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Phase Equilibria in the Ferrite Region of the System Manganese-Iron-Oxygen

Abstract: An important factor in growing crystals from the melt is an understanding of the phase relationships for systems involving the necessary elements. This investigation deals with the determination and interpretation of these relationships in the ferrite region of the system Mn-Fe-O and points out the conditions necessary to grow crystals along the Mn_3O_4-Fe_3O_4 join.

The results are presented in terms of a phase diagram which shows isotherms, isobars, and fractionation curves, the data necessary to predict the exact crystallization path of compositions which fall in the ferrite region.

Several crystallization paths are discussed and their relationship to crystal growth pointed out. Liquids falling on the Mn-Fe side of the Mn_3O_4-Fe_3O_4 join are deficient in oxygen and on cooling will precipitate a lower oxide phase in addition to a stoichiometric ferrite. On the other hand, ferrite crystals separating from liquids whose compositions fall on the oxygen side of the join can have excess oxygen (cation vacancies).

Introduction

Well-defined single crystals of the double-oxide ferrites of the type MO-Fe_2O_3 (where M signifies a single divalent cation) are valuable for fundamental research on magnetic interactions in solids. The basic information obtained from their study is of importance in developing and improving computer components. Although single crystals themselves are not particularly suited for computer use, considerable effort has been devoted to their preparation for basic research.

By using the phase diagram for the system iron-oxygen[1,2] as a guide, Smiltens[3] had shown that good crystals of Fe_3O_4 (magnetite) could be grown from the melt. Since Fe_3O_4 is essentially a double-oxide ferrite, it was felt that this same method could be used to grow crystals of other ferrites. Before this can be done, however, it is important that one know the phase relationships at liquidus temperatures for the systems containing the elements of the desired crystal. Since this information was not available for other double-oxide ferrite systems, a program was initiated to obtain the phase equilibria data necessary for the growth of good crystals.

Because the manganese ferrites are of interest from both a theoretical and a practical viewpoint, the ferrite region of the manganese-iron-oxygen system was chosen to be investigated first. This paper describes the results of a phase-equilibria investigation at liquidus temperatures in this system.

• *Experimental procedure*

Homogeneous mixtures with various concentrations of manganese and iron were made up by mixing reagent grade Fe_2O_3 and MnO_2 under alcohol in an agate mortar. Each mixture was fired twice in air, first at 1000°C for 24 hours and, after regrinding, at 1500°C for 20 hours. These mixtures were then ground to about 60 mesh and used as starting materials for the quenching experiments.

A modified platinum-wound Baker furnace was used for quenching. A gas-tight alumina tube, on which was wound a 75Pt - 25Rh booster winding, was inserted vertically inside the heating area. This tube was sealed at both ends by water-cooled brass caps through which the sample could be raised or lowered.[4] The desired gas was introduced into the furnace through the bottom cap and escaped at the top into a flask containing H_2SO_4. The oxygen pressure ranged from 1/10 to 1 atmosphere. Runs at 1 atm were made by passing tank oxygen directly through the furnace and runs at 1/5 atm (air) were made by passing dry air through the furnace. Lower and intermediate oxygen pressures were obtained by mixing oxygen and nitrogen. The rate of flow of each gas was measured by means of a calibrated flow meter. The flow rate through the furnace was approximately 150 cc/min.

Temperatures were measured with Pt - Pt 10 Rh thermocouples calibrated against a standard NBS couple. Furnace temperatures were controlled automatically and determined to an accuracy of about ±4°C at temperatures above 1550°C.

The standard quenching technique[5] was modified slightly to permit its use under controlled variable atmospheric conditions. The homogeneous mixtures with a known Mn/Fe ratio were contained in platinum envelopes or small crucibles and held at constant temperature under chosen atmospheric conditions until equilibrium was reached between the gas and condensed phases. The mixtures were then quenched to room temperature by dropping them in water or mercury, the quenched specimens were polished, and the phases present identified with a metallographic microscope. Positive identification of the phases was obtained by means of X-ray diffraction using Fe radiation with a Norelco X-ray spectrometer.

The total iron content of the quenched samples was determined by reducing in a Jones reductor and titrating with standard potassium permanganate solution. Total manganese content was obtained colorimetrically. If it is assumed that the manganese is present as Mn II, ferrous iron can also be determined by titrating with permanganate. This assumption was applied only to compositions richer in iron than $MnFe_2$ and the FeO/Fe_2O_3 ratio was determined only on these compositions. For samples on which ferrous iron was determined, care was taken to prevent oxidation as they were put into solution.

Results and discussion

- *The ferrite region as shown on a triangular plot*

The manganese ferrite region can be most easily shown in terms of the triangular plot illustrated in Fig. 1. It is a compositional plot of the system Mn-Fe-O on a weight percent basis and shows the composition of the compounds existing in the binary systems Fe-O and Mn-O. The alloy phases in the system Mn-Fe have been omitted because they have no bearing on the present problem. The area along the join between Mn_3O_4 (hausmanite) and Fe_3O_4 (magnetite) is the area of our interest.

The fact that Mn_3O_4 is cubic above 1170°C has led some investigators[6,7] to believe a complete series of solid solutions exists between it and the cubic Fe_3O_4 at liquidus temperatures. If this were the case all phases encountered could be expressed in terms of these end members, and we could consider the Fe_3O_4-Mn_3O_4 join to be a binary system with respect to phase equilibria. However, the fact that both Fe_2O_3 and a MnO-FeO solid solution[8] have been found in this system suggests that a better representation would be in terms of the ternary system Mn-Fe-O. The validity of this representation, which will be used in the discussion that follows, was borne out by the experimental results.

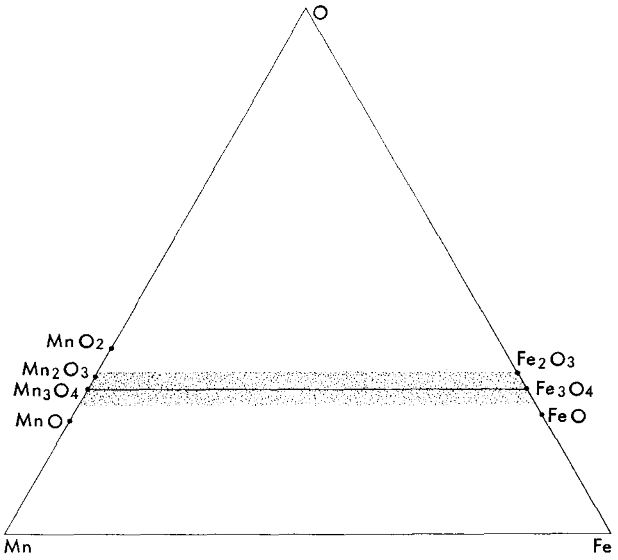

Figure 1 **Triaxial plot showing all compounds in system Mn-Fe-O. Region of interest is shaded area.**

In phase diagram work the three independent variables are temperature, pressure, and composition. The latter two are usually kept constant while the phase changes with respect to temperature are observed. In the present system, however, the situation is complicated by the fact that manganese and iron exist in variable oxidation states. Consequently the total composition of a mixture of any given Mn/Fe ratio will vary with the oxygen pressure as well as with the temperature. In order to represent the total composition variation of the condensed phases as a function of temperature and oxygen pressure on a plot like Fig. 1, it is necessary to choose a condition at which only one phase is present. The obvious choice is the condition when the temperature is the liquidus and a homogeneous liquid is the only condensed phase. Therefore in this paper, unless otherwise stated, when we speak of composition changes with respect to temperature and oxygen pressure we mean changes in liquid composition on the liquidus surface.

- *The phase-equilibrium diagram and its interpretation*

The results of selected quenching experiments are presented in terms of a partial phase diagram in Fig. 2. The area covered by this diagram includes only that small portion of the ternary in Fig. 1 which is indicated by the shaded area. This portion of the diagram was constructed by combining data of the present investigation with that published by Darken and Gurry[1,2] for the system Fe-O. The heavy dashed lines are boundary curves and are presented to show the approximate areas of the primary crystalline phases.* It should be emphasized that the exact position of these curves is not known. As will be

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*When used in this sense, "primary crystalline phase" is taken to mean the first solid phase to appear upon reaching the liquidus surface when a given composition is cooled from above the liquidus temperature under equilibrium conditions.

evident later, an accurate determination of the curve bounding the oxygen-rich side of the spinel area would involve working at high oxygen pressures at liquidus temperatures. Hay, Howat and White[8] have shown that at liquidus temperatures in the binary system MnO-FeO,* either MnO or FeO solid solution is in equilibrium with liquid. By combining their data with that obtained in the present investigation and that of Darken and Gurry,[1,2] a reasonably accurate curve can be drawn between the spinel and MnO-FeO solid solution areas.

Unfortunately, few data are available relating the composition of manganese oxides to the partial pressure of oxygen at liquidus temperatures. The melting temperature of 1565°C for Mn_3O_4, given by Wartenburg and Reusch,[9] is in agreement with the results obtained in this investigation for the melting point of manganese oxide in air. The composition of this oxide, however, corresponded to a formula of $Mn_3O_{3.8}$.

Having established where a primary crystalline phase is in equilibrium with liquid on the liquidus surface, we are in a position to consider the equilibrium cooling of a composition to below the liquidus temperature. To do this, three other relationships must be known: (a) relationship between temperature and liquid composition, (b) relationship between oxygen pressure and liquid composition, and (c) relationship between composition of the crystalline phases and the liquid composition with which it is in equilibrium. First, the temperature-liquid composition relationship is given by the isotherms. These are shown separately in Fig. 3a and by the light solid lines of Fig. 2. They were obtained by heating mixtures with known Mn/Fe ratios to successively higher temperatures, in a known atmosphere, until they were completely liquid. They were then quenched and their composition determined by chemical analysis. Secondly, the relationship between oxygen pressure and liquid composition is given by the isobars. These are shown separately in Fig. 3b and in Fig. 2 as the three heavy solid lines and represent oxygen pressures of 1/10, 1/5, and 1 atm respectively. They were determined in the same manner as the isotherms. Two schemes were used to determine the position of the isotherms and isobars on the compositional plot shown in Figs. 2 and 3. The first was to plot the total iron and manganese as determined by chemical analysis. In the other, the FeO/Fe_2O_3 ratio was determined and plotted in terms of the system $MnO-FeO-Fe_2O_3$. As previously stated these latter determinations were carried out only on compositions which were assumed to contain all the manganese as Mn II.* Although the second scheme was more precise it was limited to compositions richer in iron than Mn_1Fe_2. Thus, both the isobars and the isotherms covering compositions containing less iron than Mn_1Fe_2 (compositions to the left of the iso-Mn-Fe line, a line whose significance will be pointed out later) are only approximately determined. Finally, the relationship of compositions of liquid and crystalline phases in equilibrium involves the fractionation curves† shown as the light dashed lines in Fig. 2 and separately in Fig. 3c.

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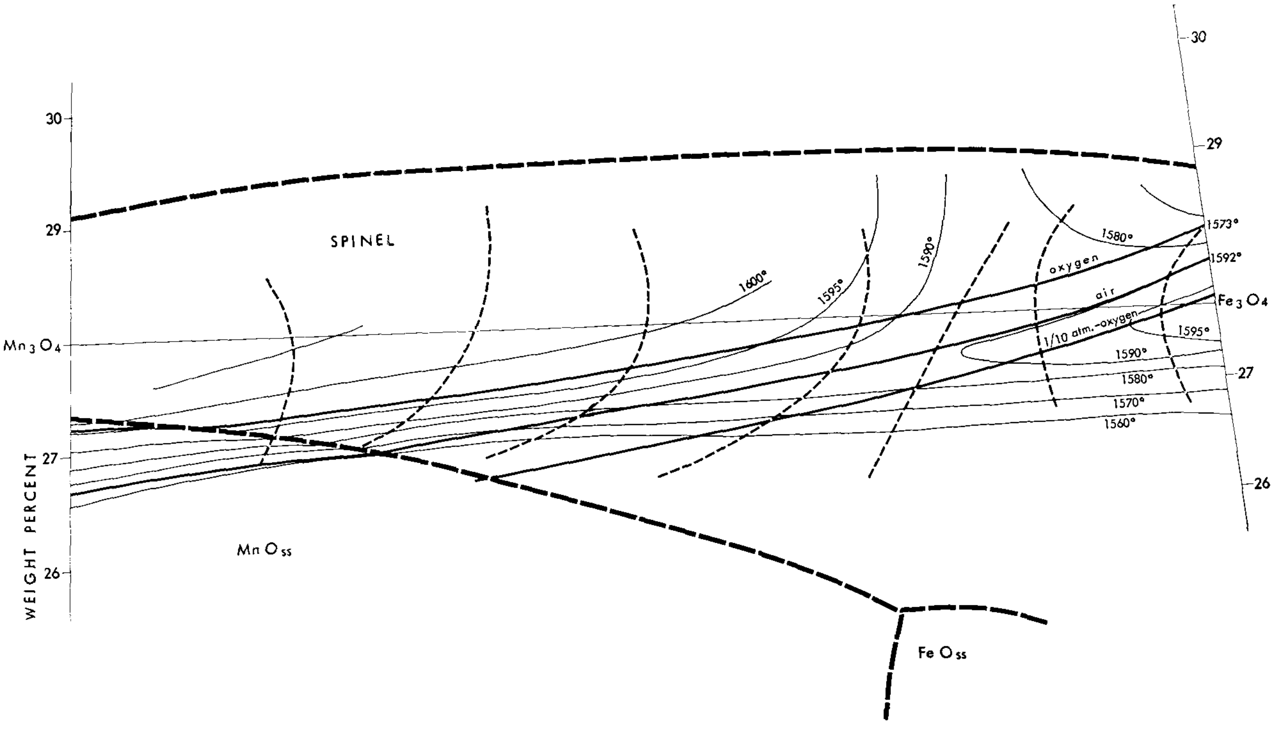
*This system can be considered binary if the incongruent melting nature of FeO is neglected.

*Should subsequent measurements of conductivity and magnetic moment show that some of the manganese is present in a higher oxidation state than 2, the position of the curves would be altered slightly.

†Fractionation curves are constructed from straight lines which join the composition of a liquid with the composition of the solid with which it is in equilibrium (conjugation lines). The conjugation lines are tangents to the fractionation curve.

Figure 2 **Phase diagram for the ferrite region of the Mn-Fe-O system.**



In order to predict the true crystallization paths of compositions in the spinel field it is necessary that the exact position of the fractionation curves be accurately known. This investigation was not primarily concerned with precisely defining crystallization paths, but rather with determining in a broader sense the feasibility of obtaining single-phase crystals. For this reason the rather laborious task of determining the relationship of compositions of liquid and crystalline phases in equilibrium throughout the whole spinel region was not attempted. However, the curves shown in Fig. 2 were determined in such a manner that they do represent, to a good approximation, this true relationship.

The method used was to heat coarsely crushed single crystals of known Mn/Fe ratio in a small-diameter platinum crucible at the desired temperature and oxygen pressure until liquid and solid were in equilibrium. The mixture was then rapidly quenched and the primary crystalline phase was mechanically separated from the fine-grained matrix and each chemically analyzed. Analysis of three different compositions, treated in this manner, indicated the fractionation curves to be as shown in Fig. 2. There is an uncertainty factor involved in this method for, even with the most rapid quenches, there was considerable grain growth of the spinel phase from the liquid, which made it difficult to pick out the primary crystalline phase. Thus a perfect separation was highly unlikely, especially for those compositions in which two crystalline phases were in equilibrium with liquid.

• *Paths of crystallization*

The preceding information should enable us to predict the approximate crystallization path for any composition which falls in the spinel area. It should be pointed out that the phase diagram in Fig. 2 can be used to show the equilibrium crystallization under two different conditions. They are: (a) constant total composition of the condensed phases, and (b) constant total oxygen pressure. The first condition involves mostly principles used in fully condensed systems, which are described in detail elsewhere.[10, 11] However, the oxygen pressure would have to be changed continuously with temperature during crystallization in order to maintain equilibrium among the phases while the total composition of the condensed phases remained constant. This seems to be impractical, for it is very difficult to achieve experimentally.

The second method of crystallization is to keep the oxygen pressure constant while lowering the temperature.[4] This procedure is the one actually used in the growth of our ferrite crystals. It should be emphasized that the actual growth of the crystal is completed when all liquid has disappeared and that this paper is concerned with only this aspect of crystal growth. However, in order to cool the crystal from just below the solidus to room temperature without altering its oxygen content, it is necessary to change the oxygen pressure as a function of temperature.

Since the liquid composition is determined by the Mn/Fe ratio, the temperature, and the oxygen pressure, it is obvious that during crystallization, at constant oxygen pressure, the liquid composition must follow the isobars along the liquidus surface. Thus the isobars at the same time become the curves of equilibrium crystallization. This relationship holds regardless of the temperature and the composition of the crystalline phase separating out. When the isobar intersects a boundary curve, the crystalline phase which had been in equilibrium with liquid is dissolved and a new crystalline phase is formed unless the point of intersection is a temperature minimum on the liquidus surface for that particular isobar. In the latter case the liquid will disappear when the boundary is reached.

The discussion of an actual crystallization path of a given mixture may be simplified by first noting the significance of lines of constant Mn/Fe ratio. These are straight lines drawn from the oxygen corner of the triangle to meet the Mn-Fe join. Each such line specifies a composition of a definite Mn/Fe ratio. Its usefulness lies in the fact that, for a composition of a given Mn/Fe ratio, the total composition of the condensed phase is always represented by a point on this line regardless of any changes in temperature and oxygen pressure. Thus the only change in the total composition of the condensed phases would be an addition or subtraction of oxygen.

• *Compositions whose liquid is deficient in oxygen*

An actual path of crystallization is discussed with reference to Fig. 4. The data pertinent to the crystallization of the compositions under discussion are taken from

Figure 3 **(Opposite)**
Liquid composition as related to temperature, oxygen pressure and crystalline phase:

a) *Isotherms showing relationship between liquid composition and temperature. Open circles represent results of iron determinations.*

b) *Isobars showing relationship between liquid composition and oxygen pressure. The symbols ○, × and □ represent results of iron determinations for mixtures heated in oxygen, air, and 1/10 atm of oxygen, respectively.*

c) *Fractionation curves showing relationship between liquid composition and the crystalline phase with which it is in equilibrium.*

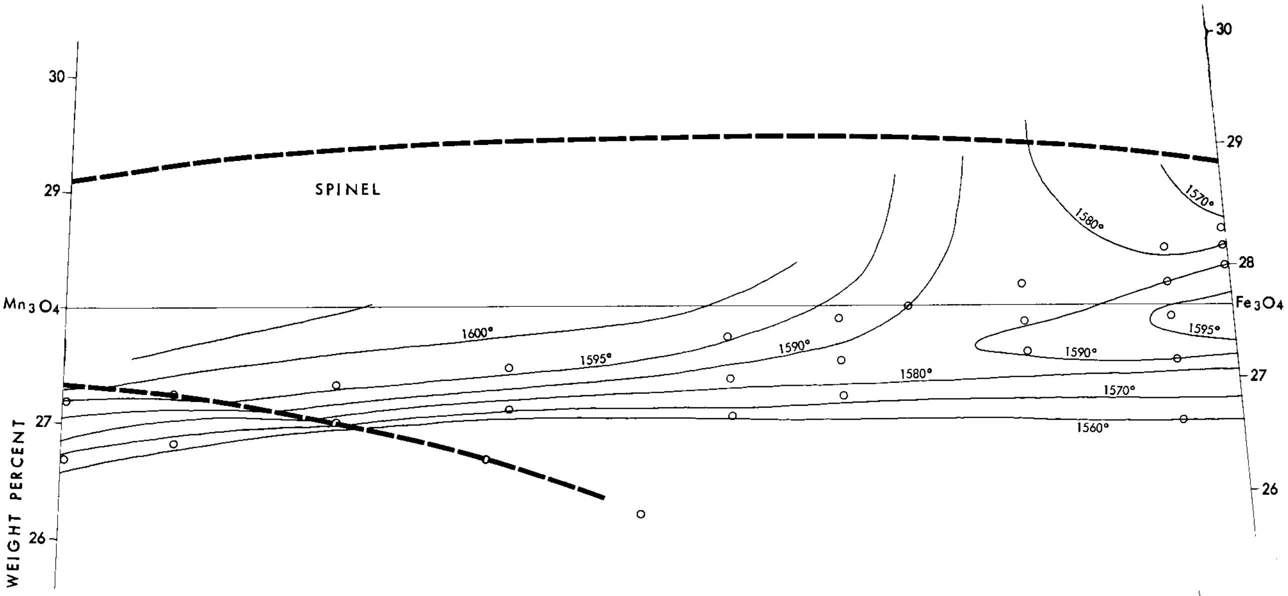


Fig. 3a

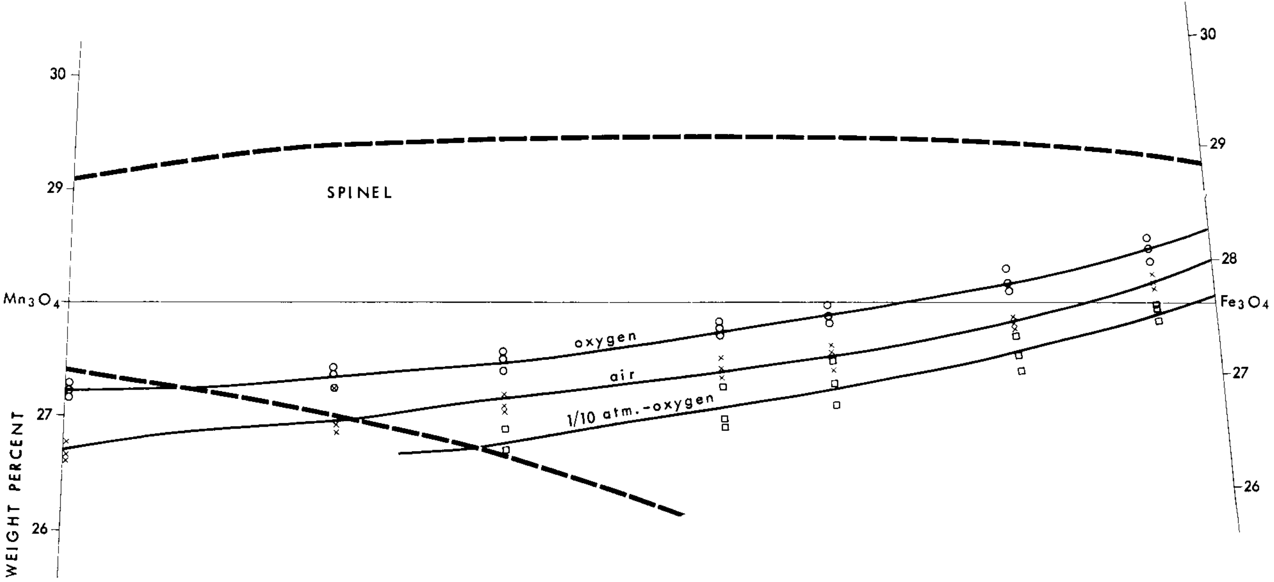


Fig. 3b

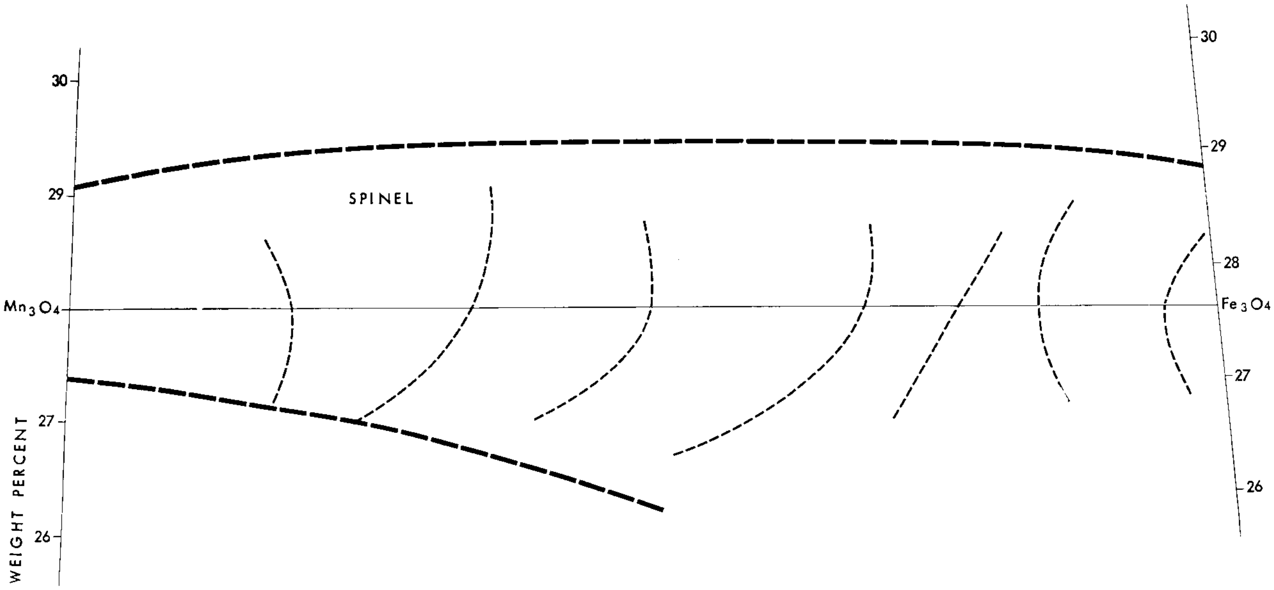


Fig. 3c

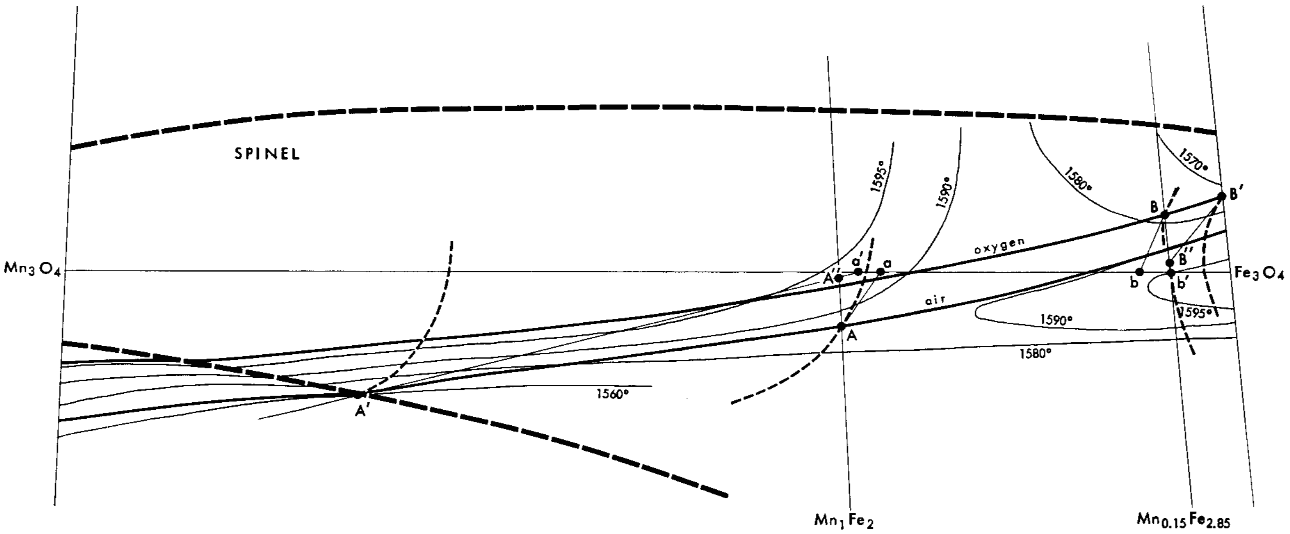


Figure 4 **Same portion of phase diagram as Fig. 2, but showing only data pertinent to crystallization paths.**

Fig. 2 and shown here. The boundary curves are the heavy dashed lines, the heavy solid lines are the isobars, the light dashed lines the fractionation curves, and the light solid lines the isotherms. The lines showing a constant Mn/Fe ratio are drawn here as light solid lines and for brevity will be called "iso-Mn-Fe lines." Let us start by cooling a mixture of composition Mn_1Fe_2 in air. It is indicated by *A*, which is the point of intersection of the Mn_1Fe_2 iso-Mn-Fe line and the air isobar. This point lies between the 1580° and the 1590°C isotherms. The mixture is therefore completely liquid above about 1587°C. When the temperature drops to 1587°, spinel crystals start separating from the liquid. The composition of these first crystals to separate is obtained by drawing a tangent to the fractionation curve which passes through point *A*. Since there was no evidence for spinel solid solution containing excess metal ions, in this case the spinel crystals which separate are stoichiometric with respect to oxygen. The oxygen-total atom ratio was 4/7. Hence the intersection of the tangent with the line joining stoichiometric Fe_3O_4 and Mn_3O_4 (point *A*) will give the composition of the spinel crystals. It is seen from this that just below 1587°C in air we have crystals of composition *a* in equilibrium with liquid of composition *A*. The first spinel crystals thus are richer in iron than the liquid, and the liquid contains less oxygen than the crystals. As the temperature drops further the liquid composition follows the air isobar until the boundary curve between spinel and MnO solid solution is reached at point *A'*. Spinel of continuously varying composition continues to be the only phase crystallizing between *A* and *A'*, and when the liquid composition reaches point *A'* the solid composition is given by *a'*, the point of intersection of the join with the tangent to the fractionation curve (conjugation line) passing through *A'*. Although the liquid composition has changed from *A* to *A'* and the solid from *a* to *a'*, the total composition remains on the iso-Mn-Fe line. At liquidus temperature it was *A;* as heat is withdrawn there is a slight over-all gain in oxygen, and the total composition will move toward the oxygen corner of the triangle along the iso-Mn-Fe line. When the liquid reaches point *A'* the total composition is *A"*. This is the point of intersection of the conjugation line and the iso-Mn-Fe line. Since *A'* is the lowest point on the liquidus surface at this particular oxygen pressure as heat is withdrawn the liquid phase disappears and MnO solid solution is formed. Thus, the final products of crystallization are a mixture of spinel of composition *a'* and MnO solid solution. During the complete crystallization process the temperature dropped from about 1587°C (point *A*) to 1563°C (point *A'*) and the total composition changed along the iso-Mn-Fe line from point *A* to *A"*.

• *Compositions whose liquid contains excess oxygen*

Since it is not uncommon to have spinels with an oxygen-total atom ratio greater than 4/7, one would expect spinels crystallized from liquids whose compositions fall on the oxygen side of the join to be deficient in metal ions. Let us now consider such a mixture whose liquid composition does fall on the oxygen side of the Mn_3O_4-Fe_3O_4 join. Point *B* represents a composition of $Mn_{.15}Fe_{2.85}$ in oxygen (the intersection of the $Mn_{.15}Fe_{2.85}$ line and the oxygen isobar). Above the liquidus we have a homogeneous liquid, and at 1578°, as heat is withdrawn, spinel of composition *b* starts to separate. The liquid composition which was *B* at 1578°C now moves along the oxygen isobar on the liquidus surface in the direction of decreasing temperature to *B'*. At a temperature of 1573°C, point *B'*, all liquid disappears and we end up with a single-phase spinel. Since the final product of crystallization is single-phase spinel, its composition will be on the Mn_3O_4-Fe_3O_4 join at point *b'* if no solid solution exists between spinel and oxygen. However, the spinel crystals formed from liquids containing an excess of oxygen have oxygen in solid solution.* This means that the exact composition will fall on the oxygen side of the join.

In this particular case, where spinel is the only phase present, its composition is the same as the total composition, and that is given by the point of intersection of the lowest temperature conjugation line and the iso-Mn-Fe line, point B''. Thus, as mixture B is cooled in pure oxygen from 1578° to 1573°C, the liquid composition changes from B to B' and the total composition from B to about B'' which, because it is single phase, is also the final spinel composition.

Summary

By way of summarizing the discussion of the crystallization paths, the point which should be emphasized is whether the spinel crystals are separating from a liquid containing a deficiency or an excess of oxygen. The first case discussed, where the liquid composition fell on the Mn-Fe side of the Mn_3O_4-Fe_3O_4 join, was an example of the former. Here the liquid did not contain sufficient oxygen to completely crystallize stoichiometric spinel and it was necessary that a lower oxygen-containing phase be formed; in this case the phase was an MnO-FeO solid solution. On the other hand, spinel crystals separating from liquids containing more oxygen than necessary to crystallize stoichiometric spinel, i.e., liquids whose composition falls on the oxygen side of the join, will have an excess of oxygen (cation vacancies). Should this oxygen content of the liquid be more than is necessary for the formation of a spinel of maximum oxygen content, a new phase richer in oxygen will form. This will be a sesquioxide phase (M_2O_3). Therefore, it is reasonable to expect that any liquid in the spinel field whose composition is on the oxygen side of the join will crystallize out spinels containing excess oxygen. But the highest oxygen pressure used in this study was one atmosphere, and since its isobar crosses the join at a composition of about $Mn_{.5}Fe_{2.5}O_4$, only oxygen-rich liquids can be formed for mixtures containing more iron than this. Thus, to form any liquid richer in manganese than $Mn_{.5}$ above the Mn_3O_4-Fe_3O_4 join would require oxygen pressures higher than one atmosphere. It is evident, therefore, that as the manganese content increases, a corresponding increase in the oxygen pressure is necessary to maintain a liquid of constant oxygen content. Finally, it should be pointed out that although the two crystallization paths just discussed are somewhat representative, it must not be concluded that similar paths would be followed by all other mixtures in the system. They were presented, rather, to show how the phase diagram indicates the relationships between the temperature and liquid composition, the oxygen pressure and the liquid composition, and the composition of the crystalline phases and the liquid composition, and also how this information can be used to predict any crystallization path. Such information is invaluable to those concerned with growing single crystals.

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*As indicated by chemical analysis and X-ray measurements of lattice parameters.