Atmospheres by loosening one of the connections. This process was repeated several times. Nitrogen was then admitted to the cylinder M until the required pressure was reached.

The percentage of hydrogen in the gas was calculated from the pressure of hydrogen and the total pressure. The compressibility factor of nitrogen was taken into account.

Cylinder No. 1.

Atmospheric pressure 779.0 mm.Hg. Room temperature 21.0°C.

Manometer reading when cylinder evacuated 779 mm.Hg

" " " hydrogen introduced 561 " "

Pressure of hydrogen introduced 218 " "

Total pressure of $H_2 + H_2 = 54.5$ Atmospheres.

Room temperature 23.0°C.

$$\text{Pressure of } H_2 \text{ at } 23^\circ C. = \frac{218 \times 296}{294} = 220 \text{ mm. Hg}$$

$$= 0.29 \text{ Atm.}$$

$$\text{Pressure of nitrogen } P_{N_2} = 54.5 - 0.29 = 54.2 \text{ Atm.}$$

The percentage of hydrogen may be calculated by using the equation:-

$$PV = \chi RTn$$

Where P = Pressure in atmospheres

V = Volume in litres

χ = Compressibility factor

R = Gas constant in litre/atm. per degree

T = Temperature in °K.

n = Number of gram molecules of gas

The value for the compressibility factor of nitrogen was taken from the curves given by B.F. Dodge⁴⁹ for the variation of compressibility factor with reduced pressure and reduced temperature.

Critical pressure for $N_2, P_c = 33.5$ Atm.

Reduced pressure for N_2 in

$$\text{Cylinder 1} \quad = \frac{54.2}{33.5} = 1.62$$

Critical temperature for $N_2, T_c = 126^\circ K$.

Reduced temperature for N_2 in

$$\text{Cylinder 1} \quad = \frac{296}{126} = 2.35$$

For these values of reduced pressure and temperature

$$K = 0.99$$

$$\text{In Cylinder 1, } n_{N_2} = \frac{54.2V}{0.99RT}$$

$$n_{H_2} = \frac{220V}{760RT}$$

$$\frac{n_{H_2}}{n_{N_2}} = \frac{220V \times 0.99RT}{760RT \times 54.2V} = 0.00527$$

$$\text{Percentage of hydrogen} = \frac{0.00527}{1+0.00527} = 0.524\%$$

$$\underline{\text{Percentage of hydrogen in Cylinder No. 1} = 0.524\%}$$

2. Mixture to contain a larger percentage of hydrogen

Both the nitrogen and the hydrogen were introduced into the cylinder in the same way as the nitrogen into Cylinder 1.

The gas from the cylinder was analysed by means of a Bone and Newitt Gas Analysis Apparatus.

Cylinder No. II

Results of analyses	15.06% H ₂
	15.12% "
	15.21% "
Mean	15.13% "

Percentage of hydrogen in Cylinder No. II = 15.13%.

SECTION VI

DETAILS OF EXPERIMENTS

SECTION VI: DETAILS OF EXPERIMENTS

In using the apparatus described in the preceding section to prepare specimens of magnesium ferrite under controlled atmospheres, a different technique had to be adopted for each series of experiments carried out under different conditions. These techniques and details of the experiments performed are given below under the appropriate headings.

(1) Preparation of Magnesium Ferrite Specimens in Oxygen Atmospheres

This series of experiments was carried out in order to determine the limits of solid solution of excess ferric and magnesium oxides in magnesium ferrite prepared in an atmosphere of oxygen at 1200°C . This was done by observing the change in lattice constant with change in the ratio of ferric oxide to magnesium oxide in the sample. The magnetic permeability and dielectric loss at various frequencies were measured for each sample.

The range of composition investigated was from $2\text{MgO}, \text{Fe}_2\text{O}_3$ or $\text{Mg}_{12.80}\text{Fe}_{12.80}\text{O}_{32.00}$ to $\text{MgO}, 2.283\text{Fe}_2\text{O}_3$ or $\text{Mg}_{4.08}\text{Fe}_{18.62}\text{O}_{32.00}$; the full list being given in the Experimental Results. For each composition a mixture of ferric and magnesium oxides was prepared by the method

previously described and 100 g. samples reacted for 6 hours at $1200^{\circ} \pm 10^{\circ}\text{C.}$ in an atmosphere of oxygen, using either the apparatus shown in Figure V or that in Figure VI. In using the latter apparatus the oxygen was not passed through the thermostat, etc., but led directly to the reaction furnace through the by-pass.

It was necessary to prepare samples as large as 100 g. in order to make the magnetic measurements. This involved the preparation of large quantities of ferric oxide and of the mixtures concerned.

For each composition one 100 g. sample was cooled slowly in the furnace and one was quenched in water.

In order to cool the sample slowly at the end of a run, the furnace was switched from the Sunvic control unit onto a transformer. The voltage from the transformer was sufficient to hold the furnace at 750°C. The furnace and sample were allowed to cool to about 800°C. before the boat containing the sample was withdrawn very slowly by means of a piece of stout nichrome wire. The stream of oxygen was kept flowing during the period of cooling.

In order to quench the sample at the end of a run, the rubber bung was removed from the end of the furnace tube and the boat rapidly withdrawn by means of a piece of stout nichrome wire onto a piece of asbestos board. The boat was

immediately grasped in a pair of crucible tongs and inverted over a galvanised iron bucket, three-quarters full of distilled water. It was found that if a cloth were placed in the bottom of the bucket of water before quenching, the process was less violent.

(2) Preparation of Magnesium Ferrite Specimens in
"Weakly Reducing" Atmospheres

The object of this series of experiments was to prepare 100 g. samples of magnesium ferrite in weakly reducing atmospheres of the order of 10^{-9} mm. Hg of oxygen at $1200^{\circ} \pm 10^{\circ}\text{C.}$, in order to study the magnetic properties of specimens prepared under these conditions. In this series, as in the one above, one 100 g. sample was quenched in water and one was cooled slowly in the furnace for each set of conditions.

The method used to obtain such atmospheres was the one based on the equilibrium existing between water vapour and nickel previously discussed in SECTION IV. The apparatus employed has been described in SECTION V, and was the modification of the one shown in Figure VI involving the introduction of a heated alumina tube, packed with nickel powder, into the gas line between the exit from the thermostat and the main reaction furnace.

In this apparatus, nitrogen was passed through the tube containing copper gauze heated at 600° to $700^{\circ}\text{C}.$, to remove traces of oxygen prior to entering the water boiler. From the water boiler the nitrogen and steam passed through the glass spiral in the thermostat, where excess water vapour condensed and ran back into the boiler. On leaving the thermostat the gas passed through electrically heated lagged tubing into the alumina tube containing nickel powder at a known temperature. The gas leaving the nickel powder furnace contained nitrogen, water vapour and a small percentage of hydrogen, which could be calculated by the method given in SECTION IV. This gas was led through electrically heated lagged tubing to the main reaction furnace, which contained the boat of ferric and magnesium oxides intimately mixed in the stoichiometric proportions required to form magnesium ferrite. The water vapour and hydrogen in the gas set up the required low partial pressure of oxygen over the reacting oxides.

In this series of experiments the actual temperature of the thermostat is immaterial, provided that it remains constant during the run. This arises from the fact that the expression for the partial pressure of oxygen, derived in SECTION IV, does not contain $P_{\text{H}_2\text{O}}$. In practice, the temperature chosen was in the range 450 to $500^{\circ}\text{C}.$

In operating this apparatus it was necessary to maintain the temperature of the electrically heated lagged tubing at least 20°C. above that of the thermostat. This was done by varying the current supplied by means of a variable resistance incorporated in the circuit. As shown in Figure VI, two three-way taps were situated in this heated tubing. These taps were greased with high vacuum silicone grease, in order to keep them gas-tight. It was essential that the whole apparatus should be gas-tight, and consequently, frequent tests were made to ensure that this was so. In order to carry out these tests, a screw-clip was tightened up on a piece of rubber tubing fitted over the glass tube emerging from the rubber bung fitted into the exit end of the main reaction furnace tube. Gas was admitted to the apparatus until the pressure inside, as measured on the manometer, was about 50 cms. of butyl phthalate above atmospheric pressure. The apparatus was considered to be satisfactory if the pressure did not fall by more than a few millimetres in five minutes. Leaks, if found, usually occurred in one of the rubber connections in the electrically heated part of the system. These rubber connections were used at some points to prevent the apparatus

from fracturing too easily, especially when fitting the rubber bungs into the furnace tube.

(3) Preparation of Magnesium Ferrite Specimens in
"Reducing" Atmospheres

This series of experiments was an extension of the one above, in which large samples of magnesium ferrite were prepared primarily for examination of their magnetic properties. Samples were prepared in the range of oxygen pressure 10^{-8} to 10^{-12} mm. Hg at $1200^{\circ} \pm 10^{\circ}\text{C}$. The method used to attain such oxygen pressures has been discussed fully in SECTION IV and was the one based on the equilibrium existing between hydrogen and water vapour, giving rise to a low partial pressure of oxygen in the reaction furnace. The required mixture of hydrogen and water vapour was obtained by passing hydrogen diluted with nitrogen through the apparatus shown in Figure VI. The diluted hydrogen was obtained from Cylinder I or II, the preparation of which has been described in SECTION V, and which contained 0.524% and 15.13% hydrogen, respectively.

In this series the stoichiometric magnesium ferrite, $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ or MgFe_2O_4 , and also the iron rich material $\text{MgO}\cdot 1.192\text{Fe}_2\text{O}_3$ or $\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$ were investigated.

For each set of conditions, one 100 g. sample was quenched in water as before and one was cooled slowly. In order to cool samples slowly, the furnace was switched off at the end of the run and the sample allowed to cool in the furnace overnight to about 100°C . When the furnace had cooled down to about 900°C ., the Bunsen burner beneath the water boiler was turned out and the gas stream changed to nitrogen. The nitrogen was passed through the tube containing copper gauze at 600° to 700°C . to remove traces of oxygen before entering the furnace. Even with the B.O.C. oxygen-free nitrogen which was used, the heated copper became oxidised gradually. Consequently, hydrogen was passed through the heated tube periodically to reduce the copper. This tube could be isolated from the rest of the system by means of the three-way taps at its ends and the reduction of the copper carried out while a run was in progress in the main apparatus. These three-way taps also served when it was necessary to fill this tube with nitrogen before turning on the heater.

The apparatus was operated as in the series above, with the exception that the gas from the cylinder was passed through tube containing palladised asbestos at 350°C ., instead of through the tube of heated copper, to remove traces of oxygen, before entering the water boiler.

In this series it was essential to know the temperature of the thermostat and for the excess water to be condensing in the glass spiral in the thermostat, in order to produce the correct partial pressure of water vapour in the gas. When the water was condensing properly it could be seen running down the tubing from the bottom of the glass spiral into the U-tube below. However, if the gas were becoming supersaturated with water vapour and passing straight through the thermostat, this condensation would not be seen. To overcome this it was necessary to turn the Bunsen burner beneath the water boiler on full. In this way so much steam passed into the thermostat that the spiral eventually became flooded with water. Once this happened, the rate of boiling in the water boiler could be reduced and the water would continue to condense in the spiral, resulting in a gas stream containing the correct amount of water vapour.

As may be seen in Figure VI, there was a three-way tap at the lowest point in the apparatus between the thermostat and the furnace. If any water should collect in the tubing, as occasionally happened at the beginning of a run when the thermostat was above $70^{\circ}\text{C}.$, it could be drained out of the apparatus through this tap.

(4) Modified Technique for Use with "Highly Reducing"
Atmospheres.

In this series of experiments, which is of interest primarily from the structural viewpoint, samples of magnesium ferrite were prepared in the oxygen pressure range 10^{-10} to 10^{-15} mm. Hg at $1200^{\circ} \pm 10^{\circ}\text{C}$. As in the series above, the materials investigated had the initial compositions $\text{MgO} + \text{Fe}_2\text{O}_3$ or MgFe_2O_4 and $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$ or $\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$. Sufficient runs were carried out to investigate the reduction of these materials.

At these oxygen pressures, which gave rise to considerable reduction, it was found to be impracticable to reach equilibrium with a sample as large as 100 g. Consequently, samples of the order of 4 g., contained in a smaller boat, were used.

The apparatus used here was the same as in the series above, the gas passed into the apparatus being either that from Cylinder II or hydrogen. Before admitting either of these gases, when the furnace was hot, the precaution of sweeping out the apparatus with nitrogen was taken.

The difference in technique in this series lay in the method of withdrawing the sample from the furnace. Previously samples had been either quenched in water or cooled slowly in order to examine the effect of this heat

treatment on the lattice constant and magnetic properties of the material. In this series of experiments at lower oxygen pressures it is the true equilibrium composition of the reduced ferrite that is being determined. It was found that under these conditions quenched and slowly cooled samples did not give concordant results on analysis. In the case of quenching this was due to aerial oxidation, and with very reduced samples to reaction with the water as well. Samples cooled slowly in the furnace changed in composition because of the changing partial pressure of oxygen during the cooling period. In view of this, another method of withdrawing the sample had to be found.

Two methods of withdrawing the sample rapidly into the cold zone of the furnace tube without the introduction of air were employed. The first of these is shown in Figure VI as the alternative method. In this method a hook of stout nichrome wire was attached to the boat, and connected to this hook was a length of fine nichrome wire. The fine wire was fastened to the glass tube connected to the inside part of the ground joint, G. By rotating the projecting portion of the inner part of the ground joint, the fine wire was coiled round the glass tube to which it was attached, so that the boat was withdrawn from the hot zone of

the furnace. In this way the boat was withdrawn to the edge of the red hot zone in about two minutes and as far as the end of the furnace tube in about twenty minutes. At the oxygen pressures used the nichrome wire did not become oxidised.

Later another device, also shown in Figure VI, was used as it was found to be more robust. In this method a length of stout nichrome wire was attached to the boat, so that one end of the wire passed through a piece of glass tubing in the rubber bung at the exit end of the furnace. The wire also passed through a piece of rubber tubing fitted over this glass tubing projecting from the bung. The gas-tight seal was made by tightening up a screw-clip on this piece of rubber tubing. At the end of the run the screw-clip was loosened slightly, but not sufficiently to allow air to diffuse into the apparatus. The boat was withdrawn by pulling the nichrome wire, while the bung was pressed hard into the furnace tube.

Mullite furnace tubes subjected to this treatment had a very short life, but an alumina tube was found to be completely satisfactory. With an alumina tube it was possible to withdraw the boat to the edge of the red hot

zone in about 15 seconds, and right to the end of the tube in about 15 minutes. After being withdrawn this far, the boat was allowed to remain in the furnace tube until it was sufficiently cool to handle, i.e., for a further 30 or 40 minutes.

(5) Study of the Effect of Firing Temperature on the Properties of Magnesium Ferrite

This series of experiments was carried out to determine the effect of the temperature of preparation of stoichiometric magnesium ferrite, $\text{MgO} \cdot \text{Fe}_2\text{O}_3$, on its lattice constant, magnetic properties and possible decomposition.

100 g. samples were prepared in an atmosphere of oxygen at atmospheric pressure, in the apparatus shown in Figure V, at temperatures of 1100° , 1200° , 1300° , 1400° and 1500°C . At the end of the run, which lasted 24 hours, the sample was quenched in water, as previously described. An additional sample was prepared at 1500°C . and allowed to cool slowly in the furnace.

(6) Fusion Methods for Preparing Magnesium Ferrite

A number of experiments were carried out in order to investigate the properties of magnesium ferrite prepared by a fusion method. The method of K.A. Hofmann and K. Hörschele²¹ was used at first to prepare a small sample of ferrite and is given below.

5 g. of hydrated magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, plus 1 g. of ammonium chloride were fused in a platinum crucible and allowed to cool. 2.5 g. of ferric oxide were added and the crucible, covered with a loosely fitting lid, heated over the full blast of a Teclu burner for $4\frac{1}{2}$ hours. When cool, the crust of the mass in the crucible was removed and found to consist of dark glistening crystals. This material was attracted by a magnet and under the microscope appeared to have a cubic form.

It was found that the platinum crucible used had been attacked slightly during the reaction; consequently, a method not involving the use of a platinum crucible was sought.

A number of similar experiments were carried out using porcelain and silica crucibles in place of platinum. In some cases the final heating was carried out in an electric muffle at 1000°C . None of these experiments gave more than a brown powder, plus in certain cases a very small amount of the crystalline product originally obtained.

Attempts were made to use commercial anhydrous magnesium chloride in place of the hydrated form, but it was found to be impossible to fuse this material over a Teclueburner or in an electric muffle at 1000°C .

The first experiment was repeated using a silica crucible in place of the platinum one and a blast Meker burner in place of the Teclu burner. The product was found to be a dark crystalline crust of ferrite as before. This experiment was repeated four times and the products combined and heated with about 50 ml. of 2.5 N. hydrochloric acid. The ferrite was allowed to settle and the supernatant liquid decanted through a filter funnel and paper; the residue was heated with two further portions of 2.5 N. hydrochloric acid, and then filtered off. The residue was washed thoroughly with water and dried at 160°C . 11 g. of a dark grey-brown crystalline substance were obtained.

In order to obtain approximately 100 g. of this material for magnetic measurements to be made, the preparation was carried out on a larger scale. The scale of the experiment was limited by the size of the silica crucible which could be kept at a sufficiently high temperature in the flame of a Meker burner. About 20 g. of a 1:2 mixture of ferric oxide and hydrated magnesium chloride were heated in

a silica crucible over a blast Meker burner for 4 hours. The combined products of about ten separate preparations were extracted several times with 2 N. hydrochloric acid and the residue filtered off and washed until the filtrate was substantially free from magnesium. The ferrite was dried, ground in an agate mortar, analysed for iron and magnesium, and an X-ray powder photograph taken.

SECTION VII

DETERMINATION OF LATTICE CONSTANTS FROM

X-RAY POWDER PHOTOGRAPHS

SECTION VII: DETERMINATION OF LATTICE CONSTANTS
FROM X-RAY POWDER PHOTOGRAPHS

X-ray powder photographs were taken of all the specimens of magnesium ferrite prepared in order to identify the phases present, and in most cases, the lattice constants determined. The technique employed and a discussion of the errors associated with X-ray powder photography follow below.

A 19 cm. "Unicam" camera of the type designed by A.J. Bradley and A.H. Jay⁵⁰ was used. This camera has the advantage that the exposed part of the film, which is in two halves, is sharply terminated by knife-edges, which serve as fiducial marks for the measurement of the positions of the reflections on the film. To prepare a specimen for examination, the finely powdered material was mixed thoroughly with gum tragacanth, moistened and rolled into rods, 1 to 1.5 cms. in length and not greater than 0.3 mm. in diameter. After being allowed to dry between microscope slides for half an hour, the specimen was mounted centrally in the camera.

In the determination of unit cell dimensions from the X-ray powder pattern of a material, the greatest precision is attained from measurements of the positions of arcs having

angles of reflection, θ , near to 90° . This arises firstly from the Bragg equation:-

$$d = \frac{\lambda}{2\sin\theta}$$

Where d = the interplanar spacing
and λ = the X-ray wave-length

As θ approaches 90° a very small change of $\sin \theta$, which corresponds to a very small change in d , results in a relatively large change in θ . Thus an error in the determination of θ results in a much smaller error in the value obtained for d .

Secondly, as θ approaches 90° the errors caused by absorption of X-rays by the specimen,^{51,52} thickness of specimen and its possible eccentricity, tend to zero⁵⁰. This also holds for a not too large shrinkage of the film and for radius errors. Errors due to the shrinkage of the film on developing and drying may be overcome if the film is assumed to shrink uniformly along its length.

The method used to determine θ in this case was that of A.J. Bradley and A.H. Jay,^{50,53} which is based on this assumption. The linear distances between the two pairs of knife-edges of the camera were measured to 0.002 cms., corresponding to 0.003° in camera angle, and the diameter to 0.01 cms., corresponding to 0.002° in camera angle. From these measurements the camera angle, θ_K , was calculated.

The angle θ is one quarter of the angle subtended by corresponding reflections on the film. Similarly, θ_K is one quarter of the angle subtended by the high-angle knife-edges. This is shown in Figure X.

The angle corresponding to any particular reflection may be derived from the equation:-

$$\frac{\theta}{\theta_K} = \frac{S}{S_K}$$

Where, S_K = the sum of the measured lengths of the two half films plus the arc distance between the low-angle knife-edges.

and S = the measured distance between the corresponding reflections on the two half films.

In this expression S has been made proportional to S_K , the sum of the lengths of the two half films after shrinking plus the arc distance between the low-angle knife-edges, but θ has been made proportional to θ_K , the true camera angle, thus, in this way a true value for θ is obtained.

In order to ensure that the correct value had been taken for the camera angle, θ_K , the camera was calibrated by taking a powder photograph of quartz, using a copper target.

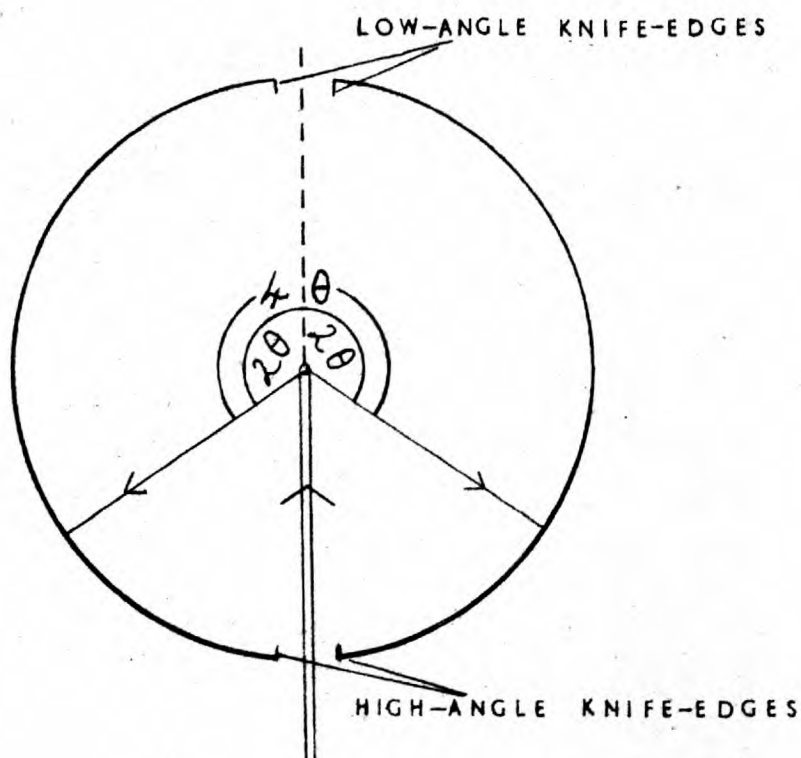
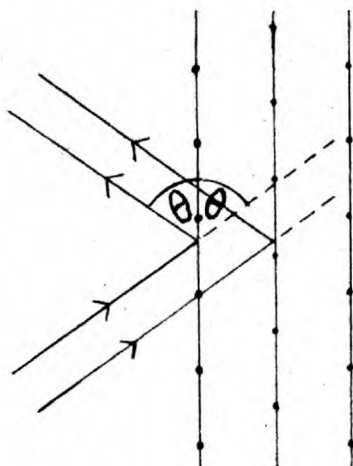


FIGURE X DIFFRACTION OF X-RAYS IN A
POWDER CAMERA

The angles of reflection, θ , for the powder pattern of quartz have been accurately determined by H. Lipson and A.J.C. Wilson^{52,53} and are given below in Table VI, together with the values obtained in the present work. The two sets of results were found to agree within the required limits. The positions of the lines on the film were measured accurately by clamping the film onto an illuminated glass screen and viewing the lines through a travelling microscope. The Vernier scale on the travelling microscope was read to 0.002 cms.

TABLE VI

Measurements of 19 cm. Camera and Values of θ for Quartz

Linear distance between low-angle knife-edges 3.129 cms.	
Arc " " " " " "	3.143 "
Linear " " high-angle " "	3.112 "
Camera angle, θ_K , = 85.287°	
Values obtained for θ	Published values of θ
61.308°	61.304° α_1
68.206° }	68.217° } α_1
68.563° }	68.578° } α_2
68.952° }	68.951° } α_1
69.327° }	69.326° } α_2
71.636°	71.632° α_1
73.316°	73.319° α_1
76.770° }	76.772° } α_1
77.400° }	77.394° } α_2

A.J. Bradley and A.H. Jay⁵⁰ have shown that the errors which arise from absorption and eccentricity together produce the proportionate error in spacing given very closely by the expression:-

$$\frac{\Delta d}{d} = \left(\frac{p \cdot \cos \phi}{R} - \frac{r}{2\theta R} - \frac{r}{2\theta AX} \right) \cdot \cos^2 \theta$$

Where, p = Displacement of specimen from centre of camera

ϕ = Direction of displacement measured from
direction of incidence.

r = the radius of the specimen

R = the radius of the film

AX = the distance from the target of the
X-ray tube to the specimen.

Thus the relative error in d is very nearly a linear function of $\cos^2 \theta$ and is zero when $\cos^2 \theta = 0$ or $\theta = 90^\circ$.

In the case of a cubic crystal, where

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$$

Where, a = the lattice constant, i.e., the length of
the side of the unit cell.

and h, k and l = the Miller indices of the plane

giving rise to the reflection of angle θ ,

the true value of a is obtained by plotting the apparent value of a calculated from each reflection against the

corresponding values of $\cos^2\theta$ and extrapolating to $\cos^2\theta = 0$, or more conveniently to $\sin^2\theta = 1$.

The method of extrapolation has been used to obtain values for the lattice constants of the samples of magnesium ferrite prepared. Figure XI shows the extrapolation of the values of $\sin^2\theta$ obtained, using an iron target, for Sample No. 8, which consisted of stoichiometric magnesium ferrite, MgFe_2O_4 , prepared in oxygen at atmospheric pressure at $1200^\circ \pm 10^\circ\text{C}$., and quenched in water. Figure XII shows the powder patterns obtained, using iron and cobalt targets, for various samples prepared.

Another method of calculation of lattice constants has been put forward by M.U. Cohen⁵⁶ and is based on solution by least squares⁵⁷. The systematic errors which arise are taken into account in the computations and the method is independent of camera calibrations such as those described above. In the case of cubic crystals, such as magnesium ferrite, graphical extrapolation is preferred, but with crystals with less symmetry the method described by Cohen has much to commend it.

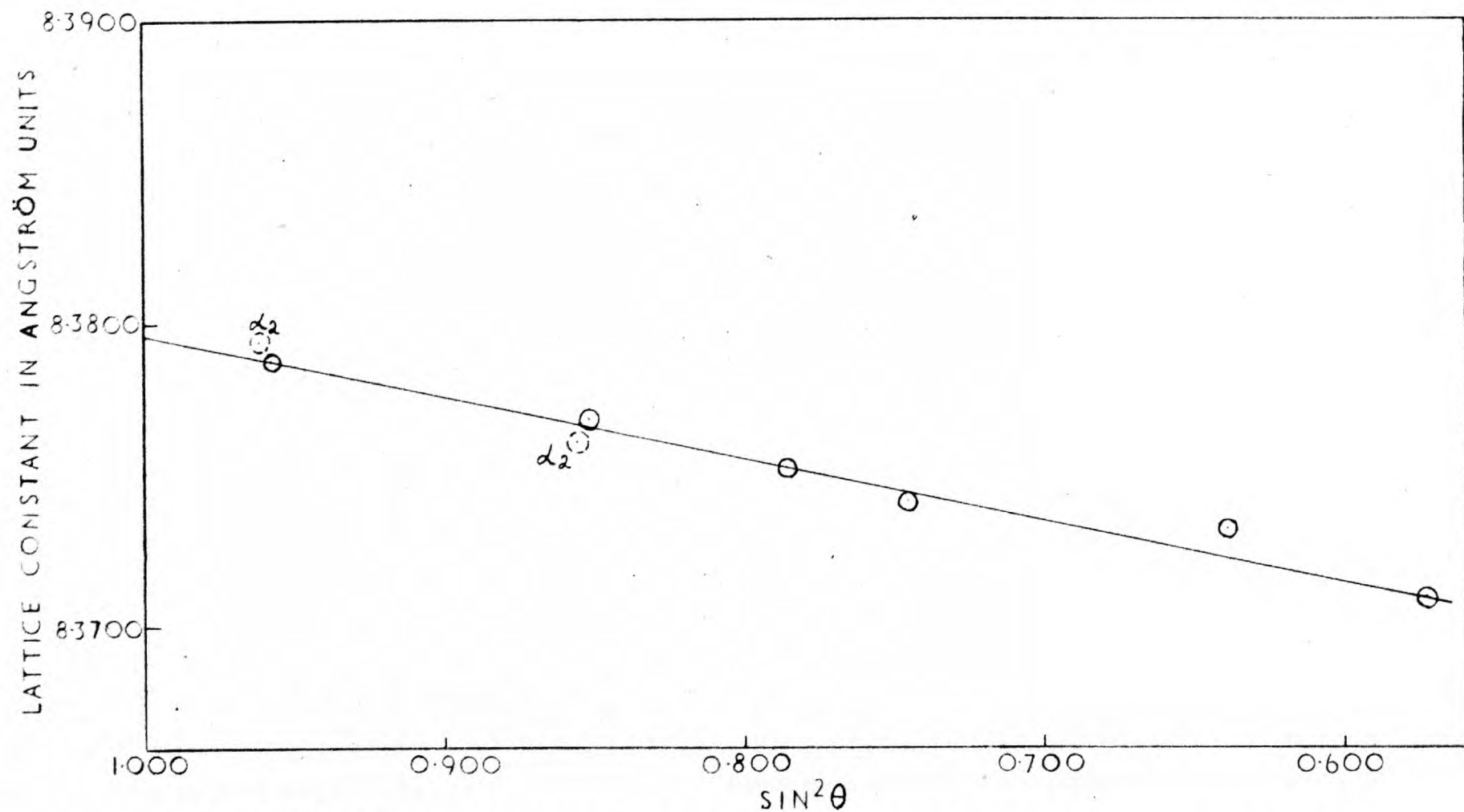


FIGURE XI DETERMINATION BY THE EXTRAPOLATION METHOD OF THE LATTICE CONSTANT OF SAMPLE No 8 (STOICHEIOMETRIC MgFe_2O_4 PREPARED IN O_2 AT $1200^\circ \pm 10^\circ\text{C}$. AND QUENCHED IN WATER)

$\{660\alpha_2-$
 $\{228\alpha_1-$
 $480\beta-$
 $800\alpha_1-$
 $\{555\beta-$
 $\{157\beta-$
 $\{355\alpha_2-$
 $\{137\alpha_1-$
 $246\alpha_1-$
 $800\beta-$
 $\{555\alpha-$
 $\{117\beta-$
 $\{355\beta-$
 $444\alpha-$
 $246\beta-$
 $226\alpha-$
 $335\alpha-$
 $260\alpha-$
 $444\beta-$
 $335\beta-$
 $135\alpha-$
 $440\alpha-$
 $\{333\alpha-$
 $\{115\alpha-$
 $440\beta-$
 $224\alpha-$
 $\{333\beta-$
 $\{115\beta-$
 $240\alpha-$
 $400\alpha-$
 $400\beta-$
 $222\alpha-$
 $113\alpha-$
 $113\beta-$
 $220\alpha-$
 $220\beta-$
 $111\alpha-$
 $111\beta-$

SAMPLE No. 8 : $MgFe_2O_4$ (Fe TARGET)

$240\alpha_1$
 $331\alpha_1$
 $400\alpha_2$
 222α
 113α
 220α
 220α
 111α

SAMPLE No. 50 : MIXED OXIDE, $(Mg,Fe)O$ (Co TARGET)

400α
 222α
 220α
 200α
 INDICES OF Fe LINES;
 MIXED OXIDE LINES
 AS IN SAMPLE No. 50

SAMPLE No. 76 : MIXED OXIDE, $(Mg,Fe)O$ + METALLIC IRON (Co TARGET)

FIGURE XII TYPICAL X-RAY POWDER PHOTOGRAPHS

Owing to the slight refraction of the X-rays by the specimen, which causes a very small deviation from the Bragg equation, a correction should be applied to the value for the lattice constant obtained by extrapolation^{58,59}. For a cubic crystal the expression for the correction reduces to:-

$$a_{\text{corrected}} = a + (1 - n)a$$

where, n = the refractive index of the specimen
for the wavelength used.

The correction to be added has a magnitude of only about 1 part in 50,000.

SECTION VIII

EXPERIMENTAL RESULTS

SECTION VIII: EXPERIMENTAL RESULTS

In SECTION VI details of the experiments carried out and the techniques employed have been described. In this section, the results obtained from these experiments and the magnetic measurements made on the specimens by the G.P.O. Research Station, Dollis Hill, N.W.2. are recorded, together with a recapitulation of the object of each series of runs and the methods employed.

Series 1. Investigation of Mixed Crystal Formation in the System $\text{MgO-Fe}_2\text{O}_3$.

In this series large samples of magnesium ferrite were prepared in oxygen at $1200^\circ \pm 10^\circ \text{C.}$ from intimate mixtures of ferric and magnesium oxides in various proportions. The object of the series was to investigate the mixed crystal formation in the $\text{MgO-Fe}_2\text{O}_3$ system, in order to determine the limits of solid solution of excess ferric and magnesium oxides in magnesium ferrite by lattice constant measurements, and also to study the magnetic properties of a range of compositions. One series of samples was quenched in water at the end of the run and one series allowed to cool slowly in the furnace. For slowly cooled samples the variation in lattice constant of the ferrite and the magnetic properties of the specimen for the compositions examined are shown in Table VII. The corresponding data for quenched samples are shown in Table VIII. The error in the magnetic measurements is estimated to be $\pm 10\%$.

TABLE VII.

VARIATION IN STRUCTURAL AND MAGNETIC PROPERTIES WITH COMPOSITION OF SLOWLY COOLED SAMPLES OF MAGNESIUM FERRITE

REACTION TEMPERATURE $1200 \pm 10^\circ\text{C}$.

SAMPLE NO.	COMPOSITION			PHASES PRESENT IN POWDER PATTERN	LATTICE CONSTANT OF FERRITE PHASE IN ANGSTROM UNITS	PERMEABILITY				PERMITTIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
	MOL RATIO	AS UNIT CELL OF 32 OXYGEN IONS	MOL % Fe_2O_3			AT LOW FREQUENCY (< 1000 kc/s.)	AT 990 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	HYSTERESIS $a \times 10^6$	RESIDUAL $c \times 10^6$	"EDDY CURRENT" $e \times 10^9$
32	$\text{MgO}, 0.500\text{Fe}_2\text{O}_3$	$\text{Mg}_{12.80}\text{Fe}_{12.80}\text{O}_{32.00}$	33.33%	* / F+ v.f. MgO	8.3740 ± 0.001	4.9	1.5	1.2	0.9	4.4	4.6	690	1300	1.2
20	$\text{MgO}, 0.756\text{Fe}_2\text{O}_3$	$\text{Mg}_{9.79}\text{Fe}_{14.80}\text{O}_{32.00}$	43.32%	F+v.v.f. MgO	8.3731 ± 0.0005	6.2	2.1	1.0	1.0	4.4	4.3	610	1900	0.6
4	$\text{MgO}, 0.895\text{Fe}_2\text{O}_3$	$\text{Mg}_{8.68}\text{Fe}_{15.54}\text{O}_{32.00}$	47.22%	Ferrite	8.3710 ± 0.001	5.5	1.2	0.95	1.0	4.2	4.4	750	2500	3.3
9	$\text{MgO}, \text{Fe}_2\text{O}_3$	$\text{Mg}_{8.00}\text{Fe}_{16.00}\text{O}_{32.00}$	50.00%	Ferrite	8.3678 ± 0.0005	5.9	1.8	0.94	0.93	4.7	4.8	350	2200	< 0.3
1	$\text{MgO}, 1.017\text{Fe}_2\text{O}_3$	$\text{Mg}_{7.90}\text{Fe}_{16.06}\text{O}_{32.00}$	50.41%	Ferrite	8.367 ± 0.002	5.2	2.2	0.9	1.0	4.4	4.9	420	1900	< 0.6
7	$\text{MgO}, 1.109\text{Fe}_2\text{O}_3$	$\text{Mg}_{7.39}\text{Fe}_{16.40}\text{O}_{32.00}$	52.57%	Ferrite	8.3610 ± 0.0005	5.3	2.3	1.1	0.96	5.1	5.3	400	2500	1.7
18	$\text{MgO}, 1.435\text{Fe}_2\text{O}_3$	$\text{Mg}_{6.03}\text{Fe}_{17.31}\text{O}_{32.00}$	58.93%	F+f. Fe_2O_3	8.359 ± 0.002	5.2	1.8	1.3	0.9	6.7	6.8	2000	6000	1.5
16	$\text{MgO}, 2.283\text{Fe}_2\text{O}_3$	$\text{Mg}_{4.08}\text{Fe}_{18.62}\text{O}_{32.00}$	69.53%	F+ Fe_2O_3	8.360 ± 0.003	4.2	1.8	2.1	1.06	8.0	8.2	800	2400	1.6

* F = Ferrite

/ f. = faint

v.f. = very faint

v.v.f. = extremely faint

TABLE VIII

VARIATION IN STRUCTURAL AND MAGNETIC PROPERTIES WITH COMPOSITION OF QUENCHED SAMPLES OF MAGNESIUM FERRITE

REACTION TEMPERATURE $1200^{\circ} \pm 10^{\circ}\text{C}$.

SAMPLE NO.	COMPOSITION			PHASES PRESENT IN POWDER PATTERN	LATTICE CONSTANT OF FERRITE PHASE IN ANGSTROM UNITS	PERMEABILITY				PERMITTIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
	MOL RATIO	AS UNIT CELL OF 32 OXYGEN IONS	MOL % Fe_2O_3			AT LOW FREQUENCY (< 1000 kc/s.)	AT 990 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	HYSTERESIS $a \times 10^6$	RESIDUAL $c \times 10^6$	EDDY CURRENT $e \times 10^9$
33	$\text{MgO}, 0.500\text{Fe}_2\text{O}_3$	$\text{Mg}_{12.80}\text{Fe}_{12.80}\text{O}_{32.00}$	33.33%	* F + v.f. MgO	8.3834 ± 0.0005	6.3	2.2	1.4	0.8	4.7	4.6	430	1200	1.4
21	$\text{MgO}, 0.756\text{Fe}_2\text{O}_3$	$\text{Mg}_{9.79}\text{Fe}_{14.80}\text{O}_{32.00}$	43.32%	F + v.v.f. MgO	8.3837 ± 0.0005	8.8	2.5	1.5	0.9	5.1	4.6	340	1700	1.3
37	$\text{MgO}, 0.870\text{Fe}_2\text{O}_3$	$\text{Mg}_{8.86}\text{Fe}_{15.42}\text{O}_{32.00}$	46.52%	Ferrite	8.3820 ± 0.0005	8.0	2.2	1.5	0.8	7.9	7.0	300	1400	0.8
8	$\text{MgO}, \text{Fe}_2\text{O}_3$	$\text{Mg}_{8.00}\text{Fe}_{16.00}\text{O}_{32.00}$	50.00%	Ferrite	8.3796 ± 0.0005	9.5	2.5	1.4	0.9	7.5	5.8	250	1300	1.2
6	$\text{MgO}, 1.109\text{Fe}_2\text{O}_3$	$\text{Mg}_{7.39}\text{Fe}_{16.40}\text{O}_{32.00}$	52.57%	Ferrite	8.3723 ± 0.0005	9.3	2.6	0.8	0.85	17	8.2	250	1500	< 0.2
19	$\text{MgO}, 1.435\text{Fe}_2\text{O}_3$	$\text{Mg}_{6.03}\text{Fe}_{17.31}\text{O}_{32.00}$	58.93%	Ferrite	8.3702 ± 0.0005	6.6	2.6	2.1	0.6	42	27	170	1200	0.6
17	$\text{MgO}, 2.283\text{Fe}_2\text{O}_3$	$\text{Mg}_{4.08}\text{Fe}_{18.62}\text{O}_{32.00}$	69.53%	F + Fe_2O_3	8.3675 ± 0.0005	4.4	2.3	1.5	0.7	22	23	150	1100	0.9

* F = Ferrite

The lattice constants shown in Tables VII and VIII are plotted against composition in Figure XIII. The limits of solid solution at $1200^{\circ} \pm 10^{\circ}\text{C.}$ are taken to lie at the two points where the curve given by the quenched samples becomes horizontal. From this curve the range of solid solution was found to extend from

42.5 Mol % to 53.5 Mol % Fe_2O_3

i.e., from $\text{MgO}, 0.75\text{Fe}_2\text{O}_3$ to $\text{MgO}, 1.15\text{Fe}_2\text{O}_3$

or from $\text{Mg}_{9.9}\text{Fe}_{14.8}\text{O}_{32.0}$ to $\text{Mg}_{7.2}\text{Fe}_{16.6}\text{O}_{32.0}$

Thus at $1200^{\circ} \pm 10^{\circ}\text{C.}$ the maximum magnesium oxide content of the mixed crystal $\text{MgO-MgFe}_2\text{O}_4$ is 33 ± 2.5 Mol percent. The maximum ferric oxide content of the mixed crystal $\text{Fe}_2\text{O}_3\text{-MgFe}_2\text{O}_4$ at $1200^{\circ} \pm 10^{\circ}\text{C.}$ is 15 ± 2.5 Mol percent.

With regard to the magnetic measurements, the values obtained for permeability are plotted in Figure XIV, those for permittivity in Figure XV, and those for the loss coefficients in Figure XVI. The loss coefficients are related by the equation

$$\frac{R}{\mu f L} = aB + c + e.f.$$

Where, R = Resistance due to the core of material under test only

μ = Permeability

f = Frequency of alternating current

L = Inductance

B = Maximum flux density in core

and a , c and e = Hysteresis, Residual and "Eddy Current" loss coefficients, respectively.

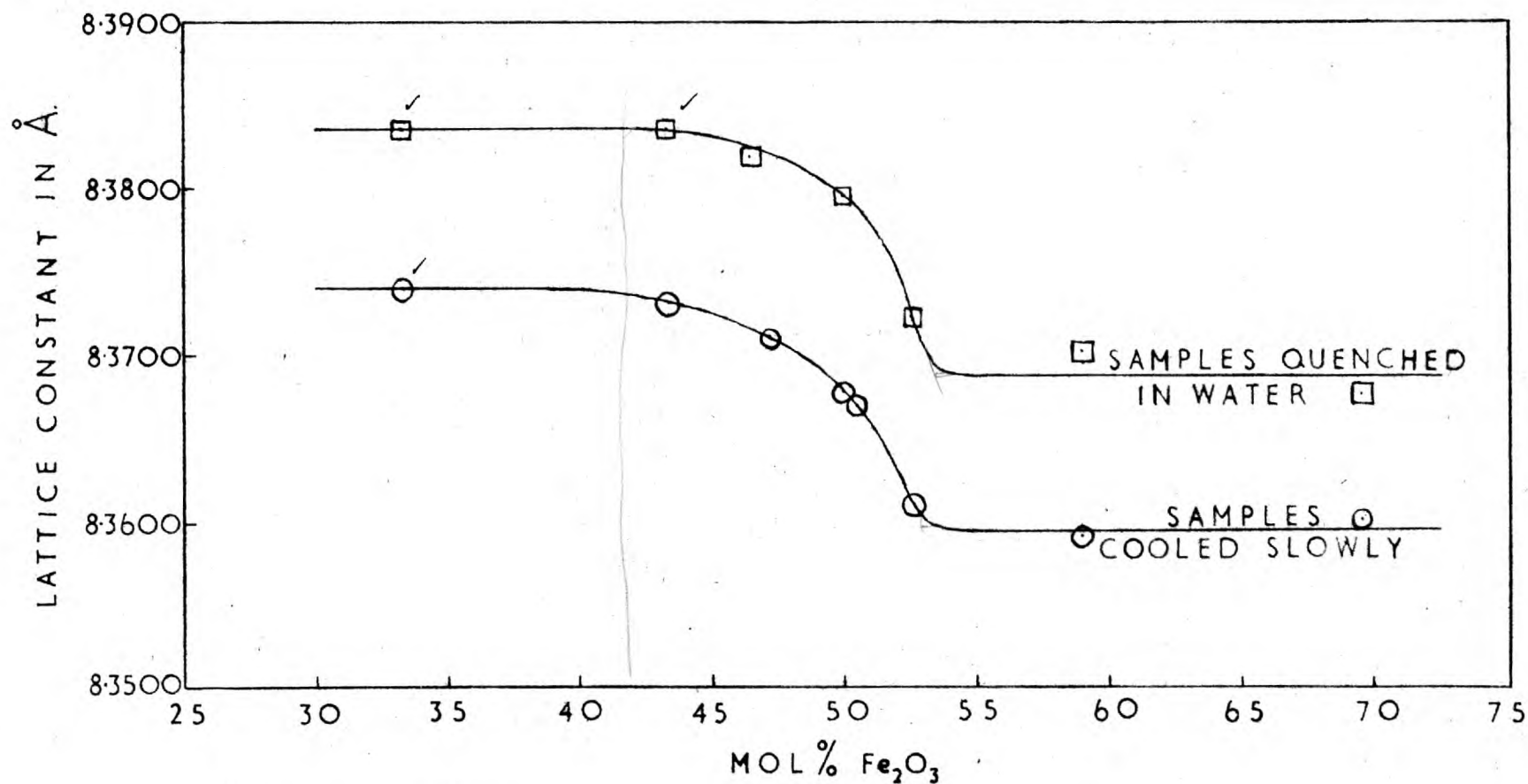


FIGURE XIII VARIATION OF LATTICE CONSTANT WITH
COMPOSITION IN THE SYSTEM MgO—Fe₂O₃

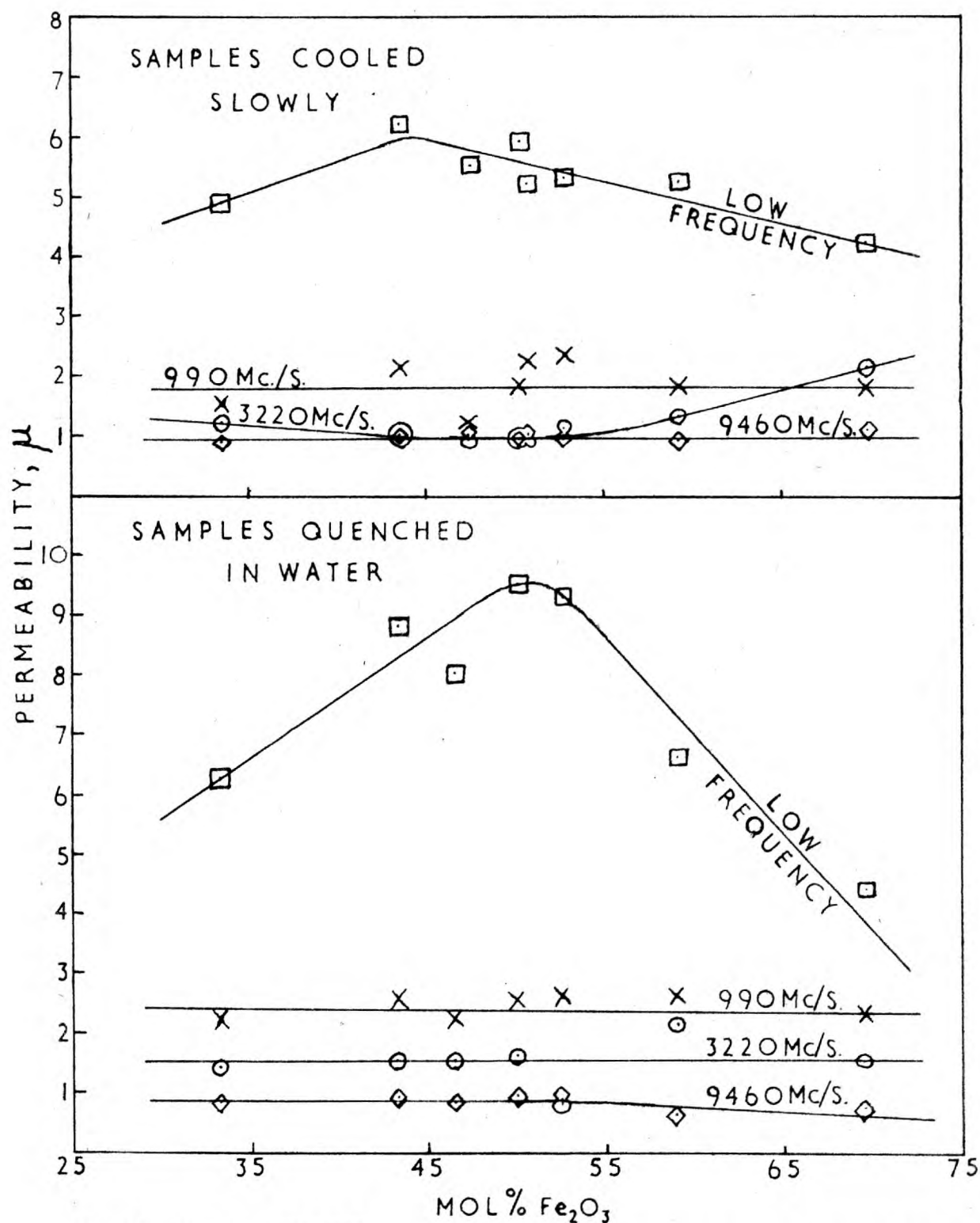


FIGURE XIV VARIATION OF μ WITH COMPOSITION OF SAMPLES PREPARED FROM MgO AND Fe_2O_3 IN OXYGEN AT $1200^\circ \pm 10^\circ\text{C}$.

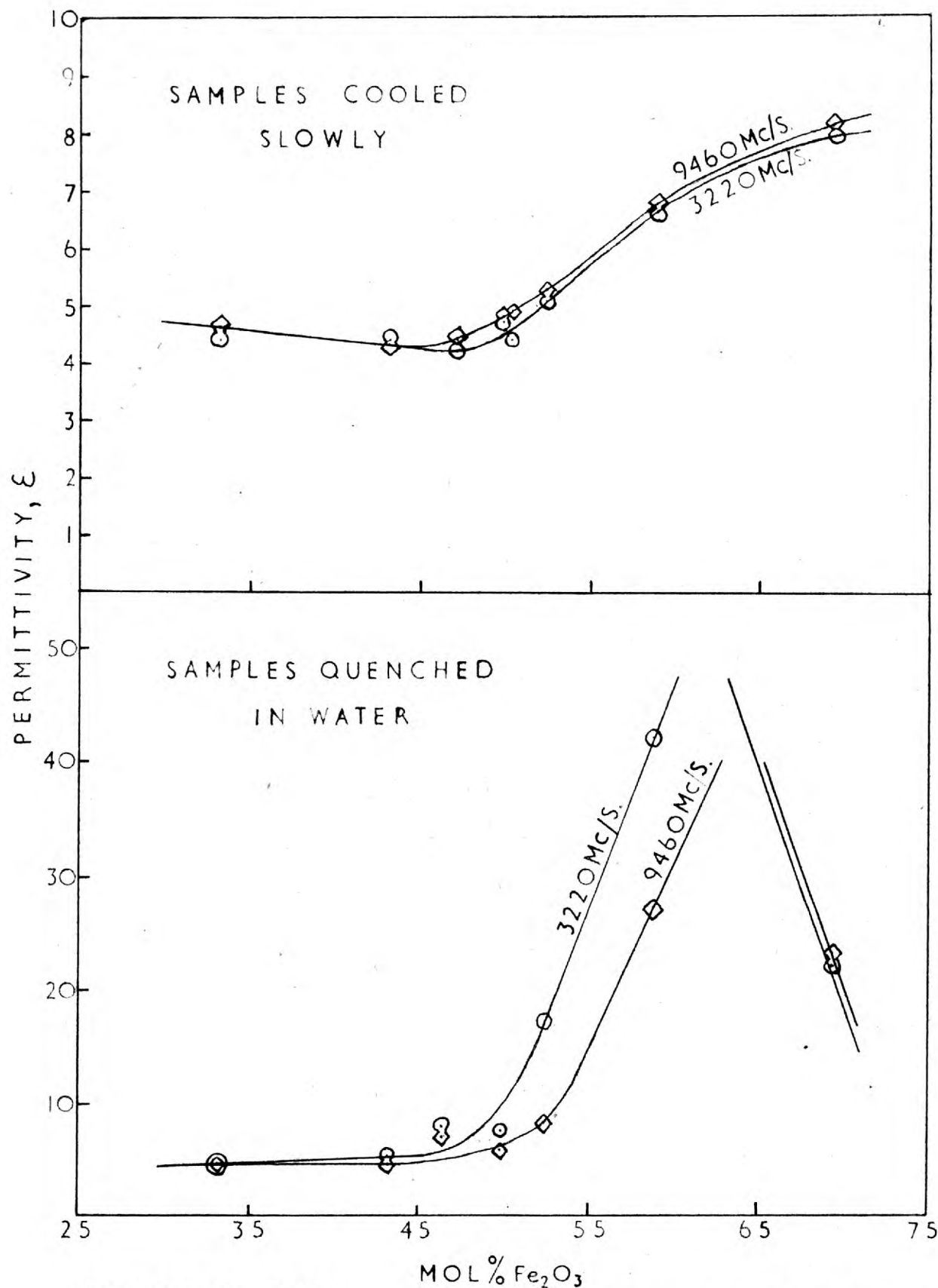


FIGURE XV VARIATION OF ϵ WITH COMPOSITION OF SAMPLES PREPARED IN O_2 AT $1200^\circ \pm 10^\circ \text{C}$.

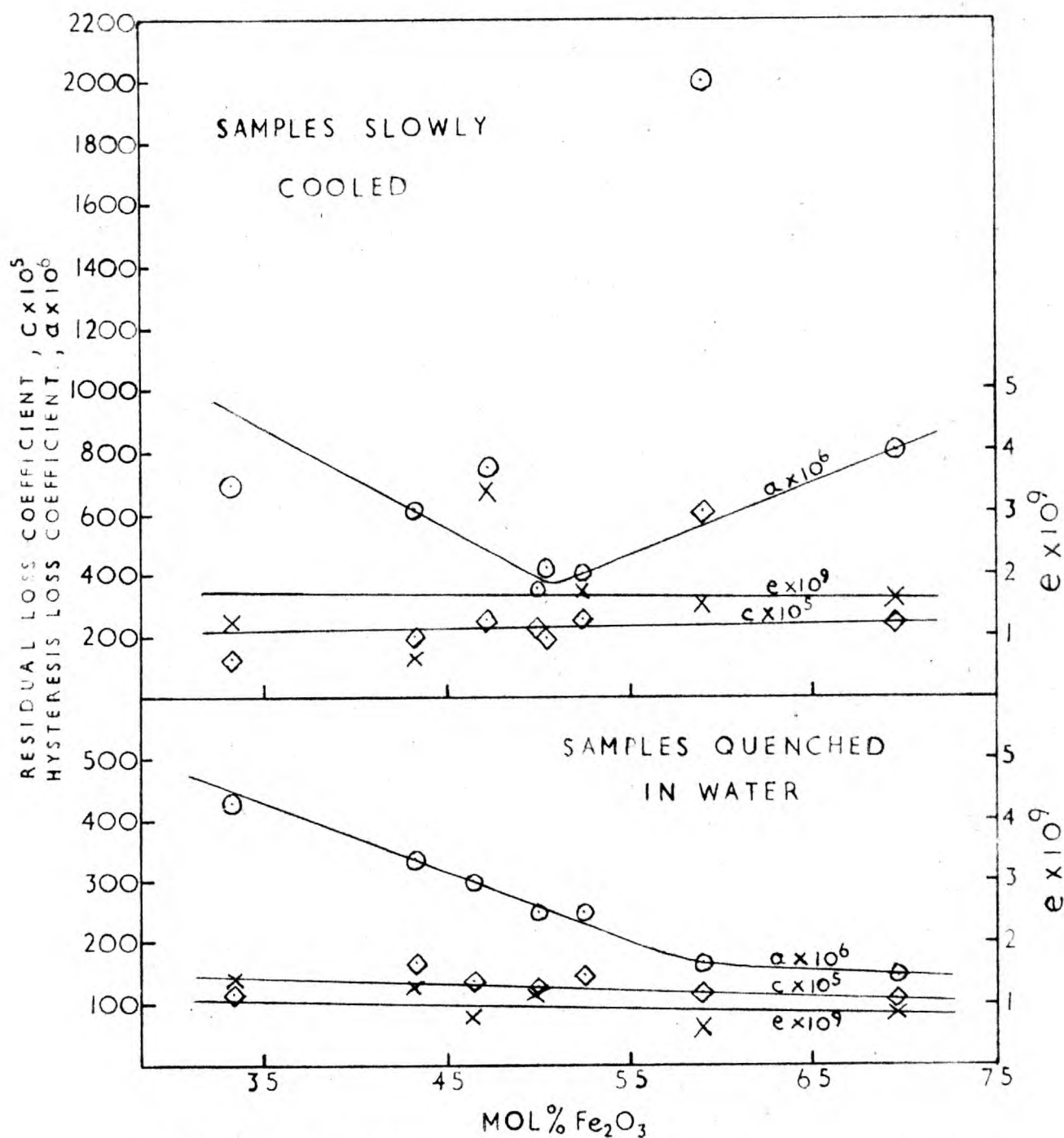


FIGURE XVI VARIATION OF LOSS COEFFICIENTS
WITH COMPOSITION OF SAMPLES PREPARED IN O_2 AT
 $1200^\circ \pm 10^\circ\text{C}$.

It should be noted that the term e , although called "Eddy current loss coefficient" in the above tables, may not correspond exactly to the eddy current losses in metals.

Series 2. Magnesium Ferrite Samples Prepared in
"Weakly Reducing" Atmospheres.

In this series large samples of magnesium ferrite were prepared from intimate mixtures of ferric and magnesium oxides in stoichiometric proportions at $1200^{\circ} \pm 10^{\circ} \text{C.}$ in an atmosphere of water vapour, hydrogen and nitrogen. This weakly reducing atmosphere was obtained, as previously described, by passing nitrogen and water vapour over nickel powder heated to a known temperature. The main object of the series was the examination of the magnetic properties of samples prepared under conditions which might produce slight oxygen deficits in the lattice. The results obtained are recorded in Table IX.

TABLE IX

MAGNETIC PROPERTIES OF SAMPLES OF MAGNESIUM FERRITE PREPARED IN "WEAKLY REDUCING" ATMOSPHERES

REACTION TEMPERATURE $1200^{\circ} \pm 10^{\circ}\text{C}$

TIME OF FIRING 6 HOURS

SAMPLE NO.	TEMPERATURE OF NICKEL	CALCULATED LOG PO_2	METHOD OF COOLING	PERMEABILITY				PERMITTIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
				AT LOW FREQUENCY (<1000 kc/s.)	At 990 Mc/s	At 3220 Mc/s	At 9460 Mc/s	At 3220 Mc/s	At 9460 Mc/s	HYSTERESIS $a \times 10^6$	RESIDUAL $e \times 10^6$	"EDDY CURRENT" $e \times 10^9$
12	$430^{\circ}\text{C}.$	-8.45	A [*]	7.7	2.3	1.3	0.9	9.6	7.8	470	1000	1.4
14	$285^{\circ}\text{C}.$	-8.80	A	4.5	1.7	0.9	1.1	6.5	6.0	1000	1800	2.2
13	$430^{\circ}\text{C}.$	-8.45	B	11.9	2.8	1.8	0.75	15.0	11.0	240	1200	0.6
15	$285^{\circ}\text{C}.$	-8.80	B	12.3	2.9	1.7	0.84	6.8	7.0	300	1200	0.6

* The three cooling techniques previously described are signified in these Tables by:-

A - Cooled slowly.

B - Quenched in water.

C - Cooled by rapid withdrawal into the cold zone of the furnace, without the inlet of air.

Series 3. Magnesium Ferrite Samples Prepared in H₂O-H₂
Atmospheres for Examination of Magnetic Properties.

- (a) From Mixtures of Composition $\text{MgO} + \text{Fe}_2\text{O}_3$
- (b) From Mixtures of Composition $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$

In this series, which was an extension of the one above, large samples of magnesium ferrite were prepared in reducing atmospheres of water vapour, hydrogen and nitrogen. These atmospheres were obtained, as previously described, by passing hydrogen diluted with nitrogen through a water boiler and a thermostat, by which means a known partial pressure of water vapour was introduced into the gas. The results obtained for samples having the initial composition $\text{MgO} + \text{Fe}_2\text{O}_3$ are given in Table X and those obtained for samples having the initial composition $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$ in Table XI.

TABLE X.

SAMPLES PREPARED FROM MIXTURES OF COMPOSITION $\text{MgO} \cdot \text{Fe}_2\text{O}_3 (\text{MgFe}_2\text{O}_4)$ IN $\text{H}_2\text{O}-\text{H}_2$ ATMOSPHERESREACTION TEMPERATURE $1200^\circ \pm 10^\circ \text{C}$.

SAMPLE NO.	$\text{N}_2\text{-H}_2$ CYLIN- DER NO.	TEMPER- ATURE OF THERMO- STAT	CALCU- LATED LOG P_{O_2}	TIME OF FIRING	METHOD OF COOLING	% Fe IN PRODUCT	CALCULATED FINAL COMPOSITION	PHASES PRESENT IN X-RAY POWDER PATTERN	PERMEABILITY				PERMIT- TIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
									AT LOW FREQUENCY (< 1000 kc/s.)	AT 990 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	HYSTER- ESIS a x 10^6	RESI- DUAL cx 10^6	"EDDY CURRENT" e x 10^9
28 ✓	I	73.55°C	-7.68	6 hrs	A	55.80%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	7.8	1.8	1.2	0.8	7.2	6.9	490	1300	0.8
26 ✓	I	60.50°C	-8.36	6 "	A	55.80%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	6.9	2.1	1.4	0.9	8.0	7.3	590	1300	1.2
22 ✓	I	44.40°C	-9.15	6 "	A	55.91%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	7.1	2.1	1.3	0.9	6.2	6.5	540	1800	0.9
24 ✓	I	28.55°C	-9.96	6 "	A	55.87%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	7.4	2.2	1.3	0.9	6.7	6.5	510	1100	1.1
48 ✓	II	65.70°C	-11.02	$7\frac{1}{2}$ "	A	58.61%	$\text{Mg}_{9.39}\text{Fe}_{18.78}\text{O}_{32.00}$	F* + M.O	2.5	1.7	1.4	1.3	17.1	17.5	320	6400	-0.8
40 ✓	II	63.30°C	-11.14	6 "	A	58.01%	$\text{Mg}_{9.05}\text{Fe}_{18.10}\text{O}_{32.00}$	F + M.O	3.5	2.1	1.7	1.3	16.7	17.2	290	2900	1.1
42 ✓	II	47.40°C	-11.92	6 "	A	58.11%	$\text{Mg}_{9.11}\text{Fe}_{18.22}\text{O}_{32.00}$	F + M.O	2.5	2.0	1.6	1.2	13.4	16.7	520	7200	2.4
29 ✓	I	73.55°C	-7.66	6 "	B	55.80%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	11.0	3.2	1.5	0.8	7.0	6.9	280	1200	0.5
27 ✓	I	60.50°C	-8.37	6 "	B	55.80%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	11.0	2.3	1.5	0.8	6.6	7.0	280	1200	0.5
23 ✓	I	44.40°C	-9.16	6 "	B	55.80%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	10.2	2.9	1.6	0.8	7.5	6.8	280	1300	0.6
25 ✓	I	28.55°C	-9.96	6 "	B	55.76%	$\text{Mg}_8\text{Fe}_{16}\text{O}_{32}$	Ferrite	9.7	2.6	1.6	0.8	6.9	7.3	300	1300	0.5
49 ✓	II	65.50°C	-11.04	12 "	B	58.86%	$\text{Mg}_{9.53}\text{Fe}_{19.06}\text{O}_{32.00}$	F + M.O	1.5	1.4	1.0	1.0	19.3	25.0	<270	-	-
39 ✓	II	63.35°C	-11.14	6 "	B	57.36%	$\text{Mg}_{8.72}\text{Fe}_{17.44}\text{O}_{32.00}$	F + M.O	3.6	2.0	1.6	1.2	19.8	15.4	550	7000	1.9
41 ✓	II	47.40°C	-11.92	6 "	B	57.29%	$\text{Mg}_{8.61}\text{Fe}_{17.22}\text{O}_{32.00}$	F + M.O	3.0	2.1	1.4	1.0	12.6	14.5	600	8300	2.3

* F = Ferrite

M.O = Mixed Oxide

TABLE XI.

SAMPLES PREPARED FROM MIXTURES OF COMPOSITION $\text{MgO} + 1.192\text{Fe}_2\text{O}_3 (\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00})$ IN $\text{H}_2\text{O}-\text{H}_2$ ATMOSPHERES

REACTION TEMPERATURE $1200^\circ \pm 10^\circ\text{C}$.

SAMPLE NO.	$\text{N}_2\text{-H}_2$ CYLINDER NO.	TEMPERATURE OF THERMOSTAT	CALCULATED LOG P_{O_2}	TIME OF FIRING	METHOD OF COOLING	% Fe IN PRODUCT	CALCULATED FINAL COMPOSITION	PHASES PRESENT IN X-RAY POWDER PATTERN	PERMEABILITY				PERMITTIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
									AT LOW FREQUENCY (< 1000 Kc/s.)	AT 990 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	HYSTERESIS $a \times 10^6$	RESIDUAL $cx10^6$	"EDDY CURRENT" $e \times 10^9$
30 ✓	I	52.70°C	-8.75	6 hrs.	A	57.82%	$\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$	Ferrite	6.6	2.2	1.7	0.9	17.2	14.1	550	2000	0.9
36 ✓	I	25.05°C	-10.13	6 "	A	57.75%	$\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$	Ferrite	5.8	2.3	1.5	0.9	16.6	11.9	480	1600	0.9
46 ✓	II	62.50°C	-11.18	6 "	A	60.63%	$\text{Mg}_{8.24}\text{Fe}_{19.65}\text{O}_{32.00}$	* F + M.O	2.5	1.7	1.4	1.2	16.4	13.8	640	9200	2.0
31 ✓	I	52.70°C	-8.75	6 "	B	57.74%	$\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$	Ferrite	8.3	2.3	1.6	0.8	14.2	15.0	320	1200	0.6
34 ✓	I	36.00°C	-9.57	6 "	B	57.82%	$\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$	Ferrite	8.5	2.4	1.6	0.8	16.8	13.4	460	2000	0.7
35 ✓	I	25.05°C	-10.14	6 "	B	57.76%	$\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$	Ferrite	8.0	2.2	1.6	0.8	16.0	13.8	320	1400	0.6
45 ✓	II	62.30°C	-11.19	6 "	B	59.25%	$\text{Mg}_{7.62}\text{Fe}_{18.16}\text{O}_{32.00}$	F + M.O	3.1	1.8	1.5	1.2	16.0	17.0	580	8100	1.0

* F = Ferrite

M.O - Mixed Oxide

The magnetic measurements recorded in Tables IX and X have been plotted against $\log P_{O_2}$, the curves for permeability being shown in Figure XVII, those for permittivity in Figure XVIII and those for the various loss coefficients in Figure XIX. The lattice constants of samples listed in Tables IX and X which have not been reduced, i.e., consisting entirely of the ferrite phase, are recorded in Table XII.

TABLE XII

LATTICE CONSTANTS OF UNREDUCED SAMPLES OF $MgFe_2O_4$

PREPARED IN H_2O-H_2 ATMOSPHERES

REACTION TEMPERATURE $1200^\circ C \pm 10^\circ C$.

SAMPLE NO.	CALCULATED $\log P_{O_2}$	METHOD OF COOLING	LATTICE CONSTANT IN ANGSTROM UNITS
26 ✓	-8.36	A	8.3724 ± 0.0005
12 ✓	-8.45	A	8.3759 ± 0.0005
22 ✓	-9.15	A	8.3750 ± 0.001
24 ✓	-9.96	A	8.3746 ± 0.001
13 ✓	-8.45	B	8.3835 ± 0.0005
15 ✓	-8.80	B	8.3822 ± 0.0005
23 ✓	-9.16	B	8.3822 ± 0.0005
25 ✓	-9.96	B	8.3826 ± 0.0005

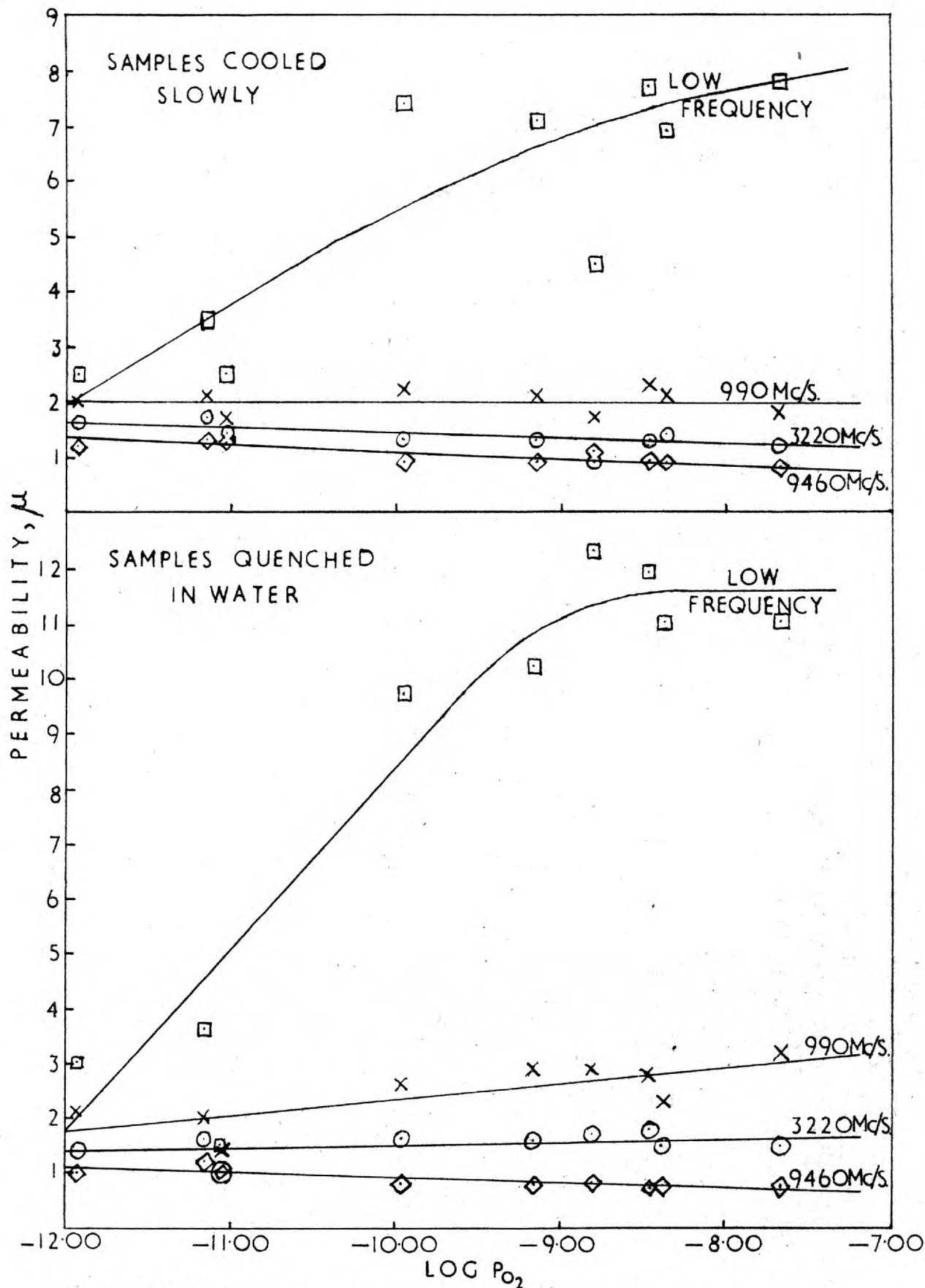


FIGURE XVII VARIATION OF μ WITH LOG P_{O_2} FOR
 SAMPLES PREPARED FROM $MgO + Fe_2O_3$ AT $1200^\circ \pm 10^\circ C.$

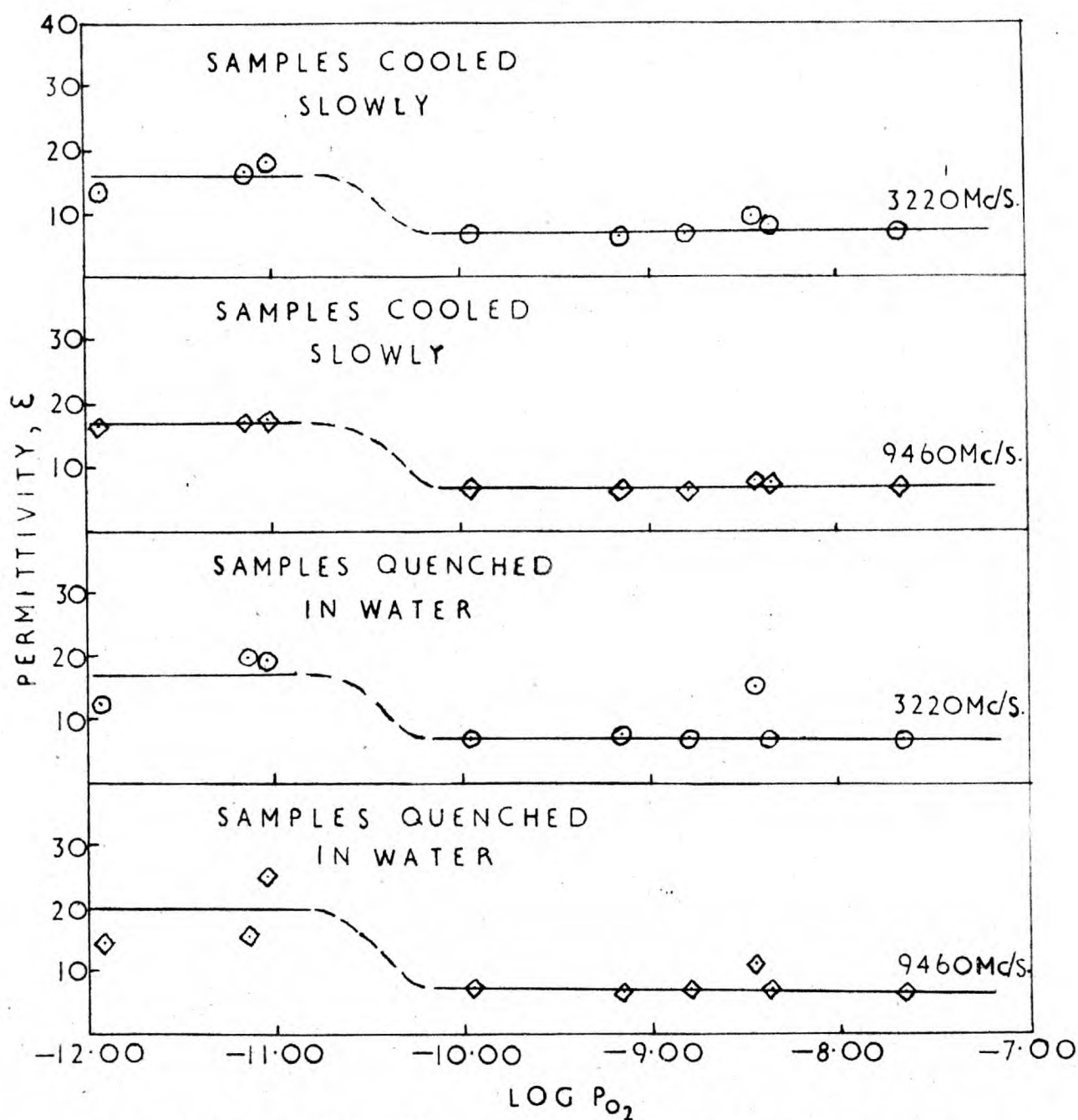


FIGURE XVIII VARIATION OF ϵ WITH $\log P_{O_2}$
 FOR SAMPLES PREPARED FROM $MgO + Fe_2O_3$
 AT $1200 \pm 10^\circ C$.

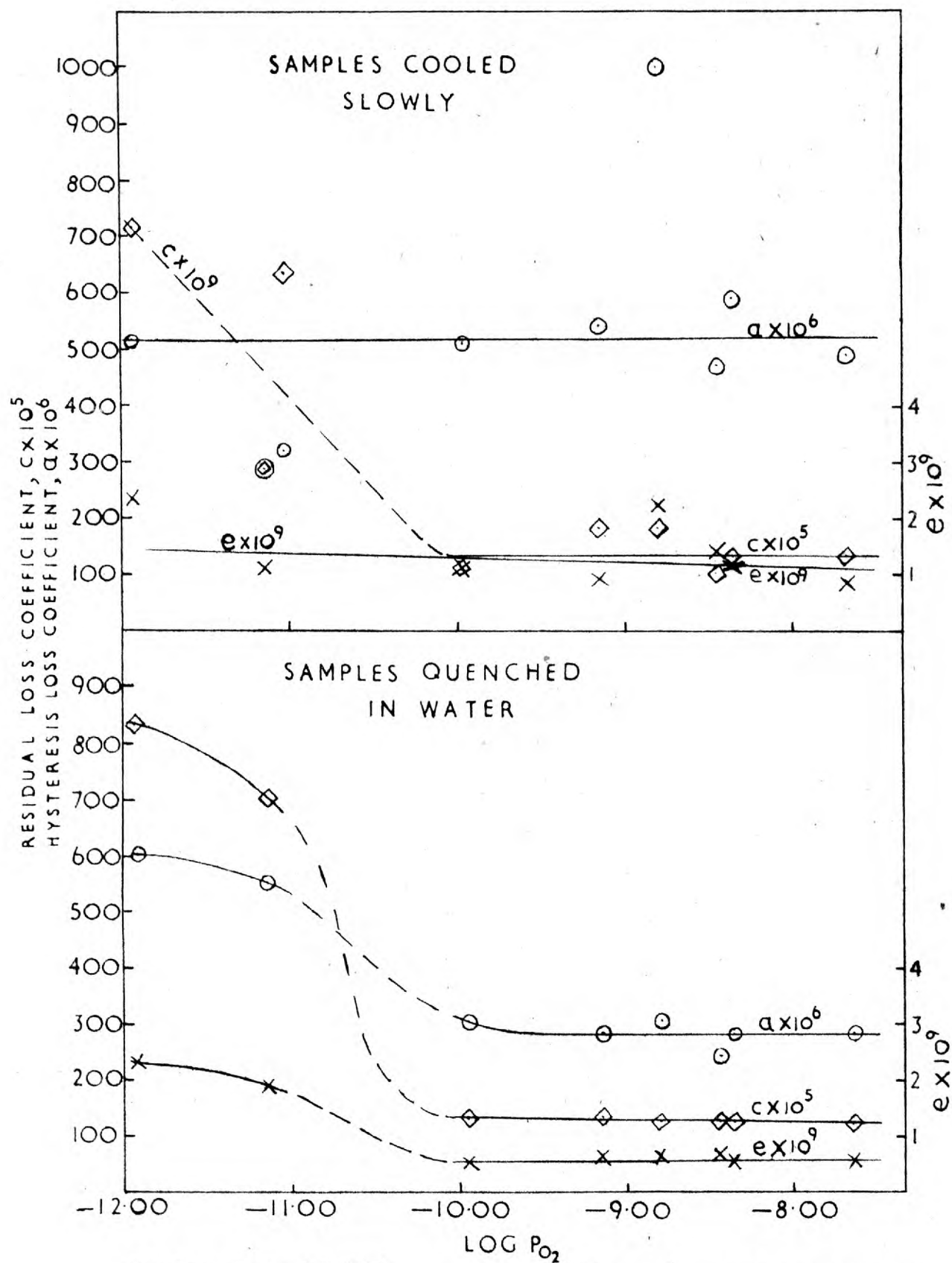


FIGURE XIX VARIATION OF LOSS COEFFICIENTS WITH LOG P_{O_2} FOR SAMPLES PREPARED FROM $MnO + Fe_2O_3$ AT $1200^\circ C$.

Series 4. Investigation of the Reduction of Magnesium
Ferrite in H₂O-H₂ Atmospheres

(a) Initial Composition $\text{MgO} \cdot \text{Fe}_2\text{O}_3$

(b) Initial Composition $\text{MgO} \cdot 1.192\text{Fe}_2\text{O}_3$

This investigation, unlike the preceding ones, involved the preparation of small samples in H₂O-H₂ atmospheres with the intention of examining their composition and structure by chemical and X-ray analysis. The required reducing atmospheres were obtained by the method used in Series 3, with the exception that in some runs the atmosphere consisted entirely of hydrogen and water vapour, without the diluent nitrogen. The special techniques which were employed in this series have been described in SECTION VI. The results obtained for samples having the initial composition $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ are shown in Table XIII, and those obtained for samples having the initial composition $\text{MgO} \cdot 1.192\text{Fe}_2\text{O}_3$ in Table XIV. The nature of the products of reduction will be considered in the General Discussion, but it should be mentioned here that the mixed oxide phase referred to in the tables below is (Mg,Fe)O.

TABLE XIII

SAMPLES PREPARED FROM MIXTURES OF COMPOSITION $\text{MgO} + \text{Fe}_2\text{O}_3 (\text{MgFe}_2\text{O}_4)$ IN $\text{H}_2\text{O}-\text{H}_2$ ATMOSPHERES

REACTION TEMPERATURE $1200 \pm 10^\circ\text{C}$.

SAMPLE NO.	GAS CYLINDER	TEMPERATURE OF THERMOSTAT	CALCULATED LOG P_{O_2}	TIME of FIRING	METHOD OF COOLING	% Fe IN PRODUCT	CALCULATED FINAL COMPOSITION	MEAN VALENCY OF IRON IN PRODUCT	PHASES PRESENT IN X-RAY PATTERN	LATTICE CONSTANT OF MIXED OXIDE PHASE IN ANGSTROM UNITS
73 ✓	II	82.80°C .	-9.99	7 hrs	C	57.09%	$\text{Mg}_{8.59}\text{Fe}_{17.18}\text{O}_{32.00}$	2.73	* F + M.O.	4.255 ± 0.002
64 ✓	II	82.00°C .	-10.07	7 "	C	57.65%	$\text{Mg}_{8.87}\text{Fe}_{17.74}\text{O}_{32.00}$	2.61	F + M.O.	4.255 ± 0.003
59 ✓	II	80.10°C .	-10.20	$7\frac{1}{2}$ "	C	58.78%	$\text{Mg}_{9.48}\text{Fe}_{18.96}\text{O}_{32.00}$	2.37	F + M.O.	4.258 ± 0.001
77 ✓	II	77.90°C .	-10.33	7 "	C	59.34%	$\text{Mg}_{9.81}\text{Fe}_{19.62}\text{O}_{32.00}$	2.26	Mixed Oxide	4.262 ± 0.001
55 ✓	II	75.00°C .	-10.51	$7\frac{1}{2}$ "	C	59.43%	$\text{Mg}_{9.87}\text{Fe}_{19.74}\text{O}_{32.00}$	2.24	Mixed Oxide	4.265 ± 0.001
50 ✓	II	51.90°C .	-11.71	$7\frac{3}{4}$ "	C	60.03%	$\text{Mg}_{10.23}\text{Fe}_{20.46}\text{O}_{32.00}$	2.13	Mixed Oxide	4.276 ± 0.002
44 ✓	II	31.00°C .	-12.74	6 "	A	60.40%	$\text{Mg}_{10.47}\text{Fe}_{20.94}\text{O}_{32.00}$	2.05	Mixed Oxide	4.283 ± 0.001
51 ✓	II	29.55°C .	-12.82	$8\frac{1}{2}$ "	C	61.73%	$\text{Mg}_{11.40}\text{Fe}_{22.80}\text{O}_{32.00}$	1.81	M.O. + Fe	4.279 ± 0.001
53 ✓	II	26.55°C .	-12.98	$7\frac{1}{2}$ "	C	69.88%	$\text{Mg}_{21.50}\text{Fe}_{43.00}\text{O}_{32.00}$	0.49	M.O. + Fe	4.243 ± 0.002
47 ✓	H_2	51.00°C .	-13.40	7 "	C	71.72%	$\text{Mg}_{26.02}\text{Fe}_{52.04}\text{O}_{32.00}$	0.23	M.O. + Fe	4.214 ± 0.002
62 ✓	H_2	43.90°C .	-13.74	8 "	C	71.30%	$\text{Mg}_{24.82}\text{Fe}_{49.64}\text{O}_{32.00}$	0.29	M.O. + Fe	4.223 ± 0.002
58 ✓	H_2	27.60°C .	-14.57	10 "	C	72.12%	$\text{Mg}_{27.16}\text{Fe}_{54.32}\text{O}_{32.00}$	0.18	M.O. + Fe	4.210 ± 0.002

* F = Ferrite

M.O. = Mixed Oxide

Fe = Metallic Iron

TABLE XIV

SAMPLES PREPARED FROM MIXTURES OF COMPOSITION $\text{MgO} \cdot 1.192\text{Fe}_2\text{O}_3$ ($\text{Mg}_{6.99}\text{Fe}_{16.67}\text{O}_{32.00}$) IN $\text{H}_2\text{O}-\text{H}_2$ ATMOSPHERES

REACTION TEMPERATURE $1200^\circ \pm 10^\circ\text{C}$.

SAMPLE NO.	GAS CYLINDER	TEMPERATURE OF THERMOSTAT	CALCULATED LOG P_{O_2}	TIME OF FIRING	METHOD OF COOLING	% Fe IN PRODUCT	CALCULATED FINAL COMPOSITION	MEAN VALENCY OF IRON IN PRODUCT	PHASES PRESENT IN X-RAY PATTERN	LATTICE CONSTANT OF MIXED OXIDE PHASE IN ANGSTROM UNITS
79 ✓	II	88.20°C.	-9.56	6 hrs	C	59.07%	$\text{Mg}_{7.54}\text{Fe}_{17.97}\text{O}_{32.00}$	2.72	$\overset{\#}{\text{F}} + \text{M.O.}$	4.262 ± 0.002
74 ✓	II	85.70°C.	-9.80	7 "	C	59.94%	$\text{Mg}_{7.92}\text{Fe}_{18.88}\text{O}_{32.00}$	2.55	$\text{F} + \text{M.O.}$	4.266 ± 0.002
66 ✓	II	82.00°C.	-10.05	7½ "	C	60.68%	$\text{Mg}_{8.26}\text{Fe}_{19.70}\text{O}_{32.00}$	2.41	$\text{F} + \text{M.O.}$	4.262 ± 0.002
68 ✓	II	75.80°C.	-10.46	8 "	C	61.18%	$\text{Mg}_{8.51}\text{Fe}_{20.28}\text{O}_{32.00}$	2.32	$\text{F} + \text{M.O.}$	4.261 ± 0.001
70 ✓	II	43.00°C.	-12.14	7½ "	C	62.49%	$\text{Mg}_{9.21}\text{Fe}_{21.96}\text{O}_{32.00}$	2.08	Mixed Oxide	4.283 ± 0.001
76 ✓	II	32.10°C.	-12.69	8¼ "	C	68.69%	$\text{Mg}_{14.08}\text{Fe}_{33.57}\text{O}_{32.00}$	1.07	$\text{M.O.} + \text{Fe}$	4.266 ± 0.0005
71 ✓	II	27.50°C.	-12.93	8 "	C	74.64%	$\text{Mg}_{24.47}\text{Fe}_{58.34}\text{O}_{32.00}$	0.26	$\text{M.O.} + \text{Fe}$	4.232 ± 0.001
72 ✓	H ₂	45.30°C.	-13.67	7½ "	C	76.08%	$\text{Mg}_{29.21}\text{Fe}_{69.65}\text{O}_{32.00}$	0.08	$\text{M.O.} + \text{Fe}$	4.211 ± 0.001

F = Ferrite

M.O. - Mixed Oxide

Fe = Metallic Iron

The results in Tables XIII and XIV may be plotted to obtain the reduction isotherms, that is, the curves showing variation in composition with oxygen pressure at one temperature, for the two compositions examined at $1200^{\circ} \pm 10^{\circ}\text{C}$. This is done in Figure XX by plotting $\log P_{\text{O}_2}$ against the mean valency of the iron in the product.

Series 5. Decomposition of Magnesium Ferrite on Heating in Oxygen

In this series large samples were prepared from intimate mixtures of ferric and magnesium oxides in the stoichiometric proportions $\text{MgO} + \text{Fe}_2\text{O}_3$ in oxygen at the temperatures 1100° , 1200° , 1300° , 1400° and 1500°C ., as previously described. At the end of the run the sample was quenched in water. An additional sample was prepared at 1500°C . and allowed to cool slowly. The iron content of the products was determined by analysis and the extent of decomposition is expressed as the percentage of ferrous oxide in Table XV, in which the magnetic measurements made on the specimens are also recorded.

TABLE XV

SAMPLES PREPARED FROM MIXTURES OF COMPOSITION $MgO \cdot Fe_2O_3 (MgFe_2O_4)$ IN OXYGEN

SAMPLE NO.	TEMPERATURE OF FIRING	TIME OF FIRING	METHOD OF COOLING	% Fe IN PRODUCT	CALCULATED FINAL COMPOSITION	% FeO IN PRODUCT	PERMEABILITY				PERMITTIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
							AT LOW FREQUENCY (1000 Kc/s.)	AT 990 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	HYSTERESIS $a \times 10^6$	RESIDUAL $c \times 10^6$	"EDDY CURRENT" $e \times 10^9$
69	1100°C.	24 hrs	B	55.80%	$Mg_{8.00}Fe_{16.00}O_{32.00}$	NIL	6.4	2.5	1.4	0.9	4.9	5.1	190	2000	0.6
8	1200°C.	6 "	B	55.80%	$Mg_{8.00}Fe_{16.00}O_{32.00}$	NIL	9.5	2.5	1.4	0.9	7.5	5.8	250	1300	1.2
67	1300°C.	26 "	B	55.75%	$Mg_{8.00}Fe_{16.00}O_{32.00}$	NIL	13.0	2.2	1.5	0.9	7.1	6.5	290	1500	0.6
65 & 80	1400°C.	24 "	B	55.94%	$Mg_{8.04}Fe_{16.08}O_{32.00}$	1.5±0.5%	12.4	2.4	1.7	0.8	8.3	7.6	340	1800	1.5
63 & 78	1500°C.	24 "	B	56.00%	$Mg_{8.07}Fe_{16.14}O_{32.00}$	2.6±0.5%	11.1	2.6	1.7	0.8	10.0	9.4	380	2500	1.2
61	1500°C.	9 "	A	55.86%	$Mg_{8.00}Fe_{16.00}O_{32.00}$	NIL	9.7	2.3	1.2	1.0	6.6	7.2	550	2300	4.4

The percentage of ferrous oxide in the quenched samples has been plotted against the temperature of preparation in Figure XXI. The variation with temperature of preparation of permeability is shown in Figure XXII, and of permittivity and loss coefficients in Figure XXIII.

Series 6. Sample of Magnesium Ferrite Prepared by a Fusion Method.

In SECTION VI the various experiments carried out in order to prepare magnesium ferrite by fusion methods have been described. These experiments culminated in the preparation of a large sample by a modification of the method of K.A. Hofmann and K. Höschele²¹. The method used consisted in heating 20 g. batches of a 1:2 mixture of ferric oxide and hydrated magnesium chloride in a silica crucible for 4 hours over a blast Meker burner. The product was extracted several times with 2 N. hydrochloric acid and analysed for iron and magnesium. The composition, magnetic properties and lattice constant of the material are recorded below in Table XVI.

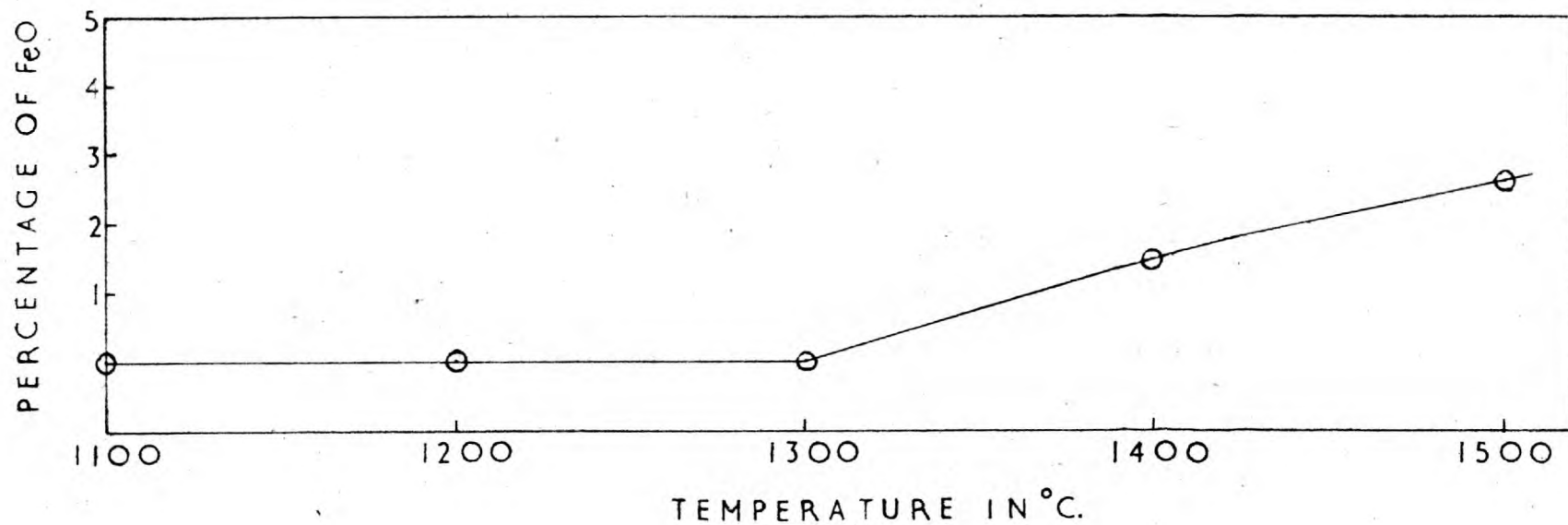


FIGURE XXI DECOMPOSITION OF MgFe_2O_4 ON HEATING IN O_2

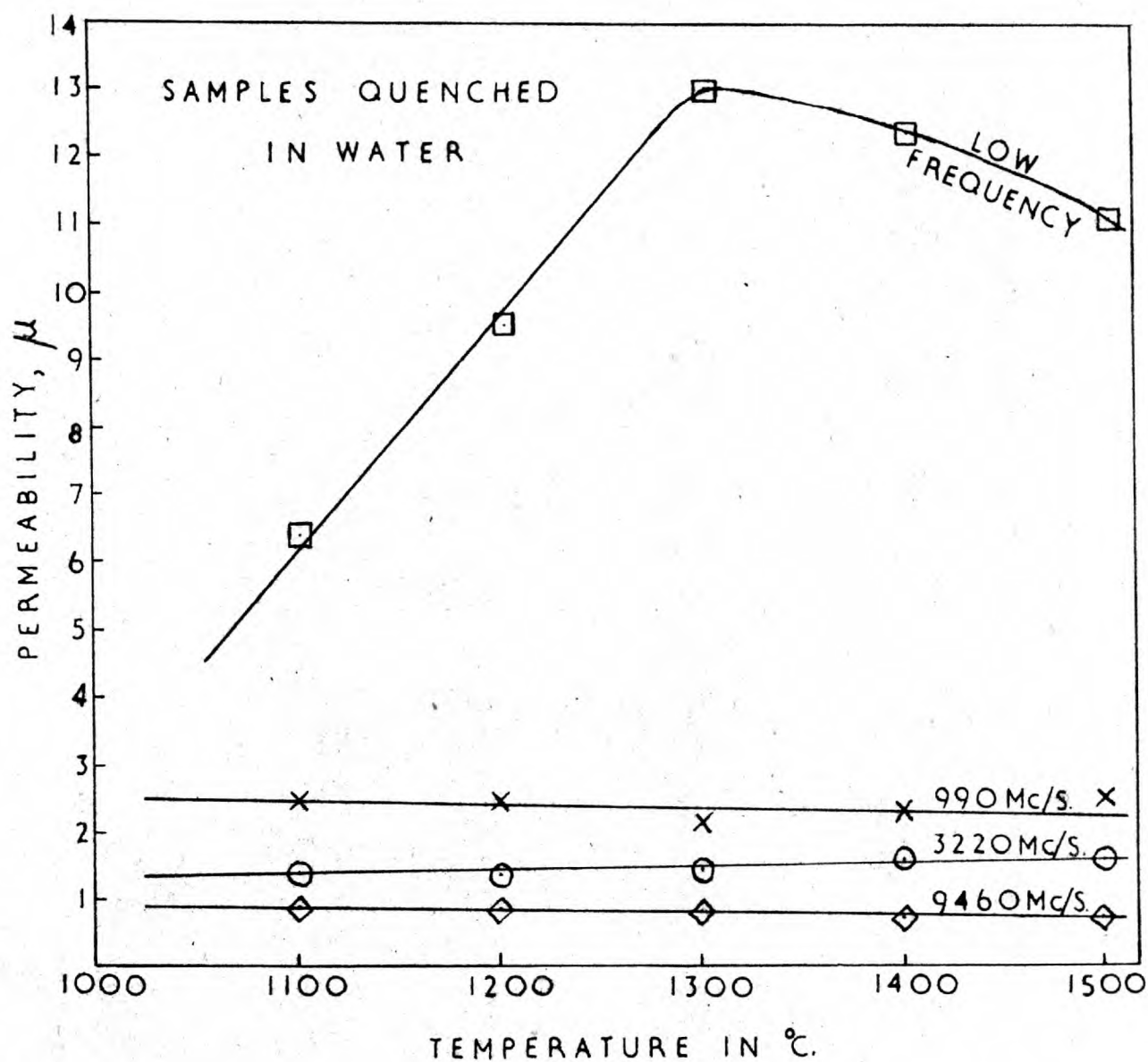


FIGURE XXII VARIATION OF μ WITH
TEMPERATURE OF PREPARATION OF MgFe_2O_4 IN OXYGEN

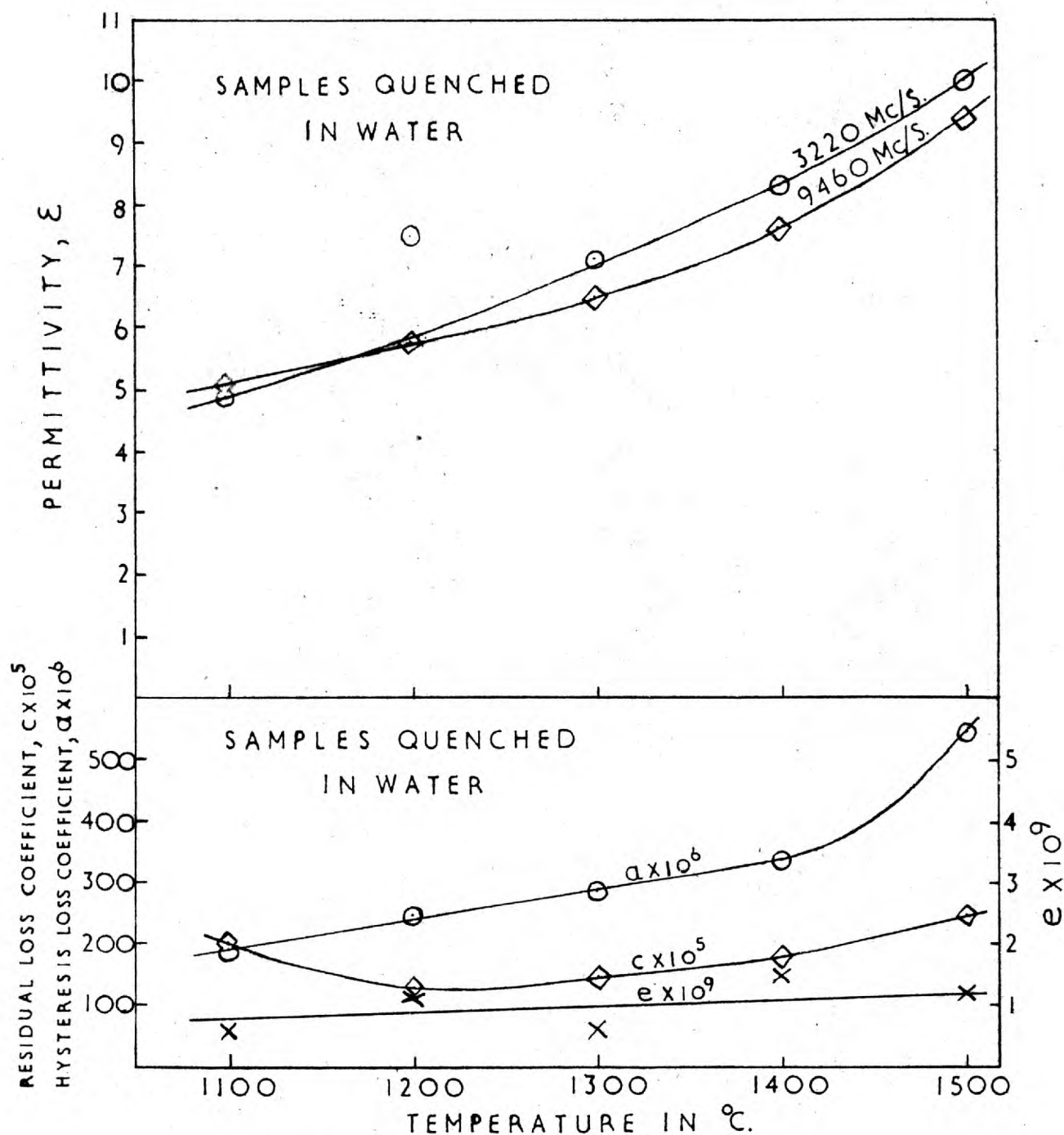


FIGURE XXIII VARIATION OF ϵ AND LOSS COEFFICIENTS WITH TEMPERATURE OF PREPARATION OF $MgFe_2O_4$ IN OXYGEN

TABLE XVI

PROPERTIES OF MAGNESIUM FERRITE PREPARED BY A FUSION METHOD

SAMPLE NO.	% Fe IN PRODUCT	% Mg IN PRODUCT	CALCULATED FINAL COMPOSITION	PHASES PRESENT IN X-RAY PATTERN	LATTICE CONSTANT OF FERRITE PHASE.	PERMEABILITY				PERMITTIVITY		LOSS COEFFICIENTS AT LOW FREQUENCY		
						AT LOW FREQUENCY (1000 Kc/s.)	AT 990 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	AT 3220 Mc/s	AT 9460 Mc/s	HYSTERESIS $\times 10^6$	RESIDUAL $\times 10^6$	"EDDY CURRENT" $\times 10^9$
3	57.25%	10.64%	Mg _{7.09} Fe _{16.60} O _{32.00}	F + f. Fe ₂ O ₃	8.374 $\pm$ 0.001	4.7	1.8	1.1	0.9	4.6	4.5	95	1300	2.8

SECTION IX

GENERAL DISCUSSION

SECTION IX: GENERAL DISCUSSION

(1) Magnetic Data

A mathematical treatment of the theoretical aspects of the magnetic properties of magnesium ferrite is outside the scope of this work, nevertheless, the various effects observed in the magnetic measurements will be examined qualitatively. Before discussing these effects, the way in which ferromagnetism arises will be considered.

It is now generally accepted that all ferromagnetic substances consist of small spontaneously magnetised regions or domains⁶⁰, which vary in size, but appear to be filamentary with lengths of perhaps 1 mm. to some centimetres. The spontaneous magnetisation in each domain is aligned with the direction of easy magnetisation of the crystal, which depends on the nature of the material and in the case of iron is the 100 axis in the face-centred cubic lattice. Except in perfect single crystals, the domains are not oriented parallel to one another. When the material is in the unmagnetised state, the vector sum of the magnetic moments of the individual domains is zero. However, when placed in a magnetic field, the material has a resultant magnetic moment which arises in two ways.

Firstly, those domains of magnetisation opposed to the field become unstable and reorient in the sense of the field, but still along the direction of easy magnetisation, that is, the magnetic vector turns through 180° . The reorientation begins at the boundary of an adjacent domain already oriented in the field direction and propagates across the domain. This process of reversal of direction of magnetisation in the individual domains causes discontinuities in the rise of magnetic induction with field strength, which are known as Barkhausen jumps. In a recent paper C. Kittel⁶¹ suggests that the Barkhausen jumps correspond to irregular fluctuations in the motion of a domain boundary under the influence of an applied magnetic field, rather than to a complete domain reversal.

Secondly, those domains having their direction of easy magnetisation at an angle with the magnetising force are made to align themselves parallel to that force. This process may be considered to take place either by movement of domain boundaries, so that a correctly oriented domain grows at the expense of a neighbouring domain having its direction of easy magnetisation inclined to the field, or by rotation of the direction of magnetisation in the domain. In either case, this second process of aligning domains with the magnetising force takes place less easily and rapidly than the reversal process.

Between neighbouring domains there are regions in which the direction of magnetisation varies from one direction of minimum energy to another. These regions are the Bloch zones, which move as a domain grows into its neighbour. The magnetic stresses introduced by the reorientation of the domains in the direction of the magnetising force produce mechanical stresses that give rise to the changes in dimensions of the specimen observed in magnetostriction.

It is now necessary to consider what causes the domains to have magnetic moments and how it is that they become spontaneously magnetised. In ferromagnetic materials the electron-spin moments of free electrons give rise to a resultant spin angular momentum quantum number, S , which may have integer and half-integer values and is responsible for the magnetic moment. For iron, cobalt and nickel the electrons concerned lie in the uncompleted 3d shell and have powerful interaction forces between them. If there are equal numbers of electrons in the energy levels of this shell with right-hand and left-hand spins, there is no resultant spin angular momentum, i.e., $S = 0$. But, if as a result of heat motions a few of the electrons migrate from the right-hand to the left-hand spin, the exchange forces lower the energy level of the left-hand group. Thus, more electrons pour into the left-hand level, which sinks as this happens,

until it is full. At this point the top of the left-hand spin energy level coincides with the top of the partially filled right-hand spin group. The material has thus spontaneously magnetised itself to the extent of the difference in numbers of electrons in the two levels. The direction of the spontaneous magnetism, i.e., right-hand or left-hand spins, is governed by pure chance in any given specimen. It may be this factor among others that leads to the spontaneous magnetisation of any extensive specimen in oppositely oriented domains. Such magnetisation can occur only if the temperature is below some critical value, above which the exchange forces cannot take control against the thermal migrations of the electrons. This critical temperature corresponds to the Curie point.

Having considered the origin of ferromagnetism, the effects observed with samples of magnesium ferrite prepared under various conditions will now be discussed.

(a) Values of Permeability

The values obtained for permeability at room temperature are all of a low order, the highest being 13. This is to be expected from consideration of the facts that the Curie point of magnesium ferrite lies at 310° - 315°C . and that the permeability of a substance is at a maximum at a temperature just below the Curie point and falls rapidly

below that temperature. It has been shown by J.L.Snoek³⁶ that the Curie point of the mixed spinel $(\text{Mg,Zn})\text{Fe}_2\text{O}_4$, in which there are equimolecular proportions of magnesium and zinc, is only a little above 100°C . This implies that the interaction forces causing the electron spins to align are more readily overcome by the thermal agitation of the electrons, or as Snoek expresses it, the crystal anisotropy has probably been "killed". The permeability of this mixed spinel is approximately 100 when prepared at 1200°C . and 600 when prepared at 1400°C .

(b) Effect of Oxygen Pressure.

No rational changes in the permeability, permittivity or loss coefficients were observed with decrease in oxygen pressure until the stage where reduction could be detected by chemical analysis was reached. Samples prepared at these very low oxygen pressures exhibited effects in their magnetic properties which can be attributed to the increased concentration of lattice defects and the accompanying increase in electrical conductivity. The nature of these lattice defects will be considered later in this discussion.

It has been observed that the loss coefficients of the reduced samples are generally larger than those of the unreduced samples. In order to appreciate the significance of this, it is necessary to consider how the various losses arise

Firstly, the hysteresis loss corresponds to the energy required for the movement of domain boundaries in the reorientation of domains. In a substance with a large concentration of lattice defects the movement of a domain boundary will be arrested when a serious defect is encountered. A greater magnetising force will be required to surmount such an obstacle, thus increasing the hysteresis loss. Secondly, the residual loss represents the lag of the induction, B , behind the field, H , and corresponds to some sort of "viscosity" in moving a domain boundary to a new position. If a moving domain boundary has a number of lattice defects in its path, before it encounters a more serious defect, such as that considered to increase the hysteresis loss, then the residual loss will be increased. The very high values of residual loss coefficient obtained for the reduced samples presumably arise in this way. Finally, the eddy current loss has to be considered. It was pointed out in presenting the experimental results that the term e , although called "eddy current loss coefficient", may not correspond exactly to the eddy current losses in metals. However, it is sufficient here to consider that in some way electro-magnetic fields are induced in the crystal which are not parallel to the external field. The effect of such induced fields would be to attempt to orient electron

spins in their own directions. The values obtained for eddy current loss coefficients of the reduced samples are higher than those of unreduced samples and this presumably arises from the increased conduction resulting in larger induced electro-magnetic fields in the crystal.

It is apparent that an increase in any of these loss coefficients results in fewer electron spins being oriented in the direction of the external field. Thus, the total magnetic induction is reduced and consequently the permeability is lower. The lowering of the permeability that would be expected to accompany the increase in losses in the reduced samples has been in fact found for measurements made at low frequency. This effect, however, is not marked at high frequencies and the reason for this will be discussed later.

Another effect observed with reduced samples is that the permittivity, or dielectric constant, is greater than in unreduced samples. At first sight, it appears to be difficult to reconcile this with the increased conductivity of the reduced samples. However, when it is realised that it is the apparent permittivity of the specimen that is being measured, the phenomenon may be explained as follows. A semi-conducting material may be considered to consist of regions in which some of the electrons are in shallow energy

troughs, i.e., they may readily be raised to the conduction band, the number of electrons in this energy level being determined by the Boltzmann distribution law. As the concentration of lattice defects increases the number of electrons in the conduction band also increases. However, the migration of these electrons is limited by the boundaries of the regions, which may be considered to be high potential energy barriers. When the specimen is placed in a field, these electrons move elastically to the boundaries, thereby increasing the total capacity, and consequently, the apparent permittivity of the specimen.

(c) Effect of Composition.

A number of effects produced by variation of the composition of the material in the range $\text{MgO}, 0.5\text{Fe}_2\text{O}_3$ to $\text{MgO}, 2.283\text{Fe}_2\text{O}_3$ have been observed mainly in the low frequency measurements.

The permeability was found to be at a maximum in the region of stoichiometric composition. This presumably arises from the concentration of lattice defects being at a minimum in the stoichiometric ferrite, thus allowing a greater number of domains to be aligned with the field. This is supported by the values obtained with slowly cooled samples for the hysteresis loss coefficient which has a minimum value at the stoichiometric

composition. The hysteresis loss coefficient of quenched samples also rises with increasing MgO content, but does not appear to rise in Fe_2O_3 -rich samples. The other two loss coefficients do not show any change with variation in composition.

The permittivity exhibits effects with change in composition which are not readily explained. In the case of quenched samples the permittivity rises to a maximum of more than 42 at 3220 Mc/s. and more than 27 at 9460 Mc/s. in the range of composition $\text{MgO}, 1.5\text{Fe}_2\text{O}_3$ to $\text{MgO}, 1.9\text{Fe}_2\text{O}_3$. With the slowly cooled samples the permittivity rises with increasing iron content.

It is clear that these results cannot be directly related to the limits of mixed crystal formation, which have been determined by X-ray examination. However, it is not to be expected that the appearance of a second phase, either of MgO or Fe_2O_3 , will have any very marked effect on the magnetic properties of the material, as the second phase will act only as a diluent, the more noticeable effects being produced by the progressive increase in lattice defects before the limiting concentration is reached.

(d) Effect of Quenching

The most noticeable effect of quenching in water is that the permeability is greater for the quenched samples than for the corresponding slowly cooled ones, the effect being far

less marked at high frequencies. This implies that in the quenched samples more domains have their electron-spin moments oriented in the direction of the field. Now, it has been shown by X-ray examination that the quenched samples have a larger lattice parameter than the slowly cooled ones. This is not merely due to "freezing" the thermally expanded lattice, as even on very rapid cooling this cubic lattice would shrink if it were perfect.

The retention at room temperature of the expanded lattice by quenched samples is probably due to some rearrangement of ions or the retention of the lattice defects which were present before quenching. In this case, it is possible that the higher permeability of the quenched samples arises from the greater ease of reorientation of electron-spin moments by domain boundary movement in the more open lattice.

(e) Effect of Temperature of Preparation

A number of interesting effects have resulted from varying the temperature of preparation in the range 1100° to 1500°C., some of which are analogous to those obtained at low oxygen pressures.

The loss coefficients exhibit a general rise with increasing temperature of preparation, which is explained, as in the case of the reduced samples prepared at low oxygen pressures, by increases in the concentration of lattice defects, which also increase the conductivity,

This increase in conductivity is again accompanied by an increase in permittivity, which rises steadily from 5 at 1100°C. to 10 at 1500°C., as the concentration of defects becomes progressively greater.

In the case of permeability, variation in the temperature of preparation produces, at low frequency, a maximum value of 13 at the temperature of preparation of 1300°C. This maximum permeability may arise from the combination of two factors. Firstly, the permeability would be expected to decrease at higher temperatures of preparation of the ferrite owing to the increase in losses accompanying the increase in defects. On the other hand, it might be expected that the samples quenched from the higher temperatures would have the higher permeability owing to the greater ease of domain boundary movement in the more open lattice, which has already been discussed. Thus, the maximum permeability observed at 1300°C. may arise from the combination of these two conflicting factors in such a way that, at a quenching temperature below 1300°C. the permeability is lower because of the greater difficulty of reorienting domains in the lattice of smaller dimensions, and above 1300°C. the permeability is lower because of the greater losses arising from the increased lattice defects.

(f) High Frequency Effects

The values obtained for permeability at high frequencies are much lower than those obtained at low frequency. This can be explained by reconsidering the two processes by which the magnetic moments of the domains in the unmagnetised state become oriented in the direction of the magnetising force when placed in an external field. The first mechanism is a rapid one, in which the magnetic vector reverses its direction, i.e., the spin magnetic quantum number changes its sign, but not its numerical value. The second process, however, is less rapid as it involves the alignment of domains with the external field. Thus, at high frequency of alternation of field direction this slower process is unable to take place to the same extent as at low frequency, thereby lowering the permeability. At ultra high frequency the first process will also be restricted.

The decrease in permeability in reduced samples, observed in low frequency measurements, has been shown to be due to increases in the loss coefficients arising from the lattice defects. However, at high frequencies even the unreduced samples have a very low permeability, and the effect of the increased losses in the reduced samples is not apparent owing to the very short time available between each alternation of field for the reorientation of domains. The high frequency of alternation has thus become the predominant factor lowering the permeability.

Finally, the observed lowering of permittivity with increase in frequency is accounted for by the lack of time for the free electrons to move elastically to their full extent, thus not allowing the full apparent capacity to be developed.

(2) Mixed Crystal Formation in the System $\text{MgO-Fe}_2\text{O}_3$

The variation in lattice constant with change in composition in the system $\text{MgO}+\text{Fe}_2\text{O}_3$ has been shown in Tables VII and VIII for slowly cooled and quenched specimens, respectively. The curves obtained in Figure XIII by plotting the lattice constant against composition are not of the form required by Vegard's Law⁶². This law maintains that in a solid solution the change in lattice constant should be directly proportional to the change in composition, i.e., the values of lattice constant should lie on a straight line, between the limits of solid solution. A.H. Jay and K.W. Andrews³³ have shown that the MgO-FeO system also deviates, but to a lesser extent, from this law.

The horizontal portions at each end of these curves represent the lattice constants of magnesium ferrite saturated in one case with magnesium oxide, and in the other case with ferric oxide. The excess oxide which the lattice of the ferrite cannot accommodate appears as a separate phase. The advantage of the method used here is that the limits of solid solution are immediately discernible in the lattice constant measurements, before sufficient excess oxide is present to appear as a second

phase in the X-ray powder pattern. The method used by A.E. van Arkel, E.J. Verwey and M.G. van Bruggen^{29,14} to investigate solid solution formation in the system $\text{MgO-Fe}_2\text{O}_3$ has the disadvantage, pointed out by the authors, that it depends on the appearance of the second phase in the X-ray pattern. It is of interest to note that these investigators found that the lines of excess ferric oxide first appeared in the X-ray pattern of quenched material, prepared at $1300^\circ\text{C}.$, at the composition $\text{Mg}_{4.00}\text{Fe}_{18.67}\text{O}_{32.00}$. This is in close agreement with the composition, $\text{Mg}_{4.08}\text{Fe}_{18.62}\text{O}_{32.00}$, of the quenched sample prepared at $1200^\circ\text{C}.$, which first showed excess ferric oxide in the X-ray pattern in the present investigation. The limit of dissolution of magnesium oxide in the ferrite is given by these investigators as less than $\text{Mg}_{20.9}\text{Fe}_{7.4}\text{O}_{32.0}$ which is beyond the limit found here.

H. Forestier¹⁹ has reported from magnetic measurements that magnesium ferrite is saturated with ferric oxide at $315^\circ\text{-}400^\circ\text{C}.$ at the composition $\text{MgO}, 1.13\text{Fe}_2\text{O}_3$ or $\text{Mg}_{7.3}\text{Fe}_{16.5}\text{O}_{32.0}$. This is in good agreement with the value found in the present instance at $1200^\circ\text{C}.$, i.e., $\text{MgO}, 1.15\text{Fe}_2\text{O}_3$ or $\text{Mg}_{7.2}\text{Fe}_{16.6}\text{O}_{32.0}$. This investigator did not detect the solid solution of magnesium oxide in magnesium ferrite by measurement of the Curie point.

H.S. Roberts and H.E. Merwin²⁸ examined microscopically samples prepared in the temperature range 1000° to 1750°C. They did not detect solid solution of ferric oxide in the ferrite, but found approximately 1% of magnesium oxide to be taken into solution.

The marked similarity in the shape of the curves in Figure XIII for the quenched and slowly cooled samples indicates that the solubilities of ferric and magnesium oxides in magnesium ferrite are not dependent upon temperature to any great extent.

It is shown by the curves obtained that the solubility of magnesium oxide in the ferrite is considerably greater than that of ferric oxide. This may be attributed to the similarity in crystalline form of magnesium oxide and magnesium ferrite, which are both cubic, whereas ferric oxide is rhombic in structure. However, in the light of present knowledge, the solid solubility exhibited by the $\text{MgO-Fe}_2\text{O}_3$ system can be viewed from a different standpoint.

It is necessary first to consider the various defects which may exist in the lattice of a stoichiometric compound.

These are,

Schottky defects, which in a stoichiometric compound consist in equivalent numbers of vacant cation sites and vacant anion sites;

Frenkel defects, which consist in interstitial atoms together with an equal number of vacant lattice sites; this type of defect is usually effectively limited to either the cations or the anions in the lattice;

Substitutional defects, which consist in equal numbers of sites, proper to cations but occupied by anions, and sites, proper to anions occupied by cations; this type of defect is likely only in intermetallic compounds, where ionic repulsions would not be involved. In general, it may be assumed from energetic considerations, that all types of defect are not equally probable under a particular set of conditions.

The stoichiometric compound is, however, a limiting case, thus in real crystals the concentrations of vacant cation sites and vacant anion sites or interstitial atoms and vacant lattice sites may not be equal. The conditions of equilibrium of such lattice defects in real crystals, deviating but little from stoichiometric composition, were worked out by C. Wagner and W. Schottky^{63,64}. This theory has been extended by J.S. Anderson⁶⁵ to include phases exhibiting a wide range of compositions. By considering not only the energy expenditure to produce lattice defects, but also the energy of interaction between neighbouring pairs of defects, the conditions governing the stability of a non-stoichiometric phase have been deduced.

The relationship derived between the activity of the components and the concentration of the lattice defects reproduces satisfactorily the observed $(P,X)_T$ and $(T,X)_P$ relations of typical systems, where X is a composition parameter, leading to the explicit prediction of the occurrence of two-phase regions in equilibrium diagrams. J.S.Anderson has shown also that the formation of anomalous mixed crystals between compounds of different formula types, e.g., between yttrium fluoride, YF_3 , and calcium fluoride, CaF_2 , is governed by the same considerations as the non-stoichiometry of a "pure" compound. The replacement of one atomic species by another of similar ionic radii is possible provided that the electrostatic balance may be maintained by the creation of a second anomaly, i.e., a vacant lattice site, an interstitial atom, or a second, compensating replacement. The process of anomalous mixed crystal formation therefore creates lattice defects in just the same manner as does the valency change of one component of a "pure" compound.

G. Hägg and G. Söderholm⁶⁶ have shown by lattice constant measurements that in the $MgO-Al_2O_3$ system the single phase spinel region at $1000^\circ C$. lies between the limits 50 and 67 Mol % Al_2O_3 . They have compared the observed densities with those calculated from the unit cell dimensions on the alternative assumptions (a) accommodation of the excess oxygen interstitially, and (b) presence of vacant cation sites.

Their conclusion is that the alumina-rich spinel phase contains vacant cation sites.

In the $\text{MgO-Fe}_2\text{O}_3$ system at $1200^\circ \pm 10^\circ\text{C}$. the spinel phase has been found to be stable on the Fe_2O_3 -rich, i.e., oxygen-rich, side up to 53.5 Mol % Fe_2O_3 or $\text{Mg}_{7.2}\text{Fe}_{16.6}\text{O}_{32.0}$.

If the predominant lattice defects in this oxygen-rich range are similar to those present in the corresponding range of the $\text{MgO-Al}_2\text{O}_3$ system, then the limit of solid solubility of Fe_2O_3 in MgFe_2O_4 represents the composition at which the concentration of Schottky defects reaches the energetically permissible limit under the conditions prevailing. The mutual interaction of these defects may be regarded, qualitatively, as the driving force behind the segregation of a new phase when the critical concentration of defects is exceeded.

The MgO -rich, i.e., metal-rich, side of the spinel phase in the $\text{MgO-Fe}_2\text{O}_3$ system at $1200^\circ \pm 10^\circ\text{C}$. has been found here to extend to 42.5 Mol % Fe_2O_3 or $\text{Mg}_{9.9}\text{Fe}_{14.8}\text{O}_{32.0}$. The accommodation of the excess metal may give rise to either a substantially complete anion lattice with metal atoms in interstitial positions (unbalanced Frenkel defects) or an incomplete anion lattice and a substantially complete cation lattice (unbalanced Schottky defects). The greater probability of the predominance of unbalanced Frenkel defects is shown in a number of ways. The lattice constant increases as the proportion of excess metal increases, as would be expected if this excess metal were accommodated interstitially. Also,

D.J. Bevan, J.P. Shelton and J.S. Anderson⁶⁷ have shown by conductivity measurements at various oxygen pressures, that MgFe_2O_4 is a metal-excess (electron) conductor, which on loss of oxygen accommodates the excess metal interstitially. The metal-rich phase obtained on such dissociation may be regarded as being to some extent analogous to the metal-rich phase obtained here by increasing the ratio of Mg^{2+} ions to Fe^{3+} ions. On this basis, the limit of solid solubility of MgO in MgFe_2O_4 , represents the composition at which the concentration of Frenkel defects reaches a limiting value.

These defects in the non-stoichiometric range of the spinel phase of the $\text{MgO-Fe}_2\text{O}_3$ system violate the true symmetry of the spinel structure, which has been discussed in the Introduction. This loss of symmetry, however, is not sufficiently developed for extra lines to appear in the X-ray powder patterns of the single phase spinel samples.

(3) Reduction Isotherms.

The reduction of magnesium ferrite falls into three phase regions, indicated by A, B and C on the reduction isotherms of the two compositions $\text{MgO+Fe}_2\text{O}_3$ and $\text{MgO+1.192Fe}_2\text{O}_3$ in Figure XX. Phase region A consists of the ferrite phase alone and extends from high oxygen pressures to the point at which reduction is first detectable by chemical analysis.

Phase Region B extends from the latter point to the stage at which all the iron in the material is in the ferrous state. Phase Region C extends from the latter stage to the limit of reduction of iron, where all the iron is in the metallic state. Phase Region A.

The X-ray powder patterns of the samples in this region show only the lines of the ferrite phase. The work of D.J. Bevan, J.P. Shelton and J.S. Anderson⁶⁷ on the electrical conductivity of magnesium ferrite has shown that decrease in oxygen pressure is accompanied by increasing oxygen deficiency in the lattice. However, the present results indicate that the progressive increase in reduction occurring in Phase Region A is very small. The lattice constants of samples in this region, recorded in Table XII, do not show any progressive change with decreasing oxygen pressure. Further evidence on this point may be obtained from the values of permittivity in this region. It has been seen that reduction or dissociation produces an increase in permittivity. This is well illustrated in Figure XXIII, which shows the progressive increase in permittivity with increase in temperature of preparation, that is, with increasing dissociation. In Phase Region A, however, the values of permittivity do not show any such increase with decreasing oxygen pressure, until the stage at which reduction can be detected by chemical analysis is reached, as may be seen in Figure XVIII.

Phase Region B.

The X-ray powder patterns of the samples in the first part of this region show the lines of the ferrite phase and the mixed oxide phase $(\text{Mg,Fe})\text{O}$. The patterns of samples prepared in the lower oxygen pressure range of this region show only the lines of the mixed oxide phase.

It has already been mentioned in discussing the mixed crystal formation in the $\text{MgO-Fe}_2\text{O}_3$ system, that J.S. Anderson^{65,68} has derived a relationship between the activity of the components and the concentration of lattice defects, which reproduces satisfactorily the observed $(p,X)_T$ and $(T,X)_p$ relations of typical systems, e.g., the Pt-PtS-PtS_2 system. This relationship predicts the occurrence of a two-phase region, when the concentration of lattice defects reaches the energetically permissible limit under the conditions prevailing. In Phase Region A the concentration of defects, in this case Frenkel defects, increases with decrease in oxygen pressure until the limiting concentration is reached. At this stage the experimental pressure equals the critical pressure at the reaction temperature and further decrease in the oxygen pressure involves the appearance of a second phase, through the mutual attraction of the defects.

The removal of O^{2-} ions from the lattice involves an effective decrease in valency of a corresponding number of cations, which are then accommodated interstitially, but at

first only in the surface layers of the lattice. The reaction proceeds by the migration of these Frenkel defects from one inter-lattice position to the next through the body of the crystal. Such movement must involve the surmounting of a certain potential barrier. It is the height of this barrier that determines the activation energy of the diffusion process. In practice, this self-diffusion becomes appreciable above $0.5 \times$ absolute melting point of the material, i.e., above the Tammann temperature⁶⁹, which for magnesium ferrite is approximately 740°C . The reaction temperature of 1200°C . employed here is well above this temperature.

On consideration of the system it may be seen that the coexistence of two solid phases is in accordance with the Phase Rule, which states:-

$$P + F = C + 2$$

Where, P = Number of phases.

F = Number of degrees of freedom.

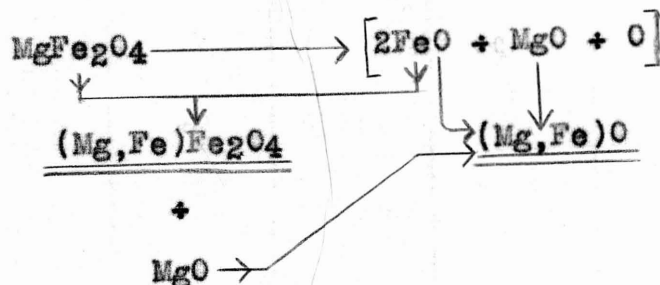
and C = Number of Components.

If there are three phases, two solid and one gaseous, in this three component system, then:-

$$F = 3 - 3 + 2 = 2$$

Thus such a system has two degrees of freedom. This agrees with the observed characteristics of the system, the variables of which are temperature, pressure and two concentrations, two of which must be fixed to define the system completely.

The nature of these two phases has now to be considered. The reduction of magnesium ferrite leads to the formation of ferrous iron, which, when the limiting concentration of defects has been reached, will appear as ferrous oxide together with the corresponding amount of magnesium oxide. These two oxides are known to form a complete mixed crystal range³³, thus the MgO and FeO formed in the decomposition will form the mixed oxide (Mg,Fe)O. On this basis, the two solid phases would be (Mg,Fe)O and MgFe_2O_4 , saturated with defects, which is in agreement with the X-ray patterns, which show the lines of the mixed oxide and a spinel. However, on reconsidering the stage where the magnesium ferrite was regarded, for the purpose of discussion, to have partly decomposed to ferrous oxide and magnesium oxide, it will be seen that this spinel phase may not be pure MgFe_2O_4 . In the system magnesium ferrite and ferrous oxide are coexisting and it is reasonable to suppose that replacement of the Mg^{2+} ions of the ferrite by Fe^{2+} ions will take place. This would lead to the formation of the mixed spinel $(\text{Mg,Fe})\text{Fe}_2\text{O}_4$ plus magnesium oxide formed from the displaced Mg^{2+} ions. The formation of the two phases $(\text{Mg,Fe})\text{Fe}_2\text{O}_4$ and $(\text{Mg,Fe})\text{O}$ is set out schematically below, but it is not implied that the actual reduction proceeds by the mechanisms shown.



The positions of the lines in the X-ray patterns of MgFe_2O_4 and FeFe_2O_4 are very similar and thus the pattern of the mixed spinel $(\text{Mg,Fe})\text{Fe}_2\text{O}_4$ would not be expected to show any appreciable variation in the positions of the lines with composition. However, the lattice constants, and hence the positions of the lines, of the mixed oxide $(\text{Mg,Fe})\text{O}$ show considerable variation with composition; the lattice constant varying from 4.200Å for pure MgO to 4.300Å for pure FeO. The curve for the variation of the lattice constant of this mixed oxide with composition has been reliably determined by A.H. Jay and K.W. Andrews³³. The lattice constant of the mixed oxide phase in all the samples has been determined and consequently the composition of this phase may be obtained from the results of these investigators. Once the composition of this phase is known, the composition of the other solid phase may be calculated from a knowledge of the overall composition of the material, as determined by chemical analysis.

In this calculation it is necessary to ignore the mixed crystal formation between the two phases, which will necessarily contain their respective limiting concentrations of defects. The extent of the non-stoichiometry arising from this will be considered by analogy with the parallel system $\text{Fe}_3\text{O}_4\text{-FeO}$, for which data are available. The results of R. Schenck and T. Dingmann³⁰, S. Hilpert and J. Beyer⁷⁰ and A. Matsubara⁷¹ show that the limiting composition of the oxygen-rich FeO phase, i.e., Wüstite, is $\text{Fe}_{0.9}\text{O}_{1.0}$ in the temperature range $800^\circ\text{-}1200^\circ\text{C}$. A. Matsubara⁷¹ gives the limiting composition of the oxygen-deficient Fe_3O_4 phase at 1175°C . as $\text{Fe}_{3.05}\text{O}_{4.00}$. Thus the mixed crystal formation in the system $\text{Fe}_3\text{O}_4\text{-FeO}$ is small, and consequently it will be assumed that the mixed crystal formation in the very similar system $(\text{Mg,Fe})\text{Fe}_2\text{O}_4\text{-(Mg,Fe)O}$ is also small.

On this assumption the results obtained here have been used in conjunction with the results of A.H. Jay and K.W. Andrews to calculate the approximate compositions and the relative proportions of the two solid phases, which are recorded below in Table XVII.

TABLE XVII

APPROXIMATE COMPOSITIONS OF SOLID PHASES IN PHASE REGION B
IN REDUCTION OF $\text{MgO}+\text{Fe}_2\text{O}_3(\text{Mg}_8\text{Fe}_{16}\text{O}_{32})$

SAMPLE NO.	LOG P_{O_2}	CALCULATED FINAL COMPOSITION	LATTICE CONSTANT OF MIXED OXIDE PHASE	APPROXIMATE COMPOSITION OF SOLID PHASES		
				MIXED OXIDE FROM LATTICE CONSTANT	MOL % OF MIXED OXIDE	CALCULATED COMPOSITION OF SPINEL PHASE
73	-9.99	$\text{Mg}_{8.59}\text{Fe}_{17.18}\text{O}_{32.00}$	4.255	$\text{Mg}_{19.4}\text{Fe}_{12.6}\text{O}_{32.0}$	22%	$(\text{Mg}_{5.5}, \text{Fe}_{2.5})\text{Fe}_{16}\text{O}_{32}$
64	-10.07	$\text{Mg}_{8.87}\text{Fe}_{17.74}\text{O}_{32.00}$	4.255	$\text{Mg}_{19.4}\text{Fe}_{12.6}\text{O}_{32.0}$	33%	$(\text{Mg}_{3.8}, \text{Fe}_{4.2})\text{Fe}_{16}\text{O}_{32}$
59	-10.20	$\text{Mg}_{9.48}\text{Fe}_{18.96}\text{O}_{32.00}$	4.258	$\text{Mg}_{18.2}\text{Fe}_{13.8}\text{O}_{32.0}$	52%	$\text{Fe}_8\text{Fe}_{16}\text{O}_{32}$
77	-10.33	$\text{Mg}_{9.81}\text{Fe}_{19.62}\text{O}_{32.00}$	4.262	$\text{Mg}_{17.1}\text{Fe}_{14.9}\text{O}_{32.0}$	57%	$\text{Fe}_8\text{Fe}_{16}\text{O}_{32}$
55	-10.51	$\text{Mg}_{9.87}\text{Fe}_{19.74}\text{O}_{32.00}$	4.265	$\text{Mg}_{16.0}\text{Fe}_{16.0}\text{O}_{32.0}$	62%	$\text{Fe}_8\text{Fe}_{16}\text{O}_{32}$
50	-11.71	$\text{Mg}_{10.23}\text{Fe}_{20.46}\text{O}_{32.00}$	4.276	$\text{Mg}_{12.2}\text{Fe}_{19.8}\text{O}_{32.0}$	84%	$\text{Fe}_8\text{Fe}_{16}\text{O}_{32}$
44	-12.74	$\text{Mg}_{10.47}\text{Fe}_{20.94}\text{O}_{32.00}$	4.283	$\text{Mg}_{9.4}\text{Fe}_{22.6}\text{O}_{32.0}$	100%	-

From these results it appears that the progressive replacement of magnesium ions in the spinel by ferrous ions is substantially complete when approximately half of the ferric iron originally present has been reduced to the ferrous state. This occurs in the oxygen pressure range $\log P_{O_2}$ -10.07 to -10.20. This conclusion is borne out by the results for the system $MgO + 1.192Fe_2O_3$, in which the substantially complete replacement of the magnesium ions in the spinel appears to take place in the oxygen pressure range $\log P_{O_2}$ -9.78 to -10.05.

Magnesium ferrite and magnetite, $Fe_8Fe_{16}O_{32}$, both have the inversed spinel structure, which has been discussed thoroughly in the Introduction. In this structure the 8 bivalent cations occupy 8 of the 16 available octahedral spaces and the 16 trivalent cations are divided equally between the remaining 8 available octahedral spaces and the 8 available tetrahedral spaces, in a unit cell of 32 oxygen ions. From this it appears that during the reduction of magnesium ferrite, the octahedral spaces of the mixed spinel $(Mg,Fe)_8Fe_{16}O_{32}$ contain ferric ions, ferrous ions and magnesium ions distributed at random. When substantially all the magnesium ions are present in the mixed oxide phase, the spinel is effectively magnetite, in which the octahedral spaces contain ferric and ferrous ions distributed at random; the tetrahedral spaces containing only ferric ions.

As the oxygen pressure decreases, the proportion of the spinel phase present also decreases. When all the iron has been reduced to the ferrous state, there is no spinel phase and the mixed oxide phase has the theoretical composition $\text{MgO} + 2\text{FeO}$, or $\text{Mg}_{10.67}\text{Fe}_{21.33}\text{O}_{32.00}$, in the case of the stoichiometric ferrite and $\text{MgO} + 2.384\text{FeO}$, or $\text{Mg}_{9.45}\text{Fe}_{22.54}\text{O}_{32.00}$, in the case of the system $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$. This occurs in both cases at the oxygen pressure $\log P_{\text{O}_2}$ -12.65 to -12.75. The spinel phase will actually disappear before this stage owing to the slight solubility of this phase in the mixed oxide. By analogy with oxygen-rich FeO , the mixed oxide phase then consists of a substantially complete oxygen lattice, but an incomplete cation lattice, the electrostatic balance being maintained by the presence of the ferric ions, i.e., the mixed oxide contains unbalanced Schottky defects.

The results obtained show that the ferrite of composition $\text{MgO} + 1.192\text{Fe}_2\text{O}_3$ is initially reduced to the two phase state at a higher oxygen pressure than the stoichiometric ferrite. At the oxygen pressure at which reduction first occurs in the iron-rich material, the pure spinel is still the most stable form for the stoichiometric ferrite, as the limiting concentration of defects has not been reached, thus the latter material is not reduced. But, at this oxygen pressure in the case of the iron-rich material, the

solid solution of excess rhombic Fe_2O_3 in the cubic MgFe_2O_4 becomes less stable than the mixed oxide - mixed spinel configuration, in which the excess iron is easily accommodated in the ferrous state. Thus reduction of the iron-rich ferrite occurs at a higher oxygen pressure than reduction of the stoichiometric ferrite.

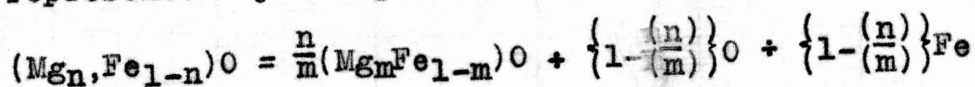
On the other hand, the oxygen pressure at which all the iron is reduced to the ferrous state is the same, within practical limits, for the two compositions examined. This arises from the fact that before this stage the phase containing the ferric iron is, in both cases, $\text{Fe}_8\text{Fe}_{16}\text{O}_{32}$.

Phase Region C.

In this region, as in Phase Region B, there are two coexisting solid phases, which are shown by the X-ray powder patterns of the samples to be the mixed oxide $(\text{Mg,Fe})\text{O}$ and metallic iron.

With decreasing oxygen pressure, oxygen is abstracted from the mixed oxide existing at the end of Phase Region B, the electrostatic balance being maintained by the conversion of ferrous ions to iron atoms, which are presumably accommodated interstitially. When the concentration of these Frenkel defects exceeds the limiting value, the mutual attraction between them leads to the appearance of a second phase, in this case metallic iron, as predicted by the theoretical considerations of J.S. Anderson. The proportion of the iron

present as a separate phase increases progressively with decrease in oxygen pressure, leaving the mixed oxide relatively richer in magnesium. The limit of this reduction would be reached at the composition $\text{MgO} + 2\text{Fe}$ in the case of the stoichiometric ferrite and $\text{MgO} + 2.384\text{Fe}$ in the case of the iron-rich material. The process of reduction may be represented by the general equation:-



Where, $m > n$

In the case of the stoichiometric ferrite $n = 0.333$, and in the case of the ferrite $\text{MgO}, 1.192\text{Fe}_2\text{O}_3$, $n = 0.295$.

The composition of the mixed oxide phase and the relative proportions of the phases may be obtained directly from the total composition determined by chemical analysis. As before, this calculation ignores the non-stoichiometry of the two phases, which, from comparison with the very similar system FeO-Fe , is assumed to be very small. The limiting compositions given by F.S. Tritton and D.J. Hanson⁷² in the FeO-Fe system are $\text{Fe}_{1.014}\text{O}_{1.000}$ for the iron-rich FeO phase at the melting point of FeO , and $\text{Fe}_{1.000}\text{O}_{0.007}$ for the oxygen-rich Fe phase at the melting point of iron.

The composition of the mixed oxide phase and the relative proportions of the phases in all the samples in Phase Region C have been calculated and are recorded in Table XVIII. The results in this table show the progressive increase in the proportion of metallic iron present and the change in composition of the mixed oxide phase, which tends to MgO , as the oxygen pressure decreases. The lattice constant of the mixed oxide phase of each sample has been measured and the theoretical composition obtained from A.H. Jay and K.W. Andrews'³³ curve of the variation in lattice constant with composition of $(\text{Mg,Fe})\text{O}$. These results also are given in Table XVIII and show fair agreement with the results obtained by chemical analysis.

TABLE XVIII

APPROXIMATE COMPOSITIONS OF SOLID PHASES IN PHASE REGION C
 IN REDUCTION OF $\text{MgO}+\text{Fe}_2\text{O}_3(\text{Mg}_8\text{Fe}_{16}\text{O}_{32})$ AND $\text{MgO}+1.192\text{Fe}_2\text{O}_3(\text{Mg}_6.99\text{Fe}_{16.67}\text{O}_{32.00})$

SAMPLE NO.	INITIAL COMPOSITION	LOG P_{O_2}	CALCULATED FINAL COMPOSITION (FROM ANALYSIS)	LATTICE CONSTANT OF MIXED OXIDE	COMPOSITION OF MIXED OXIDE FROM LATTICE CONSTANT
51	$\text{Mg}_8.00\text{Fe}_{16.00}\text{O}_{32.00}$	-12.82	$\text{Mg}_{11.4}\text{Fe}_{20.6}\text{O}_{32.0}+2.2\text{Fe}$	4.279	$\text{Mg}_{11.2}\text{Fe}_{20.8}\text{O}_{32.0}$
53	$\text{Mg}_8.00\text{Fe}_{16.00}\text{O}_{32.00}$	-12.98	$\text{Mg}_{21.5}\text{Fe}_{10.5}\text{O}_{32.0}+32.5\text{Fe}$	4.243	$\text{Mg}_{22.9}\text{Fe}_9.1\text{O}_{32.0}$
47	$\text{Mg}_8.00\text{Fe}_{16.00}\text{O}_{32.00}$	-13.40	$\text{Mg}_{26.0}\text{Fe}_6.0\text{O}_{32.0}+46.0\text{Fe}$	4.214	$\text{Mg}_{29.4}\text{Fe}_{2.6}\text{O}_{32.0}$
62	$\text{Mg}_8.00\text{Fe}_{16.00}\text{O}_{32.00}$	-13.74	$\text{Mg}_{24.8}\text{Fe}_7.2\text{O}_{32.0}+42.5\text{Fe}$	4.223	$\text{Mg}_{27.5}\text{Fe}_4.5\text{O}_{32.0}$
58	$\text{Mg}_8.00\text{Fe}_{16.00}\text{O}_{32.00}$	-14.57	$\text{Mg}_{27.2}\text{Fe}_{4.8}\text{O}_{32.0}+49.5\text{Fe}$	4.210	$\text{Mg}_{30.2}\text{Fe}_{1.8}\text{O}_{32.0}$
76	$\text{Mg}_6.99\text{Fe}_{16.67}\text{O}_{32.00}$	-12.69	$\text{Mg}_{14.1}\text{Fe}_{17.9}\text{O}_{32.0}+15.7\text{Fe}$	4.266	$\text{Mg}_{15.7}\text{Fe}_{16.3}\text{O}_{32.0}$
71	$\text{Mg}_6.99\text{Fe}_{16.67}\text{O}_{32.00}$	-12.93	$\text{Mg}_{24.5}\text{Fe}_7.5\text{O}_{32.0}+50.8\text{Fe}$	4.232	$\text{Mg}_{25.6}\text{Fe}_6.4\text{O}_{32.0}$
72	$\text{Mg}_6.99\text{Fe}_{16.67}\text{O}_{32.00}$	-13.67	$\text{Mg}_{29.2}\text{Fe}_2.8\text{O}_{32.0}+66.9\text{Fe}$	4.211	$\text{Mg}_{30.1}\text{Fe}_{1.9}\text{O}_{32.0}$

An error of $\pm 0.001\text{\AA}$ in the lattice constant of the mixed oxide corresponds to an error of $\pm 1\%$ FeO in the composition, as determined from the curve of Jay and Andrews. Such an error would give in the case of Sample No. 51 for example the range $\text{Mg}_{10.9}\text{Fe}_{20.1}\text{O}_{32.0}$ to $\text{Mg}_{11.4}\text{Fe}_{20.6}\text{O}_{32.0}$ for the composition of the mixed oxide determined from the lattice constant. If the error in the determination of iron is $\pm 0.1\%$ Fe, then the corresponding range of composition of the mixed oxide determined by analysis is $\text{Mg}_{11.2}\text{Fe}_{20.8}\text{O}_{32.0}$ to $\text{Mg}_{11.5}\text{Fe}_{20.5}\text{O}_{32.0}$.

(4) Decomposition of Magnesium Ferrite on Heating in Oxygen

The results obtained for the thermal dissociation of stoichiometric magnesium ferrite in oxygen at one atmosphere, shown in Table XV and Figure XXI, are of the same order at 1400° and 1500°C . as those of H.S. Roberts and H.E. Merwin²⁸ for decomposition in air, shown in Figure II. Roberts and Merwin detected very slight decomposition at 1100° , 1200° and 1300°C ., but decomposition was not detected at these temperatures in the present work by chemical analysis for iron. However, D.J. Bevan, J.P. Shelton and J.S. Anderson⁶⁷ have shown by electrical conductivity measurements that the dissociation of magnesium ferrite increases with decrease in oxygen pressure, giving rise to unbalanced Frenkel defects. By such

conductivity measurements it is possible to detect extremely slight departures from stoichiometry. Dissociation in the temperature range 1100° - 1500°C . is indicated also by the values obtained for the permittivity of the samples, which show a progressive rise with increase in temperature of firing. The reason for this rise in permittivity with increase in dissociation has been considered in the discussion of the magnetic results.

(5) Possible Extensions of the Work

The experimental methods which have been used here to obtain controlled atmospheres with very low effective oxygen pressures and to elucidate the phase changes in the isothermal reduction of magnesium ferrite could be applied to the investigation of other ferrites and similar systems.

A possible practical application for data of this type lies in the determination of low effective pressures in furnace atmospheres. In order to do this, the reduction isotherm of a suitable ferrite at the temperature of the furnace must be known. From the composition of a sample of ferrite or the lattice constant of the mixed oxide phase on removal from the furnace, the effective oxygen pressure of the furnace gases could then be obtained.

ACKNOWLEDGEMENTS

The research described in this Thesis has been carried out with the support of The Ministry of Supply, who purchased the more expensive equipment and provided the writer with a generous bursary. The writer is indebted to the G.P.O. Research Station, Dollis Hill, N.W.2, and especially to Dr. A. Fairweather for carrying out the magnetic measurements on the specimens.

Extensive use has been made of the X-ray equipment provided by a grant from The Royal Society to Professor H.V.A. Briscoe and Dr. A.J.E. Welch, and grateful recognition of this is given.

The writer wishes to thank the Imperial College and Professor H.V.A. Briscoe for the research accommodation and facilities provided. Professor Briscoe's kindly interest and encouragement have been very warmly appreciated. The writer is also indebted to Dr. A.J.E. Welch for his helpful supervision and invaluable assistance.

Thanks are due to Dr. K.E. Weale, of the City and Guilds College, for assistance in preparing the cylinders of mixed gases and to Professor D.M. Newitt for providing the facilities.

ACKNOWLEDGEMENTS

The writer is grateful to Mr. C.G. Garton, of The British Electrical and Allied Industries Research Association, for most helpful discussion.

The writer wishes to express his gratitude to Messrs. Goodlass Wall and Lead Industries Ltd., for their encouragement and kindly consideration during the preparation of this Thesis, and also for the typing of it.

Mr. I. David kindly took the photographs of the apparatus which are reproduced in the Thesis.

S. D. Kingman

September, 1950.

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