[CONTRIBUTION FROM THE LABORATORY FOR INSULATION RESEARCH, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Investigation of the Ferrite Region of the Phase Diagram Fe–Co–O[1]

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The cobalto-magnetite phase at 1200°, in equilibrium with a mixture of 98.13 vol. % CO_2 and 1.87 vol. % CO, is stable from $x = 0$ to 55.8, where x indicates the number of atoms of cobalt substituted for iron according to $Co_xFe_{300-x}O_{400}$. In pure oxygen the stability interval reaches from $x = 92.8$ to >120. At 1400°, in a mixture of 98.93 vol. % CO_2 and 1.07 vol. % O_2, the stability interval extends from $x = 0$ to 94.5; in pure oxygen the lower stability limit was not determined (presumably it lies near $x \simeq 70$); the upper limit for x is 113.5. The cobalto-magnetite field in the vicinity of $CoFe_2O_4$ has no width. Cobalt does not substitute for iron in the hematite phase (1200°). With x initially 100, the melt at 1626°, in oxygen, has an atomic fraction of oxygen 0.5611, which is considerably less than that required for the composition $CoFe_2O_4$.

Fundamental research on the ferromagnetic and electric properties of the ferrites, as proceeding in the Laboratory for Insulation Research, requires well-defined single crystals of these materials. After magnetite single crystals had been grown from the melt[3] and investigated over a wide temperature range,[4] a next logical step was obviously to modify this base material by cation substitution. Two of the most interesting features of Fe_3O_4 are its magnetic isotropy point at $-143°$ and an electronic order-disorder transition near $-160°$. Bickford and coworkers[5] found that the substitution of iron by cobalt shifts the isotropy point with extreme rapidity to higher temperatures. It was therefore decided to investigate the ferrite region of the phase diagram Fe–Co–O as a necessary prerequisite for the growing of cobalt-substituted ferrite single crystals.

Robin and Bénard[6] have constructed a phase diagram based on X-ray diffraction data of a series of mixed iron and cobalt oxide samples heated at temperatures up to 1000°. Such a method is not satisfactory for our purposes as it does not give sufficient information about the composition of a phase (the ratio of iron to cobalt and the crystal structure type is, in the general case, not enough). A similar objection applies to the vacuum-furnace technique used by Iida.[7] At the outset, we decided that the orthodox triangular-diagram method must be used.

Experimental

1. **Preparation of the Starting Materials.**—Remy[8] mentions that if iron is dissolved in dilute nitric acid at about 0°, the resulting iron nitrate will be mainly divalent. Clean iron rods[9] were dissolved in cold 0.4 N acid; this required about 8 days. The solution was passed through a fritted-glass filter, and the weight of the small residue was subtracted from that of the rods.

Cobalt "sponge"[10] was dissolved in 1-to-5 nitric acid and the solution was also filtered through fritted glass.

Iron–cobalt hydroxide was precipitated as follows. It is known that trivalent iron hydroxide precipitates at pH 2.2, divalent at 7, and cobalt at 8. Since the pH values for divalent iron and cobalt lie close together, a hydroxide mixture precipitated from these salts should be homogeneous. The precipitant,[11] diethylamine,[12] was distilled into warm, continuously stirred, cobalt–iron nitrate solution.[13] The precipitate was filtered, dried and then decomposed to the oxides at slowly increasing temperatures (105° after 12 hr., 140° after 24 hr.). This slow temperature rise is necessary since the residual diethylammonium nitrate starts to decompose at 120°, and hydroxide may be lost if too rapidly heated.

2. **Preparation of the Quenched Samples.**—About 0.6 g. of the oxides formed from the mixed hydroxides by drying and heating was placed in a small Pt crucible. The crucible was suspended in a 2 in. i.d., tubular globar furnace, the distance from top to the thermal center being 16 in. The temperature was controlled by a Leeds and Northrup Speedomax to ±0.6°. The thermocouples were calibrated against the melting points of gold (1063°) and palladium (1555°).

The gas mixtures in which the samples were heated were introduced through the bottom of the furnace after their volumes had been measured by capillary flowmeters. The rate of flow was about one l. per minute. The carbon dioxide and monoxide were dried and freed from SO_2 and several other impurities[14] by passing through silica gel. The small amount of O_2 present in the CO_2 was removed by means of copper at 500°. The oxygen used for low-oxygen mixtures was medical grade in order to avoid obstruction of the fine capillary in the low-rate flowmeter by particles from commercial oxygen. For high-oxygen mixtures, however, the commercial grade was used. The samples were usually heated 48 hr. When a sample was to be quenched, the crucible containing the sample was dropped into mercury.

3. **Analysis of the Quenched Samples.**—After quenching, the sample was removed from the crucible and kept for 2 hr. *in vacuo* at 180° to evaporate possibly adhering mercury. Next 0.3 g. was placed in 10 ml. deoxygenated 1-to-2 H_2SO_4 in a tube under nitrogen. After sealing, the tube was placed in an aluminum block furnace at 100° until the sample dissolved. The solution was diluted with 100 ml. of water, titrated with 0.1 N $KMnO_4$, passed through a Jones reductor, and again titrated.

The atomic fraction of oxygen of the sample, O, was calculated from formula (1) (Appendix)

$$O = \frac{600 + (300 - x)(1 - \rho)}{1200 + (300 - x)(1 - \rho)} \qquad (1)$$

where

$$\rho = \frac{\text{ml. KMnO}_4\text{ of 1st titration}}{\text{ml. KMnO}_4\text{ of 2nd titration}}$$

If the sample was expected to contain some of the cobalt

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[2] Air Force Cambridge Research Center, Bedford, Mass.

[3] J. Smiltens, *J. Chem. Phys.*, **20**, 990 (1952).

[4] L. R. Bickford, Jr., *Phys. Rev.*, **78**, 449 (1950); J. K. Galt, *ibid.*, **85**, 664 (1952); B. A. Calhoun, *ibid.*, **94**, 1577 (1954); D. O. Smith, *ibid.*, **102**, 959 (1956).

[5] L. R. Bickford, Jr., J. Pappis and J. L. Stull, *ibid.*, **99**, 1210 (1955).

[6] J. Robin and J. Bénard, *Compt. rend.*, **234**, 734 (1952).

[7] Shûichi Iida, *J. Phys. Soc. Japan*, **11**, 846 (1956).

[8] H. Remy, "Lehrbuch der anorganischen Chemie," Akad. Verlagsges., Leipzig, 1949–1950, I, p. 522; II, p. 272.

[9] Westinghouse Electric Corporation, East Pittsburgh, Pa., "Puron." The major non-volatile impurities according to manufacturer: Ni, *ca.* 0.0015%; Co, *ca.* 0.001%; Cu, *ca.* 0.0008%; P, < 0.001%; Si, <0.001%.

[10] Johnson, Matthey and Co., London, England; Matthey "Spectroscopically Standardized," Fe <0.0005%.

[11] The insolubility of cobalt hydroxide in diethylamine was found independently, but it was learned later that the non-reactivity of cobalt salts with diethylamine had already been observed by F. Ephraim and R. Linn, *Ber.*, **46**, 3742 (1913).

[12] Eastman Kodak Co., Cat. No. 92, b.p. 55–56°.

[13] Prepared by mixing cobalt and iron nitrates to give the desired x in the formula $Co_xFe_{300-x}O_{400}$.

[14] "Chemical Engineers' Handbook," McGraw-Hill Book Co., New York, N. Y., 1950, p. 911.

in a higher state of oxidation than divalent, a weighed amount of Mohr's salt,[15] $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, usually 0.1 g. or less, was added to the sample before dissolving. This is oxidized by the cobalt and, when the ml. $KMnO_4$ which the Mohr's salt alone would have required is subtracted from the ml. $KMnO_4$ used in these first and second titrations, a negative ρ results. It can be shown (Appendix) that eq. 1 is also valid for such cases.

The X-ray diffraction analysis used a Norelco Geiger counter diffractometer with $FeK\alpha$ radiation. All peaks appearing on the diffractometer record were indexed as to the corresponding structure. Since the lattice constants found relate only to quenched samples, they have no general significance and are not listed here.

The Triangular Diagram of the Ferrite Region

The framework of the triangular diagram Fe–Co–O is shown in Fig. 1. The side Fe–Co was divided into 300 parts, representing 300 atoms of Fe. A line, $x = 100$, was drawn from the opposite apex O to the point on the line Fe–Co, which represents the substitution of 100 atoms Fe by Co. According to the theory of the triangular diagram, this line is the locus of all compositions with the atomic ratio of Fe to Co of $(300 - x):x$, when $x = 100$. An enlarged portion of the $FeO–CoO–Co_2O_3–Fe_2O_3$ trapezoid with a set of x = constant lines is shown in Fig. 2. The composition point, for example, of a quenched sample with $x = 89.98$ and $O = 0.5542$, is the intersection of the x = constant = 89.98 line with a vertical line at $O = 0.5542$.

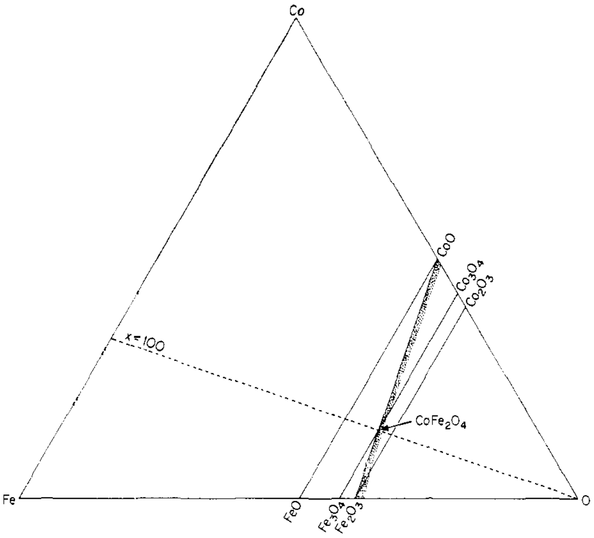

Fig. 1.—The framework of a ternary diagram Fe–Co–O, drawn in terms of atomic fractions. The line Fe_2O_3–CoO is shaded on the right-hand side to indicate that in this region some of the cobalt must be in a state of oxidation higher than divalent.

The O values for the selected isotherms are given in Table I. The 1200° (98.13 vol. % CO_2 plus 1.87 vol. % CO) isotherm was chosen for the first study because this gas mixture was used in an earlier work[3] for cooling single crystals of magnetite from 1200 to 1100°. We wished to know to what extent the addition of cobalt produces a single cobalto-magnetite[17] phase in this gas mixture. With

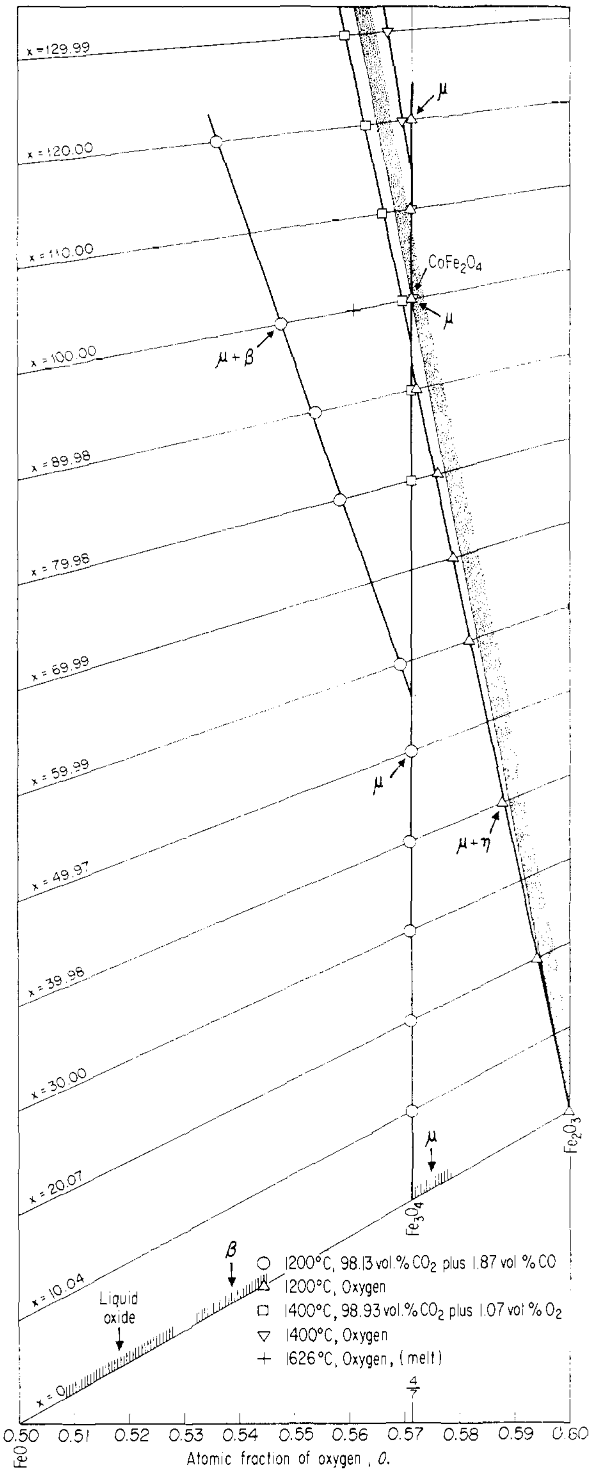

Fig. 2.—The $FeO–Fe_2O_3$ half of the $FeO–CoO–Co_2O_3–Fe_2O_3$ trapezoid showing the isotherms (these isotherms are also isobars); μ is cobalto-magnetite (spinel-type structure); β, cobalto-wüstite (rock-salt-type structure); η, hematite (corundum-type structure). The binary fields, at 1400°, on the line $x = 0$ are taken from the work of Darken and Gurry.[16]

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[15] Mallinckrodt, ferric iron, 0.01%.

[16] L. S. Darken and R. W. Gurry, THIS JOURNAL, **68**, 798 (1946).

[17] The term "cobalto-magnetite" denotes a ternary extension, by cobalt, of the binary magnetite field. Such nomenclature is established in the literature. *Cf.* N. I. Bowen and J. F. Schairer, *Am. J. Sci.*, [5] **29**, 151 (1935).

x = 10.04, 20.07, 30.00, 39.98 and 49.97, we obtain quenched samples consisting of a single cobalto-magnetite phase μ (spinel-type structure) with the atomic fraction O of oxygen between 0.5710 and 0.5714. With x = 59.99, 79.98, 89.98, 100.00, and 120.00, the quenched samples consist of two phases: cobalto-magnetite and cobalto-wüstite β (rock-salt-type structure), and the O values decrease from 0.5693 to 0.5368. The isotherm (Fig. 2) appears to consist of two straight lines. However, the portion from x = 0 to 55.8 (one phase) is not necessarily straight. The portion from x = 55.8 to beyond 120 represents a series of mechanical mixtures of two phases in equilibrium (stoichiometric[18] cobalto-magnetite with x = 55.8 and cobalto-wüstite of a composition not here determined) and according to the theory of the triangular diagram, this part of the isotherm *must* be a straight line (a "tie"). This requirement provides an excellent criterion of the correctness of the experimental method.

TABLE I

O VALUES FOR THE SELECTED ISOTHERMS

x	1200° 98.13 vol. % CO_2 1.87 vol. % CO	1200° O_2	1400° 98.93 vol. % CO_2 1.07 vol. % O_2	1400° O_2	Melt (1626°) O_2
0	....	0.5998	....	....	....
10.04	0.5714	....	....	....	....
20.07	.5712	.5940	....	....	....
30.00	.5712	....	....	....	....
39.98	.5710	.5878	....	....	....
49.97	.5713	....	..	....	....
59.99	.5693	.5818	....	....	....
69.99	....	.5788	....	....	....
79.98	.5586	.5762	0.5713	....	....
89.98	.5542	.5724	.5713	....	....
100.00	.5480	.5714	.5697	0.5716	0.5611
110.00	....	.5712	.5660	.5713	....
120.00	.5368	.5714	.5631	.5697	....
129.99	....	....	.5593	.5670	....

The 1200° isotherm in pure oxygen (drastic oxidizing conditions) gives, up to x = 92.8, two phases: stoichiometric cobalto-magnetite μ with x = 92.8, and hematite η (corundum-type structure). With x = 92.8 to 120 and over, there is only one phase: the stoichiometric cobalto-magnetite. We notice that at this temperature the cobalto-magnetite field in the vicinity of $CoFe_2O_4$ has no width.

The part of the isotherm from x = 0 to 92.8 should be discussed as to the possible substitution of cobalt for iron in hematite. This portion of the isotherm is drawn through the Fe_2O_3 point in Fig. 2, but if there were a certain amount of substitution of iron by cobalt (MN, Fig. 3) in the hematite phase, the isotherm should run as the solid line MNP. We notice that a relatively long length MN causes only a small difference in directions NP and MP'. Since we have several experimental points, we can treat the problem by the method of least squares. It can be shown[19] that the equation of a straight line in terms of the coördinates x and O is

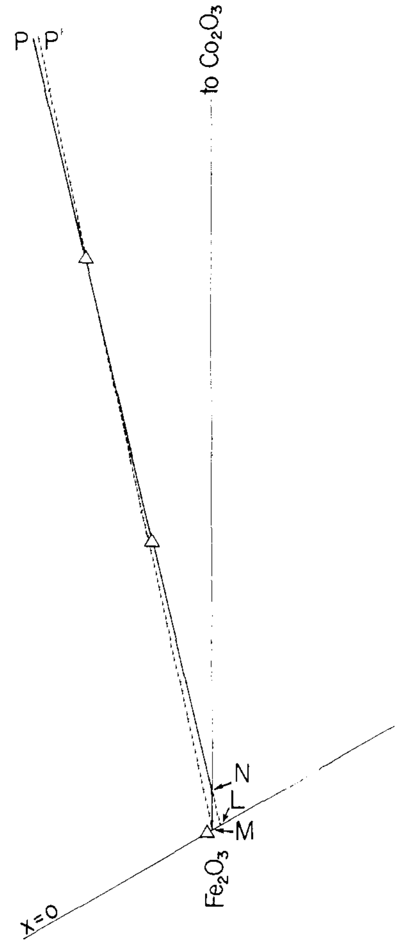

Fig. 3.—Schematic representation of the error caused by neglecting a possible, relatively small substitution NM of iron by cobalt in the hematite phase: PNM, true isotherm; P'M, erroneous isotherm.

$$O = \frac{x - B}{x - K} \tag{2}$$

where B and K are constants. The equations for calculating the most probable values of these constants are

$$\left.\begin{aligned} \sum_i x_i(1 - O_i) + K \sum_i O_i - iB &= 0 \\ \sum_i x_i(1 - O_i)O_i + K \sum_i O_i^2 - B \sum_i O_i &= 0 \end{aligned}\right\} \tag{3}$$

where i is the number of points given. In the numerical calculation the point with x = 0, O = 0.5998 was excluded, as this point might actually belong to the part MN of the isotherm; and the point with coördinates x = 79.98, O = 0.5762 was discarded because of too great a deviation. The following values for the constants were found: B = 846.14; K = 1411.08. With x = 0, eq. 2 gives O = B/K, which upon inserting the above values of the constants B and K gives O = 0.5996. Since for composition point M the atomic fraction of oxygen is 0.6000, we get a value less than zero for the distance ML. Hence, it can be concluded that cobalt does not substitute for iron in hematite at 1200°.

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[18] "Stoichiometric" in this connection means a composition corresponding to Fe_3O_4 with some Fe (not necessarily divalent) substituted by Co, but the O = 4/7.

[19] J. Smiltens, Tech. Rep. 115, Contracts Nonr-1841(10) and AF 30(635)-2872, Lab. Insulation Res., Mass. Inst. Tech., Jan., 1957.

The choice of the gas mixture (98.93 vol. % CO_2 plus 1.07 vol. % O_2) for one of the 1400° isotherms was based on the estimate that under these conditions the dissociation cobalto-magnetite → cobalto-wüstite will occur at an x value of about 100, *i.e.*, $CoFe_2O_4$. The actual dissociation was found to be at $x = 94.5$. The 1400° isotherm with pure oxygen again shows the result of drastic oxidation. In this case, the dissociation cobalto-magnetite → cobalto-wüstite occurs at $x = 113.5$. As only two points were available for the tie, they have been connected as though errorless; therefore, it cannot be decided with certainty whether this tie runs parallel to the Fe_2O_3–CoO line (as it may seem from Fig. 2) or is directed toward the CoO point. If this isotherm were extended further downwards, it would proceed along the Fe_3O_4–Co_3O_4 line and, perhaps, start bending very slightly away to the right. Somewhere around $x = 70$ it would become a tie terminating in the Fe_2O_3 point. The point at which the tie departs from the field isotherm would be one of the points of the right boundary of the cobalto-magnetite field at 1400°. An isotherm at 1458° with pure oxygen would have this tie running along the line of constant $x = 0$, as this is the condition of dissociation[16] in the binary system Fe–O; also the widening of the cobalto-magnetite field would be distinctly seen.

For an experiment in the *liquidus* region, about 1 g. of mixed oxides with $x = 100$ was placed in a 50-mesh platinum-gauze crucible and heated slowly (above 1400°, 6° rise per hr.) in oxygen until melted. At 1626° liquid oxide started to drip rapidly from the crucible. Since the residual amount of melt in the platinum gauze crucible was just about that needed to wet the gauze, it was assumed that the subsequent analysis of the melt would be representative. The atomic fraction of oxygen of the quenched melt was found to be 0.5611, *i.e.*, considerably less than that of the composition $CoFe_2O_4$ (0.5714).

From this, and from the behavior of the *solidus* isotherms, it can be concluded that to grow single crystals of $CoFe_2O_4$, oxygen pressures higher than one atmosphere may be necessary.

Acknowledgments.—The author is grateful to Professors Arthur R. von Hippel and George Scatchard for their guidance and support.

Appendix

Derivation of the Formula for Calculation of the Atomic Fraction of Oxygen.—First let us consider the case when ρ is positive. The sample then contains only divalent cobalt, and divalent and trivalent iron. If the total number of iron and cobalt atoms in the sample is taken as 300, then the number of divalent cobalt atoms is x; of divalent iron, $(300 - x)\rho$; and of trivalent iron, $(300 - x)(1 - \rho)$. The number of oxygen atoms combined with each kind of these metal atoms is: for divalent cobalt, x; divalent iron, $(300 - x)\rho$; and trivalent iron, $(3/2)(300 - x)(1 - \rho)$. The total number of oxygen atoms is, therefore, $300 + (1/2)(300 - x)(1 - \rho)$, which gives eq. 1 for the atomic fraction O of oxygen.

If ρ is negative because of trivalent cobalt, the number of trivalent cobalt atoms is $(-\rho)$ times the number of iron atoms of the sample. If ρ is negative because of tetravalent cobalt, then the number of tetravalent cobalt atoms is $(1/2)(-\rho)$ times the number of iron atoms. If this is due to n-valent cobalt, then the number of n-valent cobalt atoms is $[1/(n - 2)](-\rho)$ times the number of iron atoms. Therefore, in a general case and, again, taking the total number of metal atoms of the sample as 300, the number of n-valent cobalt atoms is $[1/(n - 2)](300 - x)(-\rho)$; of divalent cobalt atoms, $x - [1/(n - 2)](300 - x)(-\rho)$; and of trivalent iron atoms, $(300 - x)$.

The number of oxygen atoms combined with each kind of these metal atoms is: for n-valent cobalt, $(n/2)[1(n - 2)](300 - x)(-\rho)$; divalent cobalt, $x - [1/(n - 2)](300 - x)(-\rho)$; trivalent iron, $(3/2)(300 - x)$. The total number of oxygen atoms is, therefore, again $300 + (1/2)(300 - x)(1 - \rho)$ (n drops out on summation).

The presence of iron in a higher state of oxidation than trivalent can be formally transposed to a case of higher-valent cobalt as $Fe_2O_{3+m} + 2CoO = Fe_2O_3 + Co_2O_{2+m}$. If $x \rightarrow 0$ (pure iron oxide), then $m \rightarrow \infty$, but since n, which is $m + 2$, drops out, the formula is still valid.

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