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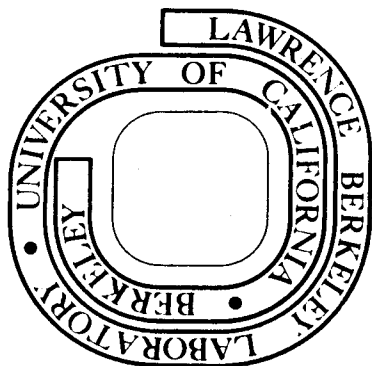
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ABSTRACT

Extensive thermogravimetric work on various spinel ferrite compositions is reported which characterizes the material loss behavior with heat treatment. Most of the work was done on the system $LiFeO_2$-$LiFe_5O_8$-Fe_2O_3, where both lithium and oxygen loss were considered. The weight loss data for other ferrites were compared and the influence of the cation distribution on the weight loss kinetics was demonstrated.

INTRODUCTION

Quantitative thermogravimetric analysis has been used by Reinjnen[1-3] to study the solid state reactions and the phase equilibria in the system $MgO-FeO-Fe_2O_3$. He gave an extensive discussion on the defect structure of ferrites and the possible equilibria that may exist in this system at high temperatures. The basic idea in all the thermogravimetric work on ferrites is that the oxygen content in the spinel at any temperature depends on the oxygen content in the ambient atmosphere. With the loss of oxygen Fe^{+3} reduces to Fe^{+2}. Likewise, oxygen may be absorbed during cooling thereby converting some of the Fe^{+2} to Fe^{+3}. A quantitative knowledge of the weight change characteristics is desired because it has a strong influence on the defect structure which, in turn, influences the sinterability and magnetic properties of the sintered ferrite.

Reinjnen in one of his papers[3] considered the reaction,

$$Fe^{+3} + 1/2\ 0^{-2} \rightleftarrows Fe^{+2} + 1/4\ 0_2(g) \qquad (1)$$
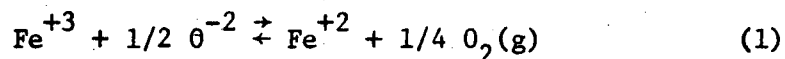
and showed that this equilibria does not represent the actual weight loss process during the heat treatment of magnesium ferrite, because at higher temperatures log(K) vs 1/T plot deviated significantly from the straight line relationship (K is the equilibrium constant for the reaction and T is the temperature in degrees Kelvin). He modified reaction 1 and suggested the following equilibria,

$$Fe^{+3} + 3/8V_c + 1/2\ 0^{-2} \rightleftarrows Fe^{+2} + 1/4\ 0_2(g) \qquad (2)$$
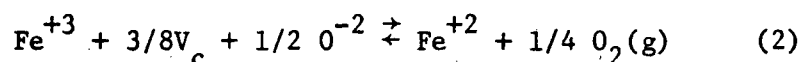
where V_c is a vacant cation site, on the assumption that the cations and vacancies have no preference for either octahedral or tetrahedral sites.[2] He also extended his discussion taking into account the detail of the spinel composition and the cation distribution, but still he found that his model was not adequate to describe all the details of the solid-oxygen equilibria in ferrites.[2] In spite of this drawback, the inherent simplicity of reaction 2 makes it extremely useful in the data analysis of the cation deficient ferrites.

The typical weight loss behavior for a Fe_2O_3 excess spinel ferrite is shown in Fig. 1 which is basically the same figure with minor changes as was shown by Reinjnen.[2] It is assumed that oxygen is the only vaporizing species in these systems. Initially two phase composition loses material to enter the single phase spinel region. Then reaction 2 continues to annihilate the excess cation vacancies so that the composition approaches the stoichiometric point (metal: oxygen = 3:4). Beyond that the composition becomes anion deficient by the continued loss of oxygen. With further increase of temperature, the weight loss increases sharply due to the reaction,

$$Fe_3O_4 \overset{\rightarrow}{\leftarrow} 3FeO + 1/2\ O_2(g) \tag{3}$$
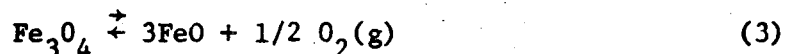
Most of the work done in this investigation is on the system $LiFeO_2-LiFe_5O_8-Fe_2O_3$, where oxygen as well as lithium loss is possible during the heat treatment. An attempt has been made to characterize the material loss behavior of the above mentioned system in relation to the starting composition. The analysis has been extended to some other

ferrites for comparison purposes.

EXPERIMENTAL PROCEDURE

(1) Powder Preparation

For the preparation of stoichiometric lithium ferrite ($LiFe_5O_8$),

suitable proportions of reagent grade Li_2CO_3 and Fe_2O_3 were mixed in a

neoprene lined ball mill for 48 h using isopropyl alcohol and teflon

balls as the mixing media. The alcohol was evaporated off and the mix-

ture was calcined at 800 C for 6 h in air. The powder was milled and

was recalcined at 800 C for 8 h in 1 atm oxygen.

$LiFeO_2$ powder was also prepared in the identical way using suitable

proportions of Li_2CO_3 and Fe_2O_3.

In order to make a series of powders with known deviation from the

stoichiometric composition, $LiFe_5O_8$ was mixed with proper proportions of

$LiFeO_2$ or Fe_2O_3 in a ball mill as described above for 24 h. Then the

mixture was calcined at 800 C for 8 h in 1 atm oxygen.

$NiFe_2O_4$ and $ZnFe_2O_4$ compositions were prepared using NiO or ZnO and

Fe_2O_3 as the starting material. The calcination temperature was 950 C

for 5 h for $NiFe_2O_4$ and 850 C for 5 h for $ZnFe_2O_4$. The calcined powder

was milled and was recalcined at 1000 C for 4 h in 1 atm oxygen.

X-ray diffraction for all of the above powders failed to detect any

undesirable second phases in any of the compositions.

(2) Thermogravimetric Analysis

The weight loss experiments were conducted in air with the weight

change recorded continuously. A platinum crucible containing the sample

in fine powder form was suspended from a platinum wire which was con-

nected to one arm of the microbalance into a kanthal wound tube furnace.

A control thermocouple was kept at the hottest part of the furnace and
the temperature was controlled by the use of a proportional controller.
The accuracy of the equipment was about +0.25 mgs which is somewhat low
compared to that claimed by Reinjnen.[1,2] Therefore, in most of the
experiments, a reasonably large quantity of powder (8gs) was used to
compensate for the low sensitivity.

In all the runs the temperature was quickly brought to 700 C and
was kept at that temperature for a sufficiently long time to reach
equilibrium. The equilibrated weight at 700 C was always assumed as the
original weight for the experiment.

(a) Constant heating rate runs. The temperature was raised at the
rate of 3 C/min to 1150 C and then the furnace was cooled to 700 C. The
weight loss was recorded continuously throughout the run. The weight
that could not be regained by cooling to 700 C has been termed as the
"irreversible weight loss".

(b) Equilibrated weight loss run. In these experiments equilibrium
was achieved at each temperature by allowing the reactions to continue
for sufficiently long time. In most of the cases the temperature was
increased in the steps of 25 C from 700 C to 1225 C.

RESULTS AND DISCUSSION

(1) Weight Loss Run at Constant Heating Rate

Weight loss in mgs/mole of powder has been plotted against tempera-
ture in Fig. 2 for various compositions which include pure $LiFeO_2$ to
20 mol% Fe_2O_3 in $LiFe_5O_8$. The data points for the 1, 3, 5 and 10 mol%
Fe_2O_3 in $LiFe_5O_8$ (which are not shown in Fig. 2) fell within the lines
due to stoichiometric and 20 mol% Fe_2O_3 in $LiFe_5O_8$ compositions. The

nature of the plots for stoichiometric and near stoichiometric powders
was identical to Fig. 1. It must be noted that while the present data
are for constant heating rate runs and equilibrium was never achieved,
Fig. 1 was drawn by Reinjnen[2] on the basis of equilibrated runs. Thus
Fig. 2 just describes the qualitative nature of the weight loss charac-
teristics and their dependence on the starting composition. The in-
creased weight loss at high temperature is most probably due to the
lithia loss rather than due to the reaction 3, because 1050 C is some-
what low for reaction 3 to occur. Increased weight loss with increasing
Fe_2O_3 content in the composition is attributed to the increased oxygen
loss. This is evident from Fig. 3 which shows that this increased loss
is almost entirely reversible.

(2) Equilibrated Weight Loss Run for the System $LiFeO_2$-$LiFe_5O_8$-Fe_2O_3

It is accepted that on heat treatment oxygen and lithium loss is
possible from lithium ferrite compositions. The amount of loss would
depend on the activity of the vaporizing species at the temperature of
the experiment. In cases where Fe_2O_3 is in solid solution with spinel
ferrites and oxygen is the only vaporizing species, reaction 2 should
describe the solid-oxygen equilibria as long as one remembers the limita-
tions of this reaction. The equilibrium constant K for the reaction 2,

$$K = \frac{a_{O_2}^{1/4} \cdot [Fe^{+2}]}{[V_c]^{3/8}} \quad (4)$$

where $[O^{-2}]$ and $[Fe^{+3}]$ concentrations have been assumed unity. On re-
arrangement,

$$a_{0_2} = \left(\frac{K \cdot [V_c]^{3/8}}{[Fe^{+2}]}\right)^4 \tag{5}$$

Thus as the cation vacancy concentration decreases or Fe^{+2} concentration increases in the single phase composition, activity of oxygen decreases sharply. As the metal:oxygen (M:O) ratio approaches 3:4, cation vacancy concentration drops to a low value. With further oxygen loss, oxygen vacancies may be created with excess cations in the interstitials. But a large deviation from the stoichiometry on the anion deficient side is not expected in the lithium ferrite system.[4] Thus activity of oxygen would reach a constant value on the single phase boundary and would maintain that through the two phase region. Figure 4 schematically shows the change of oxygen activity with the change of metal:oxygen ratio. In the same figure the expected variation of lithia activity is also shown. For simplicity it would be assumed that lithium is lost as Li_2O. In the single phase spinel composition the expected reaction associated with the lithia loss is,

$$Li^+ + 1/2 \; O^{-2} + 5/6V_o \rightleftharpoons Li_2O \; (g) \tag{6}$$
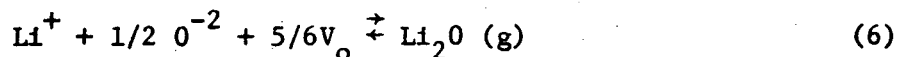
and activity of lithia should reach a low value on the cation deficient single phase boundary region, as shown in Fig. 4.

The equilibrium condition in the thermogravimetric runs in air would be determined by reaction 2, where Eq. (4) can be written as,[1]

$$K = \frac{[Fe^{+2}]}{[V_c]^{3/8}} \cdot p_{O_2}^{1/4} \tag{7}$$

where p_{O_2} is the partial pressure of oxygen in air. Since in most of the cases equilibrium was achieved, it is assumed that despite significant lithia loss from the lithium ferrite system by reaction 6, reaction 2 primarily acted as the controlling condition.

Figure 5 shows the equilibrium weight loss behavior as a function of temperature for a lithium ferrite composition with 5 mol% excess Fe_2O_3. The nature of the plot is similar to that shown in Fig. 1. As is indicated, the two phase starting composition enters the single phase region followed by increasing weight loss at higher temperatures. The irreversible weight loss for the same run is also plotted in Fig. 5. It is interesting to note that in the middle portion of the curve, which is supposedly the single phase region, the irreversible weight loss remains practically constant. It tends to indicate that lithium loss is insignificant in that region. It is also clear that the increasing weight loss at higher temperatures is at least partly due to the lithia loss as is indicated by the increased irreversible weight loss. In Fig. 6 $\log(\Delta g)$ for two lithium ferrite based compositions has been plotted against 1/T where Δg is the actual weight loss in mgs/mole of powder and T is the temperature in degrees Kelvin. For the cation deficient composition ($LiFe_5O_8$ with excess Fe_2O_3) the single phase region is characterized by the more or less straight line portion of the curve (region AB). At higher temperatures lithia loss becomes

significant and deviation from the straight line relationship occurs.
For the lithia rich composition initial weight loss is significantly
lower than that for the Fe_2O_3 rich composition. But at one point excess
lithia is lost and the composition enters the single phase region. Then
lithia and oxygen loss continues simultaneously. Figure 7 schematically
shows the compositional shift for the lithia rich (point a) and Fe_2O_3
rich (point b) starting materials and their path of entry (shown by
dotted lines with arrows) to the single phase region.

(3) Comparison of Weight Loss Behavior Amongst Various Ferrites

Oxygen loss through reaction 2 is the primary weight loss mechanism
in a cation deficient ferrite. But in the case of lithium ferrite, as
we have already seen, significant lithium loss is possible along with
the oxygen loss. So in order to compare the weight loss behavior of
lithium ferrite with that of other ferrites, it is necessary to select
the region (e.g. the spinel single phase region in Fig. 5) where lithium
loss is negligible compared to the oxygen loss. In this region it can
be assumed, like in other ferrites, that only reaction 2 determines the
weight loss. Using the simple approach used by Reinjnen,[1] at equilibrium
one can write for reaction 2,

$$\frac{\Delta g}{(\Delta g_m - \Delta g)^{3/8}} = K = A \cdot \exp(-Q/RT) \qquad (8)$$

where Δg is the actual weight loss in mgs/mole of powder, Δg_m is the
amount of oxygen to be lost per mole of powder to annihilate all the
excess cation vacancies in the system, A is a constant and Q is the

activation energy for the reaction. Using this equation, Reinjnen[1] plotted

$$[\log\left(\frac{\Delta g}{\Delta g_m}\right)\cdot 10^2 - 3/8\cdot\log\left(1 - \frac{\Delta g}{\Delta g_m}\right)\cdot 10^2]$$

against $1/T$ for a cation deficient magnesium ferrite composition and then, from the slope of the straight line portion determined the activation energy for the reaction. In the case of lithium ferrite or zinc ferrite compositions, it is quite difficult to determine the Δg_m value because of the possibility of lithium or zinc loss at high temperature. But since for a low Δg value $\log(\Delta g)$ vs $1/T$ relationship should approximate a straight line (according to Eq. (8)), comparisons can be made by internally normalizing Δg and $1/T$ values for each ferrite. The method or normalization can be described with respect to the idealized $\log(\Delta g)$ vs $1/T$ plot (Fig. 8). It is to be noted that at higher temperatures deviation from the straight line relationship (as shown by the dotted line) is expected. The normalized Δg and $1/T$ values have been defined as,

$$(\Delta g)_{nor} = \left(\Delta g/\Delta g_A\right); \text{ and } (1/T)_{nor} = (1/T_A) - (1/T)$$

where Δg_A and T_A represent the weight loss and temperature respectively at the point A. Thus we see that only the single phase regions would be considered for comparison. In Fig. 9, $\log(\Delta g)_{nor}$ values have been plotted against $(1/T)_{nor}$. It is interesting to note that the inverse spinel compositions ($LiFe_5O_8$ or $NiFe_2O_4$) show different behavior than

that shown by $ZnFe_2O_4$ or $MgFe_2O_4$ compositions. $ZnFe_2O_4$ is a normal

spinel and $MgFe_2O_4$ has cation distribution very close to normal spinel.

The increased weight loss at high temperature for lithium ferrite and

zinc ferrite compositions is probably due to lithium and zinc loss

respectively. Thus from the above discussion we see that, despite the

crude approach, Fig. 9 distinctly points out the influence of cation

distribution on the weight loss behavior in a cation deficient single

phase ferrite.

For a further comparison

$$[\log\left(\frac{\Delta g}{\Delta g_m}\right)\cdot 10^2 - 3/8 \log\left(1 - \frac{\Delta g}{\Delta g_m}\right)\cdot 10^2]$$

values for the cation deficient nickel ferrite composition have been

plotted against 1/T in Fig. 10. As has been mentioned earlier, the same

plot for lithium ferrite or zinc ferrite compositions could not be drawn

because of the difficulty in determining the Δg_m value due to lithium or

zinc loss. As was noted by Reinjnen[1] in the case of magnesium ferrite

composition, a straight line relationship has been obtained in the

single phase region of the cation deficient nickel ferrite. The points

at the single phase region have been normalized with respect to the

point "X" and have been replotted in Fig. 11, along with the data for

magnesium ferrite.[1] As expected, the nickel ferrite composition ex-

hibited a different activation energy (32.75 kcal/mol) for reaction 2

than that exhibited by $MgFe_2O_4$ (22.8 kcal/mol).[1]

SUMMARY

Extensive thermogravimetric work on various spinel ferrites led to the following conclusions:

(1) For the system $LiFeO_2$-$LiFe_5O_8$-Fe_2O_3, it has been noted that there is a strong tendency for the compositions to adjust itself through appropriate weight loss (lithium or oxygen loss as the case may be), and move into the spinel single phase region and then equilibrate with the atmospheric oxygen.

(2) In order to compare the weight loss behavior of lithium ferrite with those of other ferrites, a region was selected where lithium loss was insignificant in comparison to the oxygen loss. It has been demonstrated that the cation deficient inverse spinel compositions (e.g. Fe_2O_3 excess $LiFe_5O_8$ or $NiFe_2O_4$) exhibit a different behavior than that exhibited by normal ($ZnFe_2O_4$) or near normal ($MgFe_2O_4$) cation deficient ferrites.

(3) The activation energy for the solid oxygen equilibria in a cation deficient inverse spinel ferrite composition was found to be 32.75 Kcal/mol which is somewhat higher than that reported for magnesium ferrite composition.

ACKNOWLEDGMENT

REFERENCES

1. P. Reinjnen, "Investigations into Solid State Reactions and Equilibria in the System $MgO-FeO-Fe_2O_3$," <u>Reactivity of Solids</u>, G. M. Schwab, ed., (Elsevier Publ. Co., Amsterdam, 1965), pp 562-571.

2. P. Reinjnen, "Phase Equilibria in the System $MgO-FeO-Fe_2O_3$," Philips Res. Rep., <u>23</u>, 151-188 (1968).

3. P. Reinjnen, "Thermogravimetric Analysis Applied to Ferrites," Philips Tech. Rev., <u>31</u> [1] 24-30 (1970).

4. D. W. Strickler and R. Roy, "Studies in the System $Li_2O-Al_2O_3-Fe_2O_3-H_2O$," J. Am. Ceram. Soc., <u>44</u> [5] 225-230 (1961).

FIGURE CAPTIONS

Fig. 1. Typical equilibrated weight loss behavior for a spinel ferrite
with excess Fe_2O_3 in the composition (after Reinjnen[2]). It is
assumed that the oxygen is the only vaporizing species.

Fig. 2. Weight loss data for constant heating rate runs for various
compositions in the system $LiFeO_2-LiFe_5O_8-Fe_2O_3$.

Fig. 3. Total weight loss and irreversible weight loss at 1150°C for
various compositions. In each case the temperature was attained
in a constant heating rate run.

Fig. 4. Schematic representation of the variation of oxygen and lithia
activity with respect to metal: oxygen ratio in the system
$LiFeO_2-LiFe_5O_8-Fe_2O_3$.

Fig. 5. Equilibrated and corresponding irreversible weight loss data
for Fe_2O_3 excess $LiFe_5O_8$ composition.

Fig. 6. Logarithm of weight loss/mole of powder (Δg) has been plotted
against 1/T for equilibrated thermogravimetric runs using Fe_2O_3
excess and $LiFeO_2$ excess $LiFe_5O_8$.

Fig. 7. Schematic representation of the path of entry of the two phase
starting compositions into the single phase region.

Fig. 8. Idealized log (weight loss) vs 1/T relationship.

Fig. 9. Relationship between the normalized weight loss values
$[(\Delta g)_{nor.}]$ and normalized 1/T for various Fe_2O_3 excess spinel
ferrite compositions.

Fig. 10. $[Log (\Delta g/\Delta g_m) \cdot 10^2 - 3/8 \log (1 - \frac{\Delta g}{\Delta g_m}) \cdot 10^2]$ vs 1/T relationship
for Fe_2O_3 excess $NiFe_2O_4$ composition.

Fig. 11. Relationship between the normalized values of

$[\text{Log } (\Delta g/\Delta g_m) \cdot 10^2 - 3/8 \log (1 - \Delta g/\Delta g_m) \cdot 10^2]$ and $1/T$ for

Fe_2O_3 excess $NiFe_2O_4$ and $MgFe_2O_4$ compositions. Activation

energies calculated from the slope are 32.75 kcal/mol for
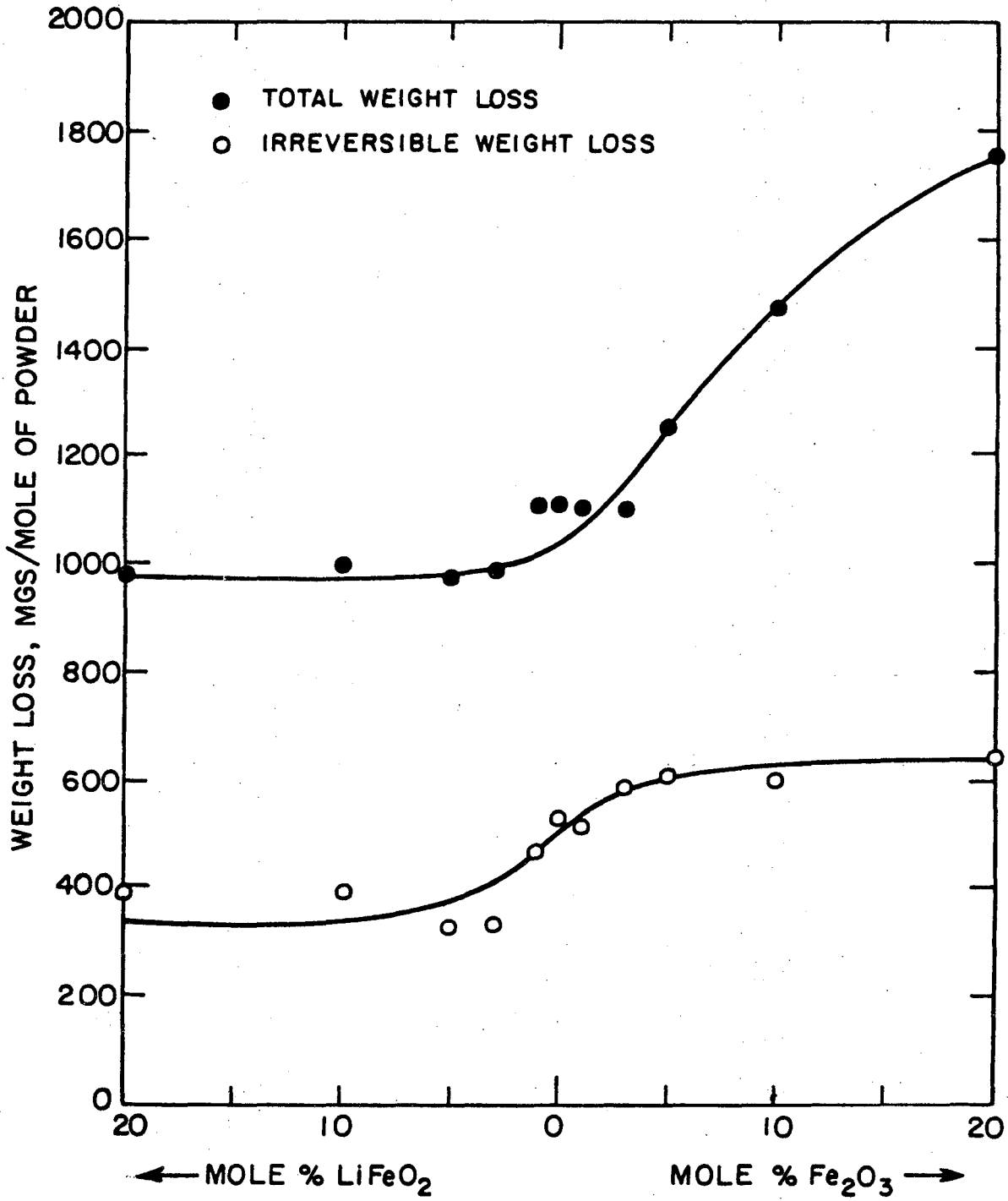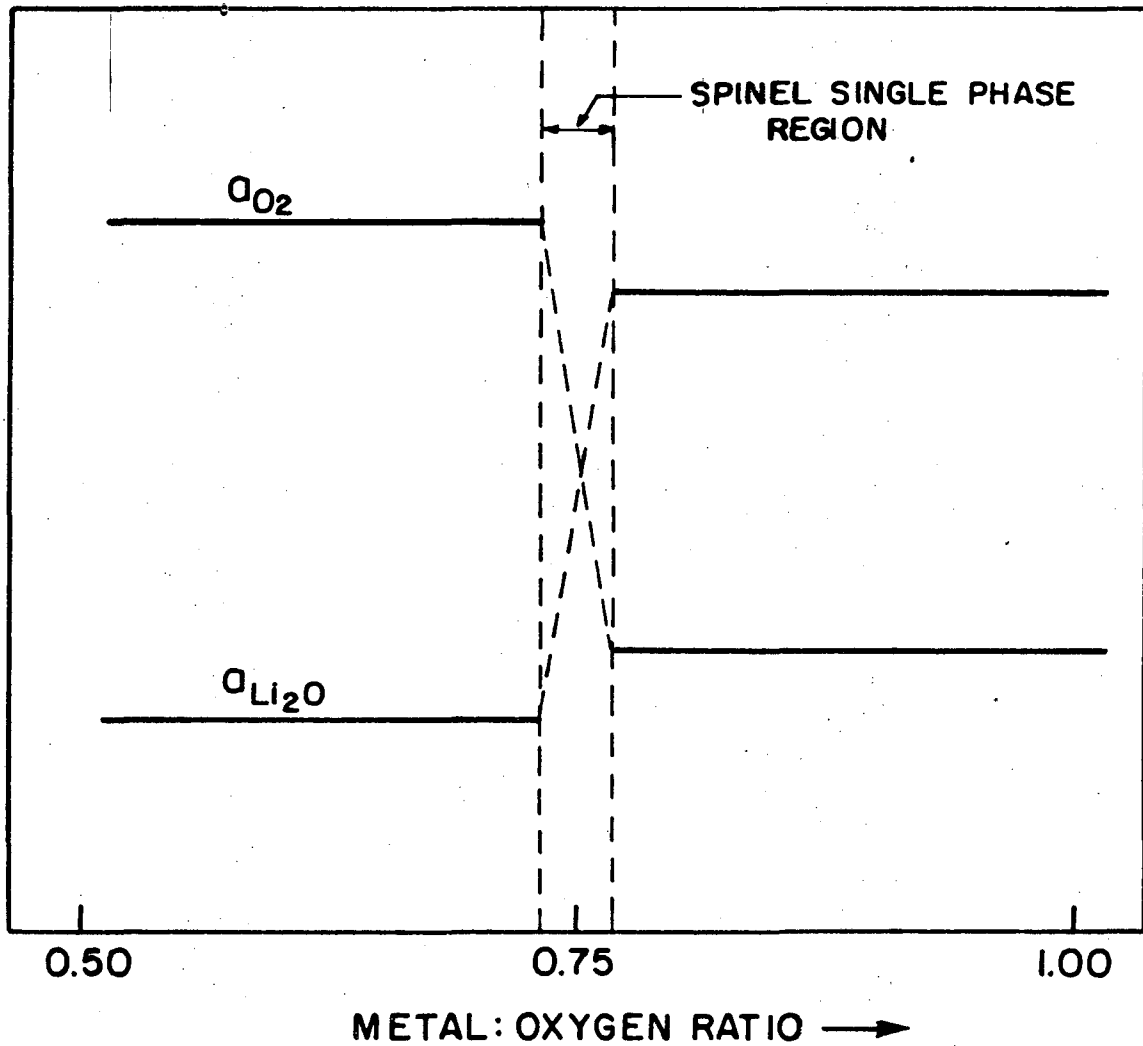
$NiFe_2O_4$ and 22.8 kcal/mol for $MgFe_2O_4$.[1]
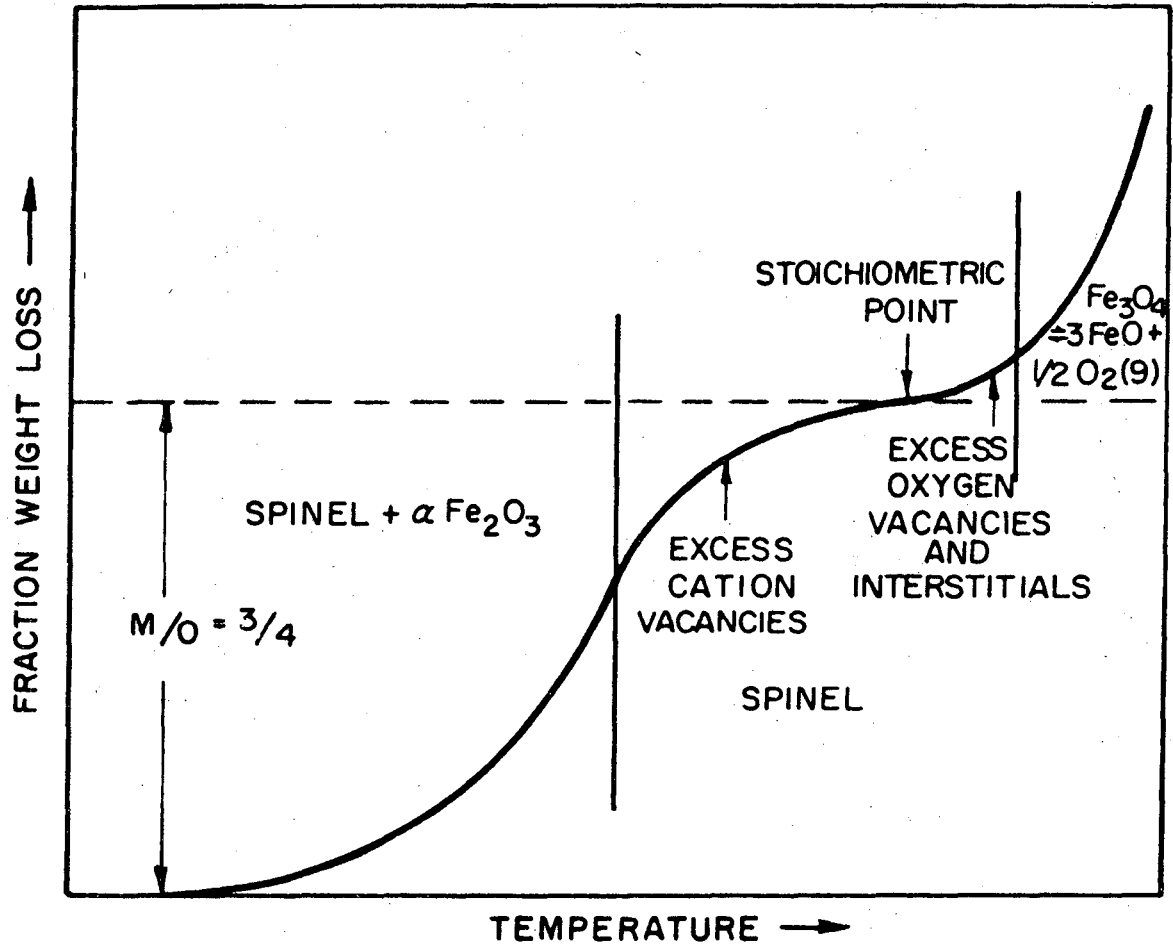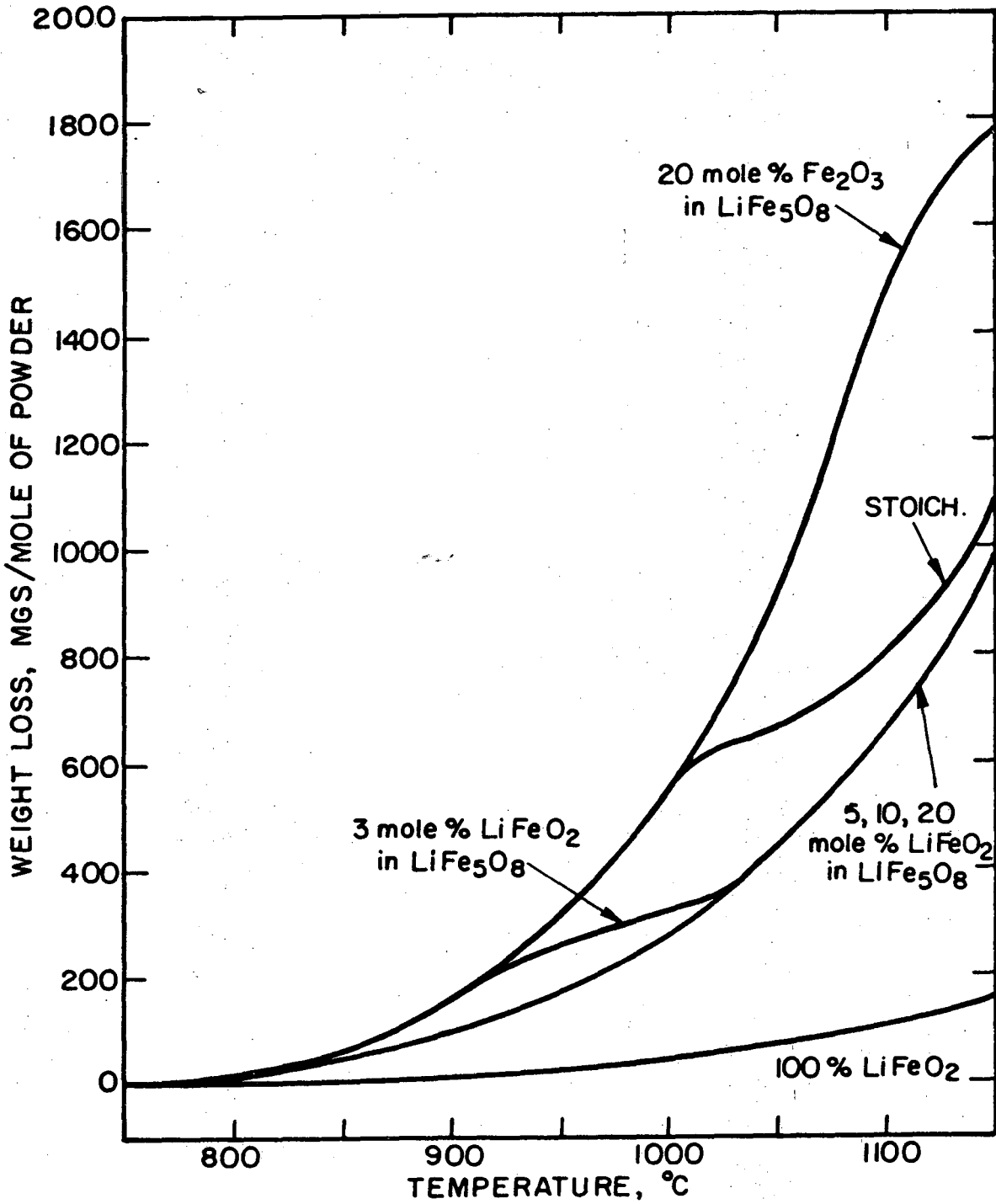
Fig. 1

Fig. 2

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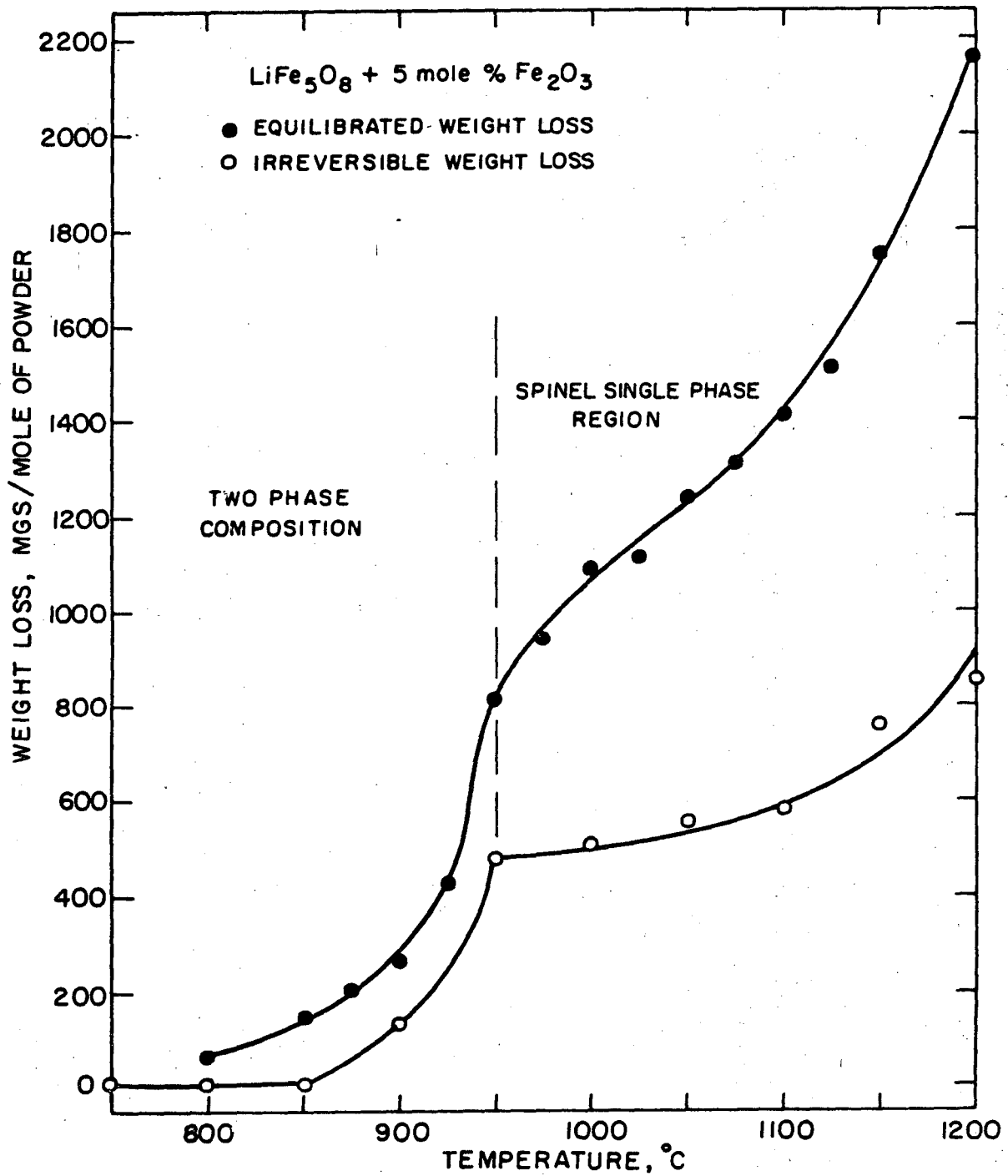Fig. 3

SPINEL SINGLE PHASE REGION

a_{O_2}

a_{Li_2O}

0.50   0.75   1.00

METAL: OXYGEN RATIO ⟶

XBL 737-1591

Fig. 4

Fig. 5
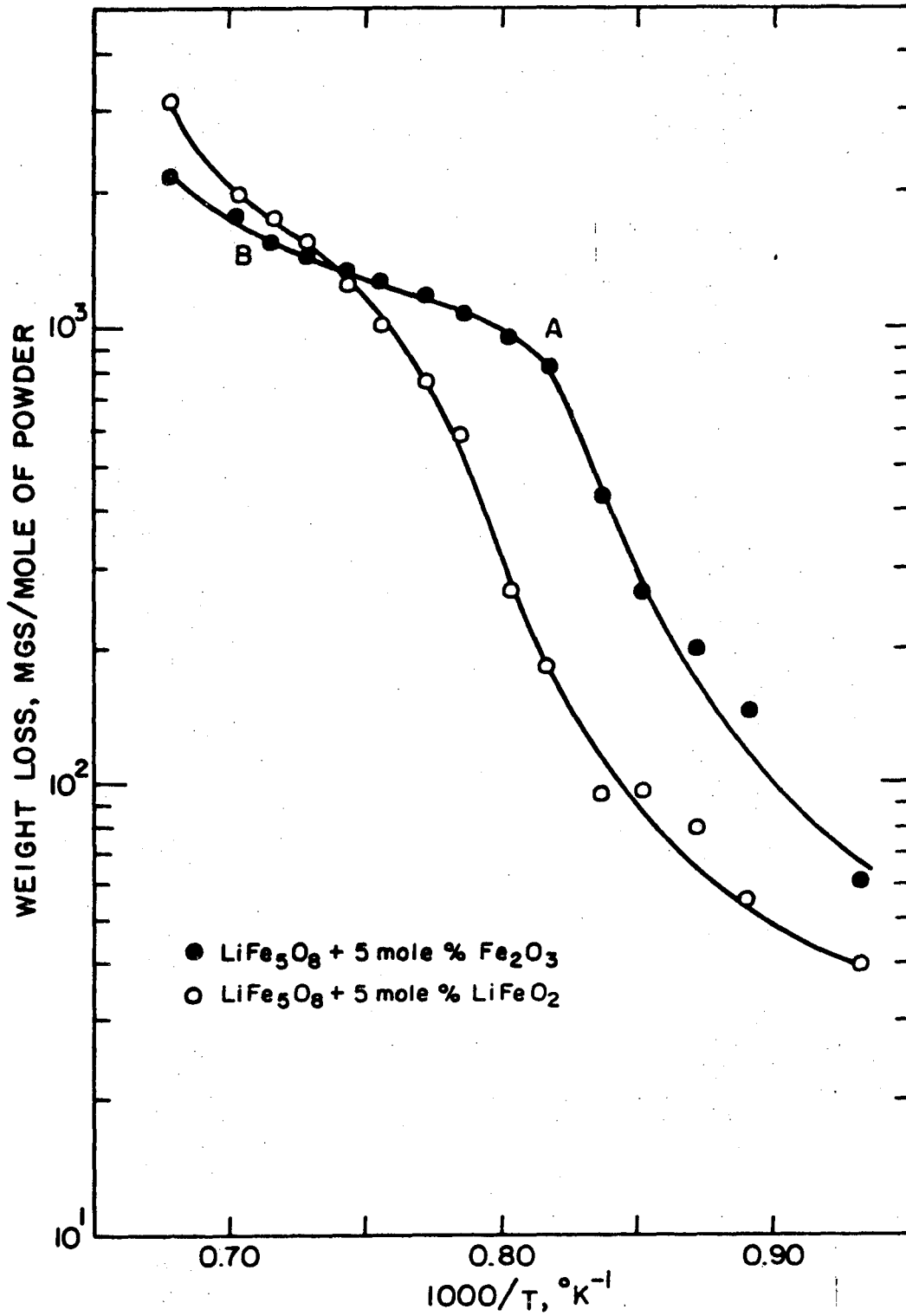
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Fig. 6
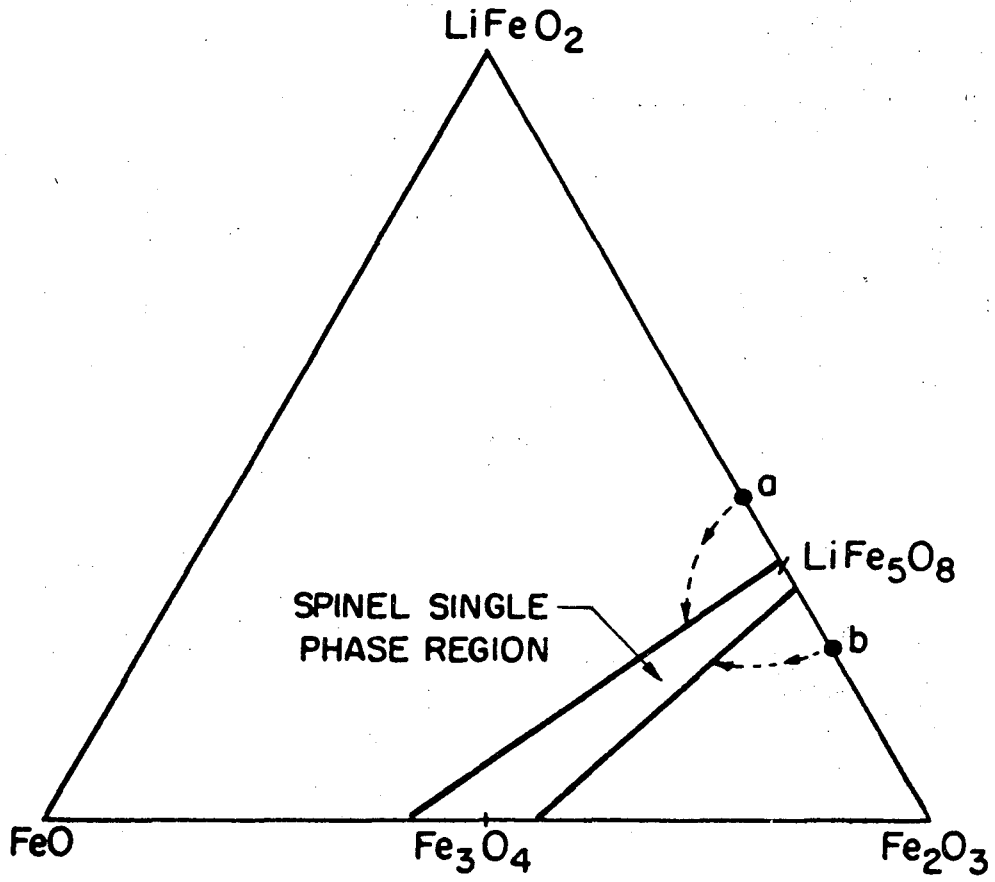
Fig. 7

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Fig. 8

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Fig. 9

Fig. 10

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Fig. 11