STUDY, DEVELOPMENT, AND PRODUCTION OF FERROSPINELS
APPLICABLE TO TUNING OF SEARCH RECEIVERS

PROGRESS REPORT NO. 10, TASK ORDER NO. EDG-6
Period Covering January 1, 1955 to June 30, 1955

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Title: STUDY, DEVELOPMENT, AND PRODUCTION OF FERROSPINELS APPLICABLE TO TUNING OF SEARCH RECEIVERS

Purpose of Task:

To further the development of ferrophophiles of different incremental permeabilities and low losses, with reference to specific applications of interest to the Signal Corps such as RF tuning units.

Procedure:

The approach to the general objective will include:

a. The preparation, under controlled conditions, of specimens of different compositions;

b. The measurement of parameters such as the incremental and initial permeabilities, the saturation inductance, the coercive force and the Q (figure of merit) at various frequencies;

c. The interpretation of these magnetic parameters in terms of the composition, reaction temperature, pressure and other conditions in the preparation of the samples;

d. The relationship of the solid state properties of the crystallite with the various measured magnetic parameters;

e. Theoretical explanations, where possible, for the relationships found in d. above.

Reports and Conferences:

a. Quarterly Task Order Reports shall be submitted reporting technical detail and progress under this Task Order;

b. Task Order Technical Reports of a final summary type are in general desirable and shall be prepared at the conclusion of investigations of each major phase. Such reports shall be prepared as decided in conference between the Electronic Defense Group and the Contracting Officer's Technical Representative in the Countermeasures Branch, Evans Signal Laboratory.
Personnel:

Electronic Defense Group:

Project Physicist: Mr. D. M. Crimes

Countermeasures Branch, Evans Signal Laboratory:

Project Engineer: Mr. Maurice S. Blum

Components and Materials Branch, Squier Signal Laboratory:

Project Scientist: Dr. E. Both

Comments:

The classification of this Task Order as Unclassified shall not preclude the classification of individual reports according to the information they contain, as determined in conference with the Contracting Officer's Technical Representative.

M. KEISER
Chief, Countermeasures Branch
Contracting Officer's Technical Representative
ABSTRACT

A study of the effect of windings on a high permeability toroidal ferrite has been made. The results are presented and analyzed. An experimental study of ferrite formation from the constituent oxides is summarized. A study to determine the effect of grain size on magnetic properties is described, together with a method for decreasing the necessary firing temperature for a completed ferrite to below 1000°C. This reduces interbatch variability and allows longer life for furnace equipment.

A nickel-zinc-iron-cobalt ferrite is described and results in crossed magnetic fields are given. An experimental study and a theoretical survey of the thermo and magnetic properties of some nickel zinc ferrites is described together with a description of a process for preparing ZnFe$_2$O$_4$.

The effect of temperature on cores with different ferrous iron content is shown for two nickel-zinc ferrites.
STUDY, DEVELOPMENT AND PRODUCTION OF FERROSPINELS
APPLICABLE TO TUNING OF SEARCH RECEIVERS

PROGRESS REPORT NO. 10, TASK ORDER NO. EDG-6
Period Covering January 1, 1955 to July 1, 1955

1. PURPOSE

The purpose of this report is to summarize the progress made by Task 6 of the Electronic Defense Group from January 1, 1955 to July 1, 1955, on Signal Corps Contract No. DA-36-039 sc63203.

The purpose of the task is to further the development of ferrospinel's of different incremental permeabilities and low losses, with reference to specific applications of interest to the Signal Corps such as RF tuning units.

The proposed program of Task EDG-6 was outlined in previous progress reports. Only those items will now be reported which have been worked on during the period.

2. PUBLICATIONS AND REPORTS

Mr. D. M. Grimes attended the meeting of the American Physical Society on solid state physics held in Baltimore, Maryland, March 17, 18 and 19.

No publications were issued during the past six months; however, a discussion was given regarding the specific heat of zinc ferrite at the Technical Conference on Magnetism, Pittsburgh, Pa., June 14, 15 and 16. This meeting was attended by Professor E. F. Westrum, Jr., Mr. D. M. Grimes, and Mr. P. E. Nace.
The following reports will be issued during the next period:

"Thermal Anomaly in Zinc Ferrite," by D. M. Grimes and E. F. Westrum, Jr.;

"Heat Capacity of Zinc and Related Ferrites," by E. F. Westrum, Jr.,
and D. M. Grimes;

"Effect of V₂O₅ on Nickel Zinc Ferrite Formation," by D. M. Grimes,
C. F. Jefferson, N. C. Kothary, L. Thomassen;

"Effect of Manufacturing Parameters on Nickel Zinc Ferrites," by C. F.
Jefferson.

3. FACTUAL DATA

3.1 Q-Meter Measurements

A series of measurements were made with the Q-meter in order to evaluate
the accuracy of such measurements. The frequency and the number of turns were
varied on Core A-324-2. This high permeability core was selected for the measure-
ments in an effort to minimize the effect of leakage inductance due to variations
in the windings. Figures 1 through 6 are plots of the data obtained. Note that
the permeability plots are greatly expanded to show detail. The $\mu_1$ curves are
smooth within $\pm 2\%$ with the exception of the permeameter curve. The $\mu_2$ and Q
curves are almost as good.

Two Boonton 160-A Q-meters were used in making these measurements. For
frequencies below 50 kc, an external signal generator was used. External mica
condensers were used to extend the tuning capacitance range of the Q-meter. Two
runs were made at each frequency using windings of 15 and 30 turns. For each run,
the old winding was removed and replaced. No. 28 A.W.G. formvar wire was used for
the windings.

The following discussion is an attempt to establish reasons for the
results of the measurements, and is, in many instances, based on speculation.
Further measurements would be necessary to check the validity of these assumptions.
FIG 2
PERMEABILITY SPECTRA FOR DIFFERENT WINDINGS
MEASURED ON Q-METER
CORE NO A-324-2
n = NUMBER OF TURNS
FIG 3
PERMEABILITY SPECTRA FOR DIFFERENT WINDINGS
MEASURED ON Q-METER
CORE NO A-324-2
n = NUMBER OF TURNS
FIG 4
PERMEABILITY SPECTRA FOR DIFFERENT WINDINGS
MEASURED ON Q-METER
CORE NO A-324-2
n = NUMBER OF TURNS
FIG 5
Q SPECTRA FOR DIFFERENT WINDINGS
MEASURED ON Q-METER
CORE NO A-324-2
n = NUMBER OF TURNS
The stray capacitance of the windings give an apparent $\mu_{1a}$ that is higher than the true value, particularly in the vicinity of the coil's self-resonance. In terms of the indicated Q-meter capacitance, $C_Q$, the effect of winding capacitance, $C_W$, is

$$\frac{C_Q + C_W}{C_Q} = \frac{\mu_{1a}}{\mu_{1t}}$$

(1)

where $\mu_{1a}$ is the apparent value and $\mu_{1t}$ is the true value. To estimate $\mu_{1t}$ we assume it to be essentially constant and equal to the low frequency of $\mu_{1a}$. For each data point for which $C_Q$ is less than roughly 100, a value of $C_W$ was calculated using Eq. 1. From these calculations an average value of $C_W$ was obtained for each winding. Table 1 gives the results of these calculations. $N$ is the number of data points used for each calculation, and $\sigma$ is the mean square deviation from the average $C_W$. The results show $C_W$ to be small except for $n = 15$ and $n = 2\mu_4$. The large $C_W$ at $n = 2\mu_4$ is attributable to the two-layer winding. For $n = 15$, the rise in the $\mu_1$ curve with frequency is probably due largely to a resonance in the material. Therefore, the $\mu_{1t}$ should have been chosen higher, which in turn would give a lower value of $C_W$.

Note that except for $n = 2\mu_4$, $\mu_1$ increases as the number of turns is decreased. This is due to the fact that the RF magnetic field, $H_{RF}$, is too large to be a "reversible" field. If a reversible field is applied to a ferrite, one measures the initial permeability (i.e., the slope at the origin of the magnetization curve). For higher fields irreversible wall displacements occur and the core cycles around a minor B-H loop. This introduces harmonic distortion, but the Q-meter measures only the fundamental component. Therefore, the permeability measured is the slope of the straight line joining the end points of the minor B-H loop. This irreversible wall motion adds to the reversible permeability, giving an incremental permeability greater than the reversible (i.e., initial) permeability. As $H_{RF}$ is increased further, the core material approaches saturation and the incremental per-
meability must decrease toward a value of one. Curve B in Figure 7 gives an approximate picture of this behavior.

| TABLE 1 |

| WINDING CAPACITANCE FOR DIFFERENT NUMBERS OF TURNS |

<table>
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<tr>
<th>n</th>
<th>M</th>
<th>Cw (µF)</th>
<th>σ (µF)</th>
<th>Estimated μlt</th>
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<tr>
<td>15</td>
<td>5</td>
<td>9</td>
<td>.75</td>
<td>330</td>
</tr>
<tr>
<td>15</td>
<td>8</td>
<td>9.5</td>
<td>1.7</td>
<td>330</td>
</tr>
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<td>30</td>
<td>2</td>
<td>2.5</td>
<td>1.5</td>
<td>310</td>
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<tr>
<td>30</td>
<td>6</td>
<td>3.3</td>
<td>.8</td>
<td>310</td>
</tr>
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<td>60</td>
<td>4</td>
<td>2.2</td>
<td>.6</td>
<td>305</td>
</tr>
<tr>
<td>85</td>
<td>4</td>
<td>3</td>
<td>.7</td>
<td>305</td>
</tr>
<tr>
<td>244</td>
<td>6</td>
<td>17</td>
<td>2.7</td>
<td>330</td>
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</table>

The Q-meter applies a voltage of about .02 volts to the series combination of the ferrite coil and the Q-meter condensor, CQ. For a coil Q of 50, there would be 1 volt across the coil. For n = 15, and ω/2π = 1 mc, ωL = 150 ohms is obtained from the data.

\[ i = \frac{e}{ωL} \approx 6.7 \text{ ma}, \text{ and } H_{RF} = \frac{ni}{2m^2} \text{ amps/meter} = .025 \text{ oersteds}. \]

For H_{RF} to be reversible, it should probably be less than .01 oersteds. Thus, we are probably operating on the rising portion of the μ_l versus H_{RF} curve.

\[ H_{RF} \propto \frac{ni}{ωL} \propto \frac{ne}{ωL} \propto \frac{ne}{ωn^2} \propto \frac{Q}{ωn}. \]

Therefore, for larger n, H_{RF} decreases and the operating point moves down the μ_l versus H_{RF} curve. The μ_l data show this effect. Table 1 shows the values of μ_l and n. Also, as the frequency decreases, H_{RF} increases. Therefore, for a given n, μ_l should start rising as the frequency decreases. This effect is shown on the curves for n = 30, 60, 85 (see Figure 1). For n = 244, the core appears to be already well within the range of rising μ_l versus H_{RF} by the time it gets away from the winding capacitance effect. μ_l then peaks sharply (see Figure 2). This may be caused by H_{RF} reaching that value which gives a peak in the μ_l versus H_{RF} curve. Then μ_l decreases as the frequency is further decreased, as predicted by the
versus $H_{RF}$ curve. Another possible explanation of the $\mu_1$ peak in the $n = 244$
curve would be the presence of a magnetostrictive resonance.

Since $H_{RF} \propto \frac{Q}{\omega n}$, $\frac{Q}{fn}$ for the various curves may be computed. $f$ represents
the frequencies at which the $\mu_1$ curves start to rise with decreasing frequency.

Table 2 shows the results. There was no apparent rise in $\mu_1$ with decreasing
frequency for $n = 15$. However, with increasing frequencies one would expect
the peaks in Figure 7 to flatten because the various irreversible wall jumps
cannot respond to the higher frequency. It takes time for wall jump to go to
completion because of viscous and/or inertial damping. At the higher frequencies
some of the wall jumps do not contribute so much, presumably because the field
reverses before the jump can be completed. The curve for $n = 15$ indicates that
the jump in the $\mu_1$ versus $H_{RF}$ curve is sufficiently blunted and broadened (see
curve C, Figure 7) so that no $\mu_1$ rise with decreasing frequency can be detected.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$f$(approx.) (mc)</th>
<th>$\frac{Q}{fn}$ $H_{RF}$</th>
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<tr>
<td>244</td>
<td>0.065</td>
<td>3.6</td>
</tr>
<tr>
<td>85</td>
<td>0.57</td>
<td>1.5</td>
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<td>60</td>
<td>0.58</td>
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<td>30</td>
<td>0.66</td>
<td>2.8</td>
</tr>
<tr>
<td>30</td>
<td>0.62</td>
<td>2.9</td>
</tr>
<tr>
<td>15</td>
<td>No $H_{RF}$ effect present</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>No $H_{RF}$ effect present</td>
<td></td>
</tr>
</tbody>
</table>

For $n = 244$, the winding capacitance effect is probably masking the
frequency at which the $H_{RF}$ effect begins. Therefore, $f = 0.065$ mc is too low a
frequency to use in computing $\frac{Q}{fn}$. If the correct frequency were known, perhaps
$Q$ would decrease to below 1.5. If the above suppositions are borne out by
$fn$
FIG 7
INCREMENTAL PERMEABILITY VS RF FIELD AMPLITUDE
additional data, then the data in Table 2 prove interesting. The value of $H_{RF}$ at which a rise in $\mu_1$ becomes apparent seems to increase with frequency. This is in accord with the model used for Figure 7.

The value of $H_{RF}$ for the frequency of the peak in the $\mu_1$-versus-frequency curve for which $n = 2^{44}$ is given by the following:

$$H_{RF} = \frac{nI}{2\pi f} = \frac{ne}{2\pi \omega L} = \frac{n\omega Qe}{2\pi f} = \frac{.02n\omega Qe}{2\pi f} \approx .038 \text{ oer.}$$

The measured values of $\omega$, $C_Q$, $\overline{f}$ and $Q$ are used. If Figure 7 were independent of frequency, the frequencies of corresponding peaks in the $\mu_1$-versus-$f$ curves would be as shown in Table 3, because $H_{RF} \propto \frac{1}{fn}$, assuming $Q$ to be essentially constant. However, the frequency dependence of the curves in Figure 7 makes the frequencies for the peaks lower than those computed in Table 3. The curves were continued to a low enough frequency to encounter the predicted peaks only at a value of $n = 2^{44}$.

Since $H_{RF}$ was too large to be reversible, the core was subjected to a history that would affect subsequent measurements unless the core was demagnetized after each measurement. Fortunately, the Q-meter tends to do this. As one

<table>
<thead>
<tr>
<th>n</th>
<th>$f(mc) \propto \frac{1}{n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2^{44}</td>
<td>.03</td>
</tr>
<tr>
<td>85</td>
<td>.086</td>
</tr>
<tr>
<td>60</td>
<td>.12</td>
</tr>
<tr>
<td>30</td>
<td>.24</td>
</tr>
<tr>
<td>15</td>
<td>.49</td>
</tr>
</tbody>
</table>
detunes from the resonant point at which a measurement has been made, the current drops to a small fraction of its resonant value. This has the effect of cycling the core around minor loops of decreasing amplitude and producing demagnetization. However, if the core is removed from the Q-meter without having detuned, the core retains some permanent magnetization which tends to lower the values of $\mu_1$ measured thereafter (Ref. 1). Perhaps this accounts for some of the inconsistencies in the data, such as the different curves obtained for the two different 15 turn windings.

Figure 1 shows data obtained with the R.F. Permeameter. These data were obtained in two different runs. In the intervening period the core was subjected to the history introduced by some Q-meter runs. The data at 2.5 and 3.5 mc were obtained on the second run; the rest of the data were obtained on the first run. Since the second run data falls low on the curve, one suspects that the core was in a nonstable remanent state introduced by the Q-meter. All of the permeameter data falls below all of the Q-meter data. This may be due to using a smaller $H_{RF}$ with the permeameter as it was used in conjunction with the General Radio Twin-T impedance bridge. Also, core history may have influenced the first run to some extent, though to a lesser extent than was the case in run two. Also, the difference between the permeameter data and the lowest Q-meter data is roughly 10%. An expected absolute accuracy of 5% is expected for each of two different sets of equipment.

One contributor to $\mu_2$ and Q is the copper resistance $R_{Cu}$.

$$\frac{1}{Q_{\text{apparent}}} = \frac{1}{Q_{\text{core}}} + \frac{1}{Q_{\text{winding}}} = \frac{\mu_2}{\mu_1} + \frac{R_{Cu}}{\omega L}$$

$$\omega L = f \cdot \frac{10^7}{\mu_1} n^2 t \mu \frac{R_2}{R_1} = fn^2 \mu_1 L_0$$

where $L_0$ is a constant.

$$R_{Cu} = nR_t$$

where $R_t = \text{ac resistance per turn}$.

$$\frac{1}{Q_{\text{measured}}} = \frac{\mu_2}{\mu_1} + \frac{R_t}{10L_0} = \frac{\mu_2_{\text{measured}}}{\mu_1}$$

$$\frac{1}{Q_{\text{measured}}} = \frac{\mu_2}{\mu_1} + \frac{R_t}{10L_0} = \frac{\mu_2_{\text{measured}}}{\mu_1}$$
If \( R_t \) is considered to be independent of \( f_n \), then \( \mu_2 \) measured should decrease and \( Q_{\text{measured}} \) should increase with increasing frequency and with increasing \( n \). These effects are observed at the lower frequencies. \( Q \) is influenced by the variation of \( \mu_1 \) with \( f \) and \( n \), but the variation of \( \mu_2 \) is the more influential.

\( R_{Cu} \) was measured at 2 mc on a polystyrene core using 86 turns of No. 28 wire and was found to be 0.013 ohms per turn. Thus, \( R_{Cu} \) for the 30 turn winding would be 0.4 ohms. At 2 mc, \( \omega L \) was 1100 ohms and \( Q \) was 39. Then, calculating \( \frac{\mu_1}{\mu_2} \) from Eq 3 gives \( Q = 39.6 \), a very minor change in \( Q \) due to copper losses. This is generally the case for \( Q < 100 \) as long as \( \mu_1 \) is high.

We know of no experimental data or hypothetical views of how \( \mu_2 \) should vary with the magnitude of \( H_{RF} \). However, one can say that \( \mu_2 \) arises in part from energy exchanges: from magnetic energy to anisotropy energy and/or elastic energy. Certainly such exchanges result in high losses in the regions of magnetostrictive resonance, domain wall resonance, and rotational resonance. However, because of the wide range in elastic parameters, domain wall parameters, domain parameters and localized fields from point to point in a sample, one expects these losses to spread into broad ranges of the frequency spectrum where it is not apparent that they are contributors. Of course these parameters vary with \( H_{RF} \). The magnetostrictive constants even change sign in some materials as the applied field increases, due to differences in the magnetic orientations. The anisotropy energy is a function of the extent to which the applied \( H_{RF} \) rotates the various magnetic dipoles from the easy directions. Of course, hysteresis losses increase with \( H_{RF} \), if \( H_{RF} \) is not a "reversible" field. Since \( H_{RF} \propto \frac{1}{\mu_{\text{am}}} \), \( \mu_2 \) should decrease and \( Q \) should increase with either increasing \( n \) or increasing \( f \). These effects are shown by the curves (Figures 1-7).

At the high frequency end of the spectrum \( \mu_2 \) undergoes an abrupt rise, even steeper than that experienced by \( \mu_1 \). \( R_t \) (Eq 3) makes an increased
contribution to $\mu_2$ at the higher frequencies because of skin effect and proximity effect. Proximity effect is probably negligible for single-layer windings on toroids because the wires are, at most, in close proximity only on the inner diameter. Only for $n = 85$ and $n = 244$ were the wires in close proximity on the inner diameter, and here the capacitance effect restricted the frequency range. Consequently, we rule out proximity effect as a significant contributor.

No. 38 A.W.G. wire has no skin effect over the range of frequencies encountered (Ref. 2). No. 10-38 Litz wire has the same dc resistance as No. 28 A.W.G. wire. Thus, this Litz wire could have been used to avoid skin effect. However, for $f = 1$ mc, and using No. 28 wire, $\frac{R_{ac}}{R_{dc}} = 1.5$ and, at 4 mc increases only to 2.2 (Ref. 3). This small amount of skin effect does not explain the steep rise in $\mu_2$, nor does it explain why it is a function of $n$.

Consider the circuit of Figure 8 where $C_W$ is the winding capacitance

![Equivalent Circuit for a Domain Wall](image)

**FIG 8  EQUIVALENT CIRCUIT FOR A DOMAIN WALL**

and $L$ and $R$ refer to the ferrite coil.

\[
Z = \frac{R + j\omega L}{1 - \omega^2 L C_W + j\omega C_W R} = \frac{R + j\omega L(1 - \omega^2 L / R)}{(1 - \omega^2 L / R)^2 + (\omega C_W R)^2} \quad \text{for} \quad \frac{\omega^2 L}{R^2} \gg 1 \quad (4)
\]

\[
= \left[ 1 - \frac{\omega}{\omega_0} \right]^{-\frac{R}{\omega_0}} + \frac{j\omega L}{\left[ 1 - \frac{\omega}{\omega_0} \right]^2} \quad \text{for} \quad (\omega C_W R) \ll (1 - \omega^2 L / R)^2 ; \quad \omega_0 = \frac{1}{\sqrt{L C_W}} .
\]
Note that $\omega^2 L C_Q \leq 1$, and $C_w \ll C_Q$ for all $C_Q$, since $C_{Q_{\text{min}}} = 27 \ \mu\text{uf}$ for the $Q$-meters used. Then the condition on Eq 4 becomes $\omega C_w R < 1$ which is rewritten as

$$\frac{\omega^2}{\omega_0^2} \ll 1,$$

which certainly is true. Equation 4 shows that while $\mu_1 \propto \frac{1}{\left( 1 - \frac{\omega}{\omega_0} \right)^2}$, $\mu_2$ is proportional to the square. Thus, $\mu_2$ should rise much faster with frequency than does $\mu_1$ as $\omega \rightarrow \omega_0$, the frequency of the coil's self-resonance. The more $n$ increases, the more $\omega_0$ is lowered and, therefore, the lower the frequency at which $\mu_2$ begins to rise. $Q = \frac{\omega L}{R} \alpha \left[ 1 - \frac{\omega}{\omega_0} \right]^2$ describes the manner in which $Q$ drops due to this winding capacitance effect (see Figure 5).

### 3.2 Iron-Rich Nickel Zinc Ferrites

A technical report including this subject is expected to be issued during the next period. A summary of the pertinent results follows.

When a ferrite is heated to a point where the diffusion process begins, the metallic cations start to penetrate the different oxygen lattices. This results in an almost immediate formation of a basic spinel structure as seen by X-ray photographs. Along with the spinel, ferrous iron is formed. As the diffusion process continues so that the permanently divalent cations are more evenly distributed, the ferrous iron content drops and the X-ray line width in the back reflection region decreases. Figure 9 shows a plot of the ferrous iron content versus firing time for a stoichiometric nickel zinc ferrite. The time required for the ferrous iron formation and the amount present depends, of course, very strongly on the firing temperature and the mixing procedure used. It does not depend upon whether water or acetone is used for the slurry.

When excess iron is added to the system, some magnetite will be formed. The percent of the excess iron converted to magnetite depends upon the temperature in much the same manner as if it were a question of the solubility of magnetite in the base nickel zinc ferrite structure. This is seen to be an equilibrium
FIG. 9
FERROUS IRON CONTENT VS FIRING TIME FOR A
STOICHIOMETRIC NICKEL-ZINC FERRITE
(FIRED AT 1200°C)
phomena since nearly the same amount of ferrous iron is found when the
material is brought to equilibrium from a lower temperature as when it is
brought to equilibrium from a higher temperature. Figure 10 shows the fraction
of the final value of the magnetite formed as a function of temperature and of
excess iron.

It is found that as the total iron increases the permeability decreases
and the Q increases. Further, there exists a frequency for a maximum Q, this
frequency increases with increasing iron content. Figure 11 shows the variation
of μ and Q with frequency for several compositions.

It is found that after the material has been annealed at 800°C, the
Q increased with the maximum Q shifting to a higher frequency (see Figure 12).
This is believed to be due to either the formation of a second phase or a
redistribution of the cations. If it is due to the formation of a second phase,
it is not evident in an examination of the surface or from X-ray photographs.
Therefore, measurements of the saturation moment will be done to test for a
cation redistribution.

3.3 Effect of Grain Size on Magnetic Properties

3.3.1 Outline of the Work. In order to extend the investigations re-
ported in Section 3.3 of Electronic Defense Group Task 6 Quarterly Progress
Report No. 8, it was first necessary to establish better polishing techniques,
so that fewer grains would be pulled out of the material while polishing. This
work was reported in Section 3.4 of Electronic Defense Group Task 6 Quarterly
Progress Report No. 9.

The object of the investigation was then to obtain two cores with the
same permeability, fired for different times at different temperatures. All of
the other variables were to be held constant. The grain sizes in these samples
FRACTION OF MAGNETITE FORMED AS A FUNCTION OF FIRING TEMPERATURE.

FRACTION OF EXCESS Fe₂O₃ CONVERTED TO Fe₃O₄
**FIG 11** FREQUENCY SPECTRA OF $\mu$ AND Q AS A FUNCTION OF TOTAL IRON CONTENT.
FIG 12

THE $\mu$, Q SPECTRA OF COMPOSITION FIVE AFTER QUENCHING FROM 1375°C AND AFTER ANNEALING AT 800°C (Ni$_{0.474}$Zn$_{0.526}$Fe$_2$O$_4$ + 0.938Fe$_2$O$_3$)
would then be compared. This approach assumed an increase in permeability with firing time. It was shortly found that the permeability goes through a maximum and then decreases, both at extended firing times and at higher firing temperatures.* For work on grain size to continue, it was necessary to understand and control or avoid this decrease in order to obtain comparative measurements.

It was thought that this decrease might be due to volatization of zinc. The volatility of ZnO seems to be quite varied judging from the conflicting reports in the literature. However, it was presumed that the zinc present was as the spinel and not as ZnO. Two methods of checking the volatility were tried. First, firing weighed samples at different temperatures showed that the samples did lose weight above 1200°. Second, Curie point measurements were taken. Since the zinc would volatilize from the surface it must be expected that the temperature falloff of permeability should not change with Zn content, but the temperature at which the permeability approached unit would. These data were inconclusive.

Since the material described above was slow cooled, it was thought that at least most of the zinc would occupy A sites, as contrasted with the quenched material described in Section 3.2. However, there is no assurance that the material is completely normal, nor can it be assumed that annealing after a high temperature fire would place all of the zinc in the A sublattice.

3.3.2 The Flux Problem. The problems introduced by the zinc seemed to demand a lower firing temperature. Our previous work had shown that V2O5 was instrumental in promoting grain growth at a specified temperature. Therefore,

* This is shown in Figures 11, 12 and 13 of Electronic Defense Group Task 6 Quarterly Progress Report No. 5.

** See Section 3.4.1 of Electronic Defense Group Task 6 Quarterly Progress Report No. 5.
lower firing temperatures were tried using cores with .75 mole of Fe₂O₃ replaced by .75 mole of V₂O₅. A series of cores were fired between 800⁰ and 1000⁰C. for four hours. This material was ball milled with acetone for six hours and dried at 110⁰C. The material was furnace cooled.

The die used was 1-11/16" OD and 1-7/16" ID. These values were chosen to obtain a ratio of minimum to maximum diameter as close to unity as possible (see Section 3.3, Ref. 1). The spinel formation in these cores occurred between 800⁰ and 850⁰. Cores fired at 800⁰ were orange red, those fired at 850⁰ were black. The 800⁰ core had expanded about 1/16" in OD, while the 850⁰ core had undergone firing shrinkage. Cores fired at or above 900⁰ have a smooth surface, those fired below 900⁰ showed a folded surface with valleys and hills in a pronounced warped pattern. The X-ray and metallographic pictures of these specimens showed no evidence of a second phase (see Figures 13 and 14). It is presumed that the reaction goes very fast in the presence of the vanadium pentoxide. CrO₃ did not have the same effect. Presumably the reaction which formed the spinel, possible exothermic, started in certain localized regions. These regions shrunk and formed a superstructure which prevented the remainder from contracting when it reacted, thus giving an irregular surface. Once this shape was formed, it could not be removed by heating at higher temperatures.

The grain size involved was quite large (20 microns diameter). The grain size of a core containing .75 mole % V₂O₅ and fired at 950⁰ was quite comparable with that of a core not containing the vanadium fired at 1350⁰ (see Figure 14).

One item of note was that the "spots" described previously* were entirely absent. These "spots" involved regions of abnormally high grain size.

* Section 3.2.4 of Electronic Defense Group Task 6 Quarterly Progress Report No. 6, April 1954.
FIG 13

X-RAY POWDER DIFFRACTION PATTERN OF A Ni-Zn FERRITE CONTAINING V₂O₅ AND FIRED AT 1000°C FOR FOUR HOURS

(SPECIMEN B-2002)
FIG 14 COMPARATIVE PHOTOMICROGRAPHS OF A POLISHED AND UNPOLISHED Ni–Zn FERRITE CONTAINING $V_2O_5$ AND FIRED AT 1000°C FOR FOUR HOURS. SPECIMEN B–4–4
It is possible that the entire ferrite now has the characteristics of the spots seen before.

Considerable difficulty was involved in making good physical specimens with the larger die. The difficulty was apparently involved with the very fast reaction. The core had to be kept at as uniform a temperature as possible. This was accomplished fairly successfully by placing a toroidal ring of alundum, large enough to completely cover the specimen, directly on top of it during the firing. All such cores made to date have been slightly elliptical, having a $D_{\text{min}}/D_{\text{max}}$ of about .9.

The surface of these cores showed a very obvious grain pattern without polishing or etching. The significance and reason for this is not at all understood. However, if the internal structure were comparable with that at the surface it would eliminate the necessity for polishing and etching each specimen. However, comparative photomicrographs show the unpolished surfaces have a smaller mean grain size and have a larger percentage voids than do polished surfaces. (See Figure 15). Therefore, it has been concluded that all measurements should be made on polished samples.

Comparative magnetic properties are shown in Figures 16 and 17 between a vanadium sample fired at $950^\circ\text{C}$. and a nickel-zinc sample fired at $1250^\circ\text{C}$. Figure 16 shows the comparative Q-meter measurements, and Figure 17 shows the comparative B-H loops.

3.4 Cobalt, Iron, Nickel, Zinc Ferrites

Although the exact nature of the loss mechanism is not presently understood, it is certain that coupling between magnetic and elastic lattices would result in energy dissipation. Two methods of energy transfer would be by magnetostrictive and by anisotropic coupling.
Specimen A-112

(500 x)

Plain nickel-zinc ferrite core, fired for four hours at 1350 degrees C.

Specimen B-2018-2

(500 x)

Nickel-zinc ferrite core containing $V_2O_5$ and fired for four hours at 950 degrees C.

Fig 15 Comparative photomicrographs of a Ni-Zn ferrite fired at 1350°C and a Ni-Zn ferrite containing $V_2O_5$ fired at 950°C.
Fig 16  Comparative Measurements of $\mu$ and $Q$ vs Frequency for Cores A-275 and B-2018-1
A-275 Ni-Zn Ferrite Core fired at 1250°C for four hours
B-2018-1 Ni-Zn Ferrite Core containing Vanadium fired at 950°C for four hours
FIG 17  COMPARATIVE B-H LOOPS OF CORES  A-275 & B-2018-1
A-275; Ni-Zn FERRITE FIRED AT 1250°C FOR FOUR HOURS
B-2018-1; Ni-Zn FERRITE CORE FIRED AT 950°C FOR FOUR HOURS
(CONTAINS V₂O₅)
The contribution of different magnetostrictive coefficients to the effective anisotropy for constant stress is:

\[ \Delta K = \frac{9}{4} \left[ (c_{11} - c_{12}) \lambda_{100}^2 - 2c_{44} \lambda_{111}^2 \right] \]

The \( c_{ij} \)'s represent the elastic moduli. The magnetostriction in a saturated, polycrystalline body is given by:

\[ \lambda = \frac{1}{5} \left[ 2 \lambda_{100} + 3 \lambda_{111} \right] \]

For other values of \( M \), Brown gets for anisotropic material:

\[ \frac{\lambda}{\lambda} = 1 - 3 \frac{\cosh \eta}{\eta} + \frac{3}{\eta^2} \]

where \( \eta \) is defined by

\[ \frac{M}{M_s} = \cosh \eta - 1/\eta \]

Values of \( K, \lambda_{100}, \lambda_{111} \) and \( \lambda \) are given in Table 4.

**TABLE 4**

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{100} )</th>
<th>( \lambda_{111} )</th>
<th>( \lambda ) (demagnetized polycrystal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Fe or Co Ferrites</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Fe(_2)O(_4)</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>CoFe(_2)O(_4)</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Since \( K \) and \( \lambda \) have different magnitudes in different ferrites, it seems that it might be possible by properly combining divalent cations to produce material with a high Curie point but small values of \( K \) and \( \lambda \). One major difficulty would be the problem of producing locally small coupling. (See Sec. 3.5).

These values allow the possibility of varying \( \lambda \) and \( K \) with \( M \) in such a manner as to change the character of the \( Q \) vs \( M \) curve.

Since tuning units, which are the ultimate objective of these investigations, operate from on or near remanence towards saturation, the above possibility becomes of considerable interest. Therefore cores containing different amounts of cobalt
and iron were made.

To test $\mu$-Q versus a parallel biasing field, the equipment developed under EDG Task 1 for use at 500Kc was used.* For transverse biasing fields the cores were wound in the usual fashion and placed between the pole faces of a magnet, as described previously (Ref. 1). The core windings led to a Q meter.

Sample results are shown in Fig. 18. Similar data have been taken on the cores containing magnetite and cobalt. The results and compositions are shown in Figures 19, 20 and 21. These cores were all fired in the following manner. They were heated rapidly to 1150°C and flushed with air at all temperatures greater than 1150°C. They were taken slowly to 1375°C, held there 30 minutes, then taken down to 1200°C for two hours. They were cooled to 1100°C, then put in a N2 atmosphere and slow cooled.

Each series contained a different total iron content. Each started with zero cobalt, and each series had a constant zinc content. Cobalt was introduced at the expense of the nickel, starting with the magnitude of 1/100 of the original nickel, then approximately doubling the amount of cobalt for each new core type. Some of the data are not included.

It is expected that transverse field data will be taken at frequencies up to 10 mc as well as parallel field data at 500 kc. The results shown are quite dramatic. The interpretation will be considered later.

3.5 Properties of $(\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4)$, Review

3.5.1 The Spinel Structure. For spherically symmetric bonding and with repulsive forces which fall off rapidly with distance, a close packed array of atoms in energetically the most stable. This can be accomplished with either a face-centered or a hexagonal close packed lattice when all atoms are identical. Either of these structures have about $74\%$ of the available space occupied.

* The experimental setup and the data on core A-105-1 are described in Electronic Defense Group Task 4 Quarterly Progress Report No. 15.
FIG 18

$\mu$ vs $Q$ VARIATION AS MAGNETIZATION CHANGES
A-105-1
FIG 19 THE VARIATION OF $\mu$, $Q$ WITH MAGNET CURRENT

TRANSVERSE FIELDS
FIG 20 THE VARIATION OF $\mu$ AND Q WITH MAGNET CURRENT, TRANSVERSE FIELDS. ($Fe_{2}O_{3}$ CONTENT IS THE INITIAL CONTENT. FINAL FERROUS IRON VALUE UNKNOWN.)
FIG 21  THE VARIATION OF $\mu$ AND Q WITH MAGNET CURRENT, TRANSVERSE FIELDS.
Fe$_2$O$_3$ CONTENT IS THE INITIAL CONTENT. FINAL FERROUS IRON VALUE UNKNOWN.
assuming spherical particles.

For face-centered cubic arrays of spherical particles, there will be inter-
stances surrounded by 6 spheres, corresponding to Coordination Number 6 for the
center of an octahedron of spheres. This type of site will be referred to as a
B site. Other interstices are surrounded by four spheres giving a Coordination
Number 4 to the center of a tetrahedron of spheres. This type of site will be
referred to as an A site.

The mineral spinel, MgAl_2O_4, has been taken as the prototype of the spinel
structure. There the larger Mg^{2+} cations are on the A sites, the smaller Al^{3+} on
the B sites, while the O^{2-} form the close-packed lattice. It is to be noted that
this is in contrast to the usual case where the largest cations have the largest
coordination numbers. One half of a unit cell is shown in Fig. 22. The spinel
structure consists of an alternating array of such blocks continuing in all three
directions. The positions of cations may not be exactly in octahedral or tetrahe-
dral centers but in positions characterized by a parameter, μ.

Many materials\(^7\) crystallize, either from the melt or during solid state
reactions, into this structure. We shall, for the most part, confine our efforts
to MFe_2O_4 where M is a divalent ion or ions.

Barth and Posnjak\(^8\) have shown that the positions of the metallic ions can be
rearranged and still preserve the spinel structure. The alternative is to have
half of the trivalent ions on A sites, the remainder and the divalent ions on B
sites.

Verwey and Heilmann\(^9\) studied the structure of several such iron containing
spinel or "ferrites" using X-ray techniques. They found that for M = Ni, Cu, Mg,
Co, Fe and Mn the divalent ions were on the B sites. For M = Zn, and Cd, the
divalent ions were on the A sites. They defined the latter as "normal" spinels
and the former as "inverted" spinels.
<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>NORMAL STRUCTURE</th>
<th>INVERSE STRUCTURE</th>
<th>COORDINATE NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgAl$_2$O$_4$</td>
<td>MFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>1 Mg$^{**}$</td>
<td>1 M$^{**}$</td>
<td>1 Fe$^{***}$</td>
</tr>
<tr>
<td>v</td>
<td>2 Al$^{***}$</td>
<td>2 Fe$^{***}$</td>
<td>1 M$^{<strong>}$, 1 Fe$^{</strong>*}$</td>
</tr>
<tr>
<td>o</td>
<td>4 O$^{**}$</td>
<td>4 O$^{**}$</td>
<td>4 O$^{**}$</td>
</tr>
</tbody>
</table>

FIG. 22
THE SPINEL STRUCTURE
They found that the lattice constants for the normal spinels were larger than for the inverse spinels. This, of course, means that the inverse ferrites are more closely packed. From a combination of lattice-constant and line-intensity measurements they determined that in a mixed ferrite of Cu and Zn the zinc stayed on the A sites, the Cu on the B sites.

Goodenough and Loeb have shown that a combination of covalent bonding and electrostatic bonding can account for the known spinel properties.

The aforementioned ferrites with inverted spinel structure possess ferromagnetic properties. Those with normal spinel structure do not. Snoek was able to make ferromagnetic materials with an array of properties mixing normal and inverted spinels.

Lithium ferrite also exists in the spinel structure. In this case the Li form an ordered f.c.c. array on the B sublattice.

3.5.2 Magnetic Properties: Two Sublattice Model. The gross magnetic properties of the ferromagnetic spinels, or ferrites, with the inverse structure has been well established. There are several major differences from the ordinary ferromagnetic behaviour. The material does not follow the Curie-Weiss law above the Curie temperature, but is concave towards the temperature axis. The saturation moment is small—less than the sum of all atomic moments.

These characteristics were explained and the temperature dependence of the spontaneous moment predicted by Néel. This was accomplished by extending the molecular field approximation of ferromagnetism. The ions located on A sites will be subjected to different crystalline forces than those on B sites. It is assumed that the B ions will exert antiferromagnetic forces on each other, as will also the A ions. However, the B ions exert an antiferromagnetic force on the A ions larger than the intra-A antiferromagnetic forces, and vice versa. The result
is that the B ions have their moments aligned as do the A ions, but in the opposite sense. Thus, the net moment arises from the difference of the B and the A moments.

Following Néel, let \( \lambda \) be the fraction of the ferric ions on the A sites, \( \mu \) the fraction on the B sites. Thus, \( \lambda + \mu = 1 \). For the inverted spinel, \( \lambda = \mu = 0.5 \). For the normal spinel \( \lambda = 0, \mu = 1 \). Let the magnetization of a gram ion of ferric ions on the A sites be denoted by \( M_a \), the magnetization of a gram ion of ferric ions on the B sites by \( M_b \). The total magnetization is then given by:

\[
M = \lambda M_a + \mu M_b
\] (5)

The molecular field approximation assumes an effective local field at each lattice site due to the surrounding ions given by:

\[
H_a = n_o (\alpha \lambda M_a - \mu M_b) \quad (6)
\]

\[
H_b = n_o (\alpha \lambda M_a - \gamma \mu M_b)
\]

The magnetic energy associated with these fields at absolute zero is given by:

\[
E = \frac{1}{2} \left[ \lambda H_a \cdot M_{as} + \mu H_b \cdot M_{bs} \right] \quad (7)
\]

Combining Equations 6 and 7

\[
E = n_o/2 \left[ \alpha \lambda M_{as}^2 + 2\alpha \mu M_{as} M_{bs} + \gamma \mu^2 M_{bs}^2 \right] \quad (8)
\]

\( E \) is an extremum for the following four cases.

I. \( M_{as} + M_{bs} = 0 \). (paramagnetism)

II. \( M_{as} = M_{bs} = \) the maximum value \( M \).

III. \( M_{as} = M; M_{bs} = - \lambda/\mu \gamma \quad M \).

IV. \( M_{as} = \mu/\lambda \alpha \quad M; \quad M_{bs} = M \).

It is to be noted that solutions III and IV represent a sublattice magnetization different from saturation at \( 0^\circ \text{K} \), and that the slope of the \( M \) vs \( T \) curve for this specimen is nonzero at \( 0^\circ \text{K} \), violating the so-called third law of
thermodynamics.

That the above ideas are essentially correct has been shown by Shull, et. al. by neutron diffraction studies of magnetite. Since then further neutron studies on NiFe₂O₄, ZnFe₂O₄, and Ni₅Zn₅Fe₂O₄ have been carried out. They, too, substantiate the Néel picture.

In spite of all this experimental agreement, it should be emphasized that even though it can be shown that the ground state for ferromagnets is very nearly that of all moments aligned, and further, that for antiferromagnets the picture of nearest neighbors with antiparallel spins is stable for extended periods of time, it is necessary to merely assume this state for ferrimagnetism.

It is to be expected that the usual equations describing wall formation in ferromagnets must be altered to consider the additional sublattice. Further, since the ferric ions on A and B sites are located in different potentials it is to be expected that crystalline-dependent properties such as the Lande' g-factor and the crystalline anisotropy would be different on each sublattice. The effects of different g-factors have been observed.

The possible magnetization curves using the two sublattice model are shown in Fig. 23.

3.5.3 Magnetic Properties: Four Sublattice Model. Yafet and Kittel considered a further subdivision of the structure by considering nearest neighbor interactions. They divided the A sublattice into two and the B sublattice into four face-centered cubic lattices. For zero anisotropy the four B sublattices can be lumped into two equivalent sublattices. The molecular fields acting on each sublattice can be written, analogous to Eq. 2, as:

\[ H_{a'} = n_0 (a_1 \vec{M}_a' + a_2 \vec{M}_a' - \vec{M}_b - \vec{M}_b') \]

\[ H_{a''} = n_0 (a_2 \vec{M}_a' + a_1 \vec{M}_a'' - \vec{M}_b' - \vec{M}_b'') \] (5)
FIG 23
POSSIBLE VARIATIONS OF M AND X WITH T.
\begin{align*}
H_b' &= n_0 (-M_2' - M_a + 2M_b' + 2M_b) \\
H_b'' &= n_0 (-M_a' - M_a + 2M_b' + 2M_b) \\
\end{align*}

This gives rise to a magnetic energy:

\[ E = -n_0 \left[(\alpha_2 - 2\alpha_2 \cos 2\phi)M_a^2 + 4M_aM_b \sin \phi \sin \psi + (\gamma_1 - \gamma_2 \cos^2 \psi)M_b^2 \right] \tag{6} \]

The angles \( \phi \) and \( \psi \) are defined in Fig. 24. This leads to the minimum energy conditions analogous to those of Néel:

I. \( \phi = \psi = 0 \). This term no longer means a paramagnetic arrangement but a doubly antiferromagnetic arrangement of spins.

II. \( \phi = \psi = \pi/2 \).

III. \( \psi = \pi/2, \sin \phi = \frac{M_b}{\alpha_2 M_a} \).

IV. \( \phi = \pi/2, \sin \psi = \frac{M_a}{M_b \gamma_2} \).

Solutions II, III and IV correspond directly to Néel's solutions. The interpretation in this theory is a triangular spin arrangement on one sublattice for solutions III and IV.

In this case the slope of the magnetization curve at \( T = 0 \) is zero.

The higher temperature behaviour can be found by assuming the usual Curie law to hold using the proper molecular fields. There is no simple relationship between the high and low temperature characteristics. It is therefore possible to go from one minimum energy condition to another as the temperature changes.

It is to be expected that there will be an extra specific heat contribution at the boundary between different minimum energy conditions because of the difference in the temperature dependence of the magnetic energy.

According to Yafet and Kittel, it is to be expected for a mixed Ni-Zn ferrite with about 10 mole % NiO and 40 mole % ZnO and 50 mole % Fe₂O₃, that
FIG 24
PROPOSED ANGULAR MAGNETIZATION ON A & B
SUBLATTICES. (AFTER YAFET & KITTEL)

FIG 25
VARIATION OF ENERGY
DIFFERENCE ON A AND B
SUBLATTICES WITH ATOMIC
NUMBER. (AFTER NÉEL)
several such transitions should occur as the temperature of the material is varied.

3.5.1 The Effect of Fluctuations of the Molecular Field. As was pointed out by Néel,\textsuperscript{19} the molecular field approximation assumes each cation to possess the average environment of the gross material. A B-site cation has 6 nearest neighbor A-sites and 6 nearest neighbor B-sites. Consider the case of RFe\textsubscript{2}O\textsubscript{4}. In the case of a simple normal spinel all 6 nearest neighbor A-sites will be occupied by R\textsuperscript{2+}, all 6 n.n. B-sites by Fe\textsuperscript{3+}. For an inverted spinel all A-sites would be occupied by Fe\textsuperscript{3+}, the B-sites would contain both R\textsuperscript{2+} and Fe\textsuperscript{3+}. For the normal spinel the molecular field approximation should remain always valid. For the inverted case differences would be manifested near the Curie point. For intermediate cases the situation is not so clear. Intermediate cases can arise for two reasons, (a) the material can be retained in metastable positions by suitable tempering and (b) the bivalent ion could be a mixture of metals forming normal and inverted ferrites.

Consider first (a) above. For each R\textsuperscript{2+} there is an Fe\textsuperscript{3+} on the other sublattice. Let the potential for the R\textsuperscript{2+} to be on the A sublattice be $\mathcal{E}_a$, on the B sublattices $\mathcal{E}_b$. Per mole of material there will be N sites available on the A sublattice and 2N on the B sublattice. Let y be the fraction of the R cations on the A sublattice.

The number of ways this can be done is:

$$W = \frac{(3N)!}{(Ny)! \left[N(1-y)\right]^2 \left[N(1+y)\right]}$$

(7)

Upon using Stirling's approximation:

$$\ln W = \text{const.} - N \left[ y \ln Ny + 2(1-y) \ln N (1-y) + (1+y) \ln N (1+y) \right]$$

The number of filled sites is given by

$$N = yN + (1-y)N.$$  

The total energy is:
E = \varepsilon_a y^N + \varepsilon_b (1-y)^N.

These three conditions must be stable with respect to variations in y. Thus:

\[ \frac{y(1+y)}{(1-y)^2} = \exp \left( -\frac{\Delta \varepsilon}{kT} \right) \]

\[ \Delta \varepsilon = \varepsilon_a - \varepsilon_b \]  \hspace{1cm} (8)

At 0^\circ K, for \Delta \varepsilon < 0, y = 0, the spinel will be normal. Conversely for \Delta \varepsilon > 0 the spinel will be inverted. This situation would be the final equilibrium state. For materials cooled in a finite time a steady state will be reached depending upon the relative magnitude of the right side of Eq. 8 and the magnitude of the ionic mobility.

Studies of the magnetic moment of magnesium ferrite as a function of temper have been carried out by Kriessman, Harrison and Callen.\textsuperscript{20} They have found that Eq. 8 does not fit their data, but rather an equation similar to it where \( \Delta \varepsilon = \Delta \varepsilon_0 - \xi y \) where \( \xi \) is a constant. This would mean that the energy necessary for a cation to go from one sublattice to the other is a function of the sublattice population. Néel considers the series Mn, Fe, Co, Ni, Cu, Zn to be one of decreasing magnitude of \( \Delta \varepsilon \) from Mn (See Fig. 25) to Cu, then becoming positive for Zn. Thus the ferrites most likely to be retained in a metastable condition would be those of Cu and Zn. That the structure insensitive properties of CuFe\textsubscript{2}O\textsubscript{4} is a function of temper is well known, this case was treated by Néel.\textsuperscript{13}

It has also been reported\textsuperscript{21} that ZnFe\textsubscript{2}O\textsubscript{4} can be made magnetic by quenching from 1400\textdegree C.

A theoretical analysis of possible cations distributions has been carried out by Smart.\textsuperscript{22}
3.6 Properties of \( \text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \), Experimental and Discussion

3.6.1 The Magnetic Moment. In conjunction with Professor S. Legvoel of the Low Temperature Laboratory, Iowa State College, magnetic moment data were taken on samples with \( x = 0.6, 0.7, 0.8 \) and 0.9. The data were taken using a Gouy type balance. Fields up to 18,200 oe were used. The temperature range from 20°K to room temperature was investigated on two samples, from 80°K to room temperature on two other samples. Curves taken for \( H = 18.2 \text{ Koe} \) and \( H = 12 \text{ Koe} \) are shown in Fig. 26.

The magnetic moment for the larger values of \( x \) increases between \( H \) of 12 and 18.5 Koe. From more detailed data, the moment is still rising at the largest value of magnetic field utilized.

For large values of \( x \), the \( \sigma \) vs \( T \) curves tails slowly toward the axis. Thus the concept of a fairly definite Curie point for the material as a whole ceases to exist.

On the samples measured, the moment goes through a definite maximum as a function of temperature. This is not quite in accordance with the paramagnetic data of Neel and Brochet\(^{23} \) which predicts that the material when cooled below its Curie temperature should follow a curve of type \( Q \), Fig. 23. Type \( Q \) material should have a monotonic decreasing magnetic moment as a function of temperature. The \( \alpha-\beta \) plane is depicted in Fig. 27 for two values of \( \lambda/\mu \). It is seen that a slight shift of the points could move the material from a region predicting type \( Q \) to one predicting type \( P \) behavior. Type \( P \), see Fig. 23, predicts a maximum in the \( M-T \) curve.

3.6.2 The Heat Capacity. Heat capacity data were taken using equipment described in Progress Report No. 1, Task 6, EDG, January, 1953.

The heat capacity of the same samples considered in the previous section
FIG 26

VARIATION OF MAGNETIC MOMENT WITH TEMPERATURE FOR Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$
in addition to one with \( x = 1 \) was measured from \( T = 5^\circ K \) to \( 300^\circ K \). The results are depicted in Figs. 28 and 29. Obviously, there is a maximum in the curves at \( T = 9.3^\circ K \). This takes the form of a sharp spike for \( x = 1.0 \), and is more spread out as \( x \) decreases. The effect is still obvious for \( x = 0.6 \). It is to be noted that the sharpness of this effect is in direct contradiction with the results of Friedberg, et. al.

According to Corliss and Hastings\(^{21}\) below the transition temperature there is some type of antiferromagnetic ordering on the \( B \) sublattice. Above that temperature all ions are oriented paramagnetically. These points will be expanded in the next section. Perhaps an equally important though negative result is the absence of any irregularities in the heat capacity curve other than the \( 9.3^\circ \) one.

3.6.3 Discussion. From the experimental results of the two previous sections we seek answers to the questions of the type of \( B \) sublattice ordering present below \( 9.3^\circ K \), if one can find experimental confirmation of Yafet and Kittel's\(^{18}\) predictions, what produces the measured variance of the \( 9.3^\circ \) peak with nickel content, and how is this related to the observed magnetic properties? Further, can an understanding of these phenomena in any way aid the interpretation of the magnetic effects described in the other sections?

First, let us consider the question of the type of magnetic ordering found on the \( B \) sublattice below about \( 9.3^\circ K \). Yafet and Kittel\(^{18}\) have shown that the lowest energy arrangement is the same for the \( B \) sublattice subdivided into two sublattices as when it is subdivided into four sublattices in the absence of anisotropy. Wannier\(^{25}\) has shown that a simple antiferromagnetic ordering cannot exist in a planar triangular lattice. Thus some more complicated ordering structure must be involved. A simple calculation shows that for minimum energy, a configuration similar to that shown in Fig. 30a would be present.
FIG. 28
LOW TEMPERATURE HEAT CAPACITY
OF Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$
FIG 29
HEAT CAPACITY OF Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$
If this is the type of ordering, then the presence of a Ni$^{2+}$ cation carrying a spin of 1 on a B site with a nearest neighbor A site Fe$^{3+}$ (for local electrical neutrality) would surely strongly alter the molecular field coefficients and thus either strongly alter or eliminate any such transition. It would also effect second nearest neighbor molecular field coefficients. To qualitatively account for this effect, assume the magnetic heat capacity of pure ZnFe$_2$O$_4$ to be a delta function with the spike at 9.3°K, the presence of Ni is assumed to eliminate the contribution to the spike from all its nearest neighbors. On the basis of this model one proceeds to calculate the height of the specific heat curve at the transition temperature. For ease in calculation we count the fraction of groups of four B site cations composed of four Fe$^{3+}$ cations and surrounded by its ten nearest neighbor A site cations all of Zn$^{2+}$. If the nickel is randomly oriented on the B sites, and the zinc is wholly on the A sublattice the probability of a specified group of four B site cations to be Fe$^{3+}$ is given by $[(1+x)/2]^4$. The probability that the ten nearest neighbor A sites to this group of four B sites be occupied by Zn$^{2+}$ is $x^{10}$. If local electric neutrality is required the probability goes to $x^8$. Thus, the probability of a specified group of four B site cations to be all Fe$^{3+}$ and surrounded by ten nearest neighbor A
site cations of Zn$^{2+}$ is, if local electrical neutrality is required, given by:

$$P(x) = \left(\frac{(1+x)/2}{2}\right)^4 \times 8$$

Table 5 lists $P(x)$ as a function of $x$.

\begin{table}[h]
\centering
\caption{Tabular Values of $P(x)$}
\begin{tabular}{|c|c|}
\hline
$x$ & $P(x)$ \\
\hline
1   & 1.000  \\
0.9 & 0.351  \\
0.8 & 0.110  \\
0.7 & 0.030  \\
0.6 & 0.007  \\
\hline
\end{tabular}
\end{table}

To compare with experiment, it would be desirable to normalize the experimental height of the peak for $x = 1$ to one, then compare the results with Table 5. Unfortunately, the height of the peak, if there is one, cannot be determined. We therefore compare by normalizing the experimental value for $x = .9$ to be .351. The measured heat capacities at 9.3$^\circ$K were corrected for the lattice contribution by extrapolating from the K. K. Kelly pamphlets. The values are given in Table 6. It is observed that $P(x)$ drops faster than experiment below $x = .9$, but is too weak a function of $x$ above. At least the curves vary in the same way.

\begin{table}[h]
\centering
\caption{Comparative Anomaly Heights}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
$x$ & $C_{9.3^\circ K}$ & $C_{1}$ & $C_{m}$ & $P'(x)$ & $P(x)$ \\
\hline
1.0 & 8     & .070  & 8     & 1.99   & 1.000  \\
.9  & 1.657 & .069  & 1.588 & .351   & .351   \\
.8  & .784  & .068  & .716  & .158   & .110   \\
.7  & .432  & .067  & .365  & .081   & .030   \\
.6  & .201  & .066  & .135  & .030   & .007   \\
\hline
\end{tabular}
\end{table}

It is known,\textsuperscript{26} that lithium ferrites contains an ordered face centered cubic array of Li$^{+1}$ cations on the B sublattice. Further, Li$^{+1}$ carries no unpaired
electrons. Thus if it be assumed that small amounts of Li also form f.c.c. structures, the effect upon the local molecular fields should be considerably different from Ni^{2+}. One possible sublattice arrangement would be for the spins of the remaining three ferric ions to be oriented as shown in Fig. 30b.*

For the case \( x = 0.9 \) above the A sublattice contains, assuming ZnFe_{2}O_{4} to be completely normal and NiFe_{2}O_{4} inverted, \( (0.9 \text{Zn}^{2+} + 0.1 \text{Fe}^{3+}) \) cations, the B sublattice contains \( (1.9 \text{Fe}^{3+} + 0.1 \text{Ni}^{3+}) \) cations. If now a lithium-zinc ferrite were made which had the same cations on the A sublattice, the B sublattice would contain \( (1.95 \text{Fe}^{3+} + 0.05 \text{Li}^{+1}) \) cations. If the Li^{+1} were randomly distributed, heat capacity results similar to the nickel-zinc ferrite would be expected. If, however, the Li^{+1} were ordered in some manner this would be expected to alter the "averaged" local fields and thus the transition temperature as well as its magnitude.

Such a sample was prepared and measured. The results are shown in Figs. 31a and 31b. The transition temperature has indeed been altered and stands at about 7.20K.

Since the height of the heat capacity curve for zinc ferrite is, according to the statistical arguments, very dependent upon any inversion the sample was made with considerable care. Weighed quantities of dried ZnO and Fe_{2}O_{3} were milled for six hours in a hardened steel ball mill using a dilute acetone slurry. After passing the slurry through a magnetic separator, the bulk of the acetone was decanted and the remainder evaporated. Fifty gram slugs were pressed, the surface layer removed, and the slugs fired for 14 hours in air at 1100\(^{0}\)C.

After furnace cooling, the slugs were broken in a hardened steel

* This was originally proposed by Dr. B. A. Calhoun, Westinghouse Research Laboratories, during a private discussion.
FIG 31b

HEAT CAPACITY OF LITHIUM FERRITE
(Li_{0.5}Zn_{0.9}Fe_{2.05}O_{4})
"diamond mortar" to pass a 30 mesh screen. These granules were again formed into slugs and refired at 1100°C for 12 hours with an intervening hour at 1200°C. The refiring was done in air within a closed furnace with ZnO slugs present. After gradual cooling of the furnace, the accompanying zinc oxide slugs were still white. The resulting ferrite granules were of a uniform brownish color throughout.

Two chemical and spectrographic analysis of the ZnFe₂O₄ by the Detroit Testing Laboratories gave the following results:

Chemical analysis

<table>
<thead>
<tr>
<th>Test No. 1</th>
<th>Test No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage by weight</td>
<td>Zn 27.35  Zn 27.00</td>
</tr>
<tr>
<td></td>
<td>Fe 46.24  Fe 46.24</td>
</tr>
<tr>
<td>Ideal 1/1 mole ratio</td>
<td>Zn 27.12</td>
</tr>
<tr>
<td></td>
<td>Fe 46.33</td>
</tr>
</tbody>
</table>

Spectrographic Analysis

.01 - .1 percent Ca, Cu, Mg
Al
Mn Ni, Si

It is believed that at least some of the difference between our results and those of Friedburg is due to differences in manufacturing techniques for the two samples. However, the difference may also be due to the extended periods necessary for thermal equilibrium to be established (up to 43 hours) below the transition temperature. Another sample prepared in the same fashion has been sent Dr. Hastings of the Brookhaven National Laboratories for neutron diffraction measurements.

According to Yafet and Kittel, one test for experimental confirmation of their theory would be the presence of irregularities in the specific heat curve for the composition we have called \( x = 0.3 \). No such irregularities exist.
However, using the statistical arguments it would be expected that the any such transition should only be local in effect. Thus, any contribution would be very broad and as such probably not possible to measure. Thus, no conclusions can be drawn.

We now turn to a consideration of the magnetic saturation data. From the shape of the $x = 0.9$ curve it is apparent that the definition of a Curie point would be rather nebulous. This, too, is to be expected from the standpoint of fluctuations in the local field, for each region would carry its own Curie point.

An item of note is the difference in value of $\sigma$ (see Fig. 26) as a function of applied field for large values of $H$. Three plausible explanations are:

(1) The small volumes of ferrimagnetic regions surrounded by antiferromagnetic regions have their magnetic moment oriented in the field direction quite analogous to a paramagnetism. (2) The local field is increased by the external field, thus inducing a larger fraction of the material to be below its Curie point than in the absence of the field. (3) Angles of the type proposed by Yafet and Kittel exist locally and are decreased by the action of the applied field.

Items (2) and (3) both yield a term too small to account for the increase in $M$. As shown by Brown, item (1) should yield a term proportional to $1/H$.

Experimentally, we find closer agreement with a term proportional to $H$. However, neither the theory nor the experimental data are believed good enough to allow a definite statement of behaviour, and the theoretical magnitude can be made large enough to account for the change observed. Therefore, explanation (1) above seems the most plausible.

In summary, it is believed that the behaviour of nickel-zinc ferrite can be qualitatively explained on the basis of a random distribution on nickel cations on the B sublattice. This model can be extended to include materials now being
used for their large permeability. It is obvious that any attempt to produce locally zero magnetostrictive constants or arisotropy would be abortive, but local regions containing opposites signs would be possible, and thus a macroscopic zero would be possible. Further the permeability dispersion curve cannot be fitted to a simple differential equation with constant coefficients. However, quite good agreement can be obtained by averaging the coefficients over a given range. The model proposed above would require such a variation in coefficients. Therefore, if sharp resonances are desired simple type ferrites must be used.

3.7 Temperature Effect on $\mu$-Q for Differing Ferrous Iron Contents

In conjunction with the studies reported in Section 3.2 of this report, it was desired to know how much of the magnetic properties could be directly linked to the ferrous iron content in the material. A step in this direction was to measure the magnetic properties as a function of temperature.

The apparatus used had been built previously. It is shown schematically in Figure 32. The temperature of the test chamber is adjusted by controlling the energy input into the heating coils. The Q-meter reading have to be corrected for losses due to the length of lead used. No correction were made for the extra capacitance introduced.

The results are shown for cores A-532-1 and A-507-1. A-532 had a stoichiometric composition, core A-507-1 was composition five (See Sec. 3.2). Figs. 33a and 33b show the results on two material types.

The real part of the permeability is quite temperature dependent for A-532-1, but the phase angle is not temperature dependent. Just the inverse is true for A-507-1. Although the phase angle undergoes a considerable change in A-507-1 between $-40^\circ$ and $0^\circ$C the permeability remains fairly constant. Also, the order of the frequency points change between these two temperatures.
FIG 32
NITROGEN CRYOSTAT
FIG 33b

Q vs TEMPERATURE
4. CONCLUSIONS

4.1 Q-Meter Measurements

It has been possible to account for the variation of the permeability spectrum as a function of the number of turns wound on the specimen. This in turn imposes quite serious limitations on the Q-meter measurement as a method of obtaining accurate results. The important points are the variation in size of the applied ΔH with frequency, the capacitive effects of the windings, and the effective wire resistance.

4.2 Iron-Rich Nickel Zinc Ferrites

Since a technical report including this subject is to be issued shortly, the results have not been described in detail in this report. The important points are the variation of μ and Q with quenching and annealing, the variation of μ and Q with ferrous iron content, the variation of ferrous iron with time and temperature, and thus its apparently important role in the spinel formation. The equilibrium value of ferrous iron as a function of nickel-zinc content and temperature was not previously known. This provides an opportunity for study of materials with controlled ferrous iron content. (See Sec. 3.7).

4.3 Effect of Grain Size on Magnetic Properties

Aside from the preliminary data discussed in Task 6 Quarterly Progress Report No. 8, Section 3.3, the important points to date arise from the difficulties involved. First, the difficulty of the decreasing permeability with time has emphasized the problems of zinc volatility and zinc cation placement. This would result in intraspecimen variations.

To circumvent this difficulty, V₂O₅ was added to the mix. It has been found that this decreases the necessary firing temperature up to 400°C.
constitutes proof that mineralizers or fluxes exist which augment the spinel formation reaction. Since this is the case, small quantities will greatly effect the resulting properties, whether added accidentally or purposefully. What other agents act in this manner (B₂O₃, Cr₂O₃ and MoO₃ do not) is not known but it can be immediately predicted that raw materials containing V₂O₅ as an impurity will produce quite different cores than those made without this impurity! The proper firing temperature is a function of the amount of V₂O₅ present.

4.4 Cobalt, Iron Nickel, Zinc Ferrites

The analysis of the curves presented in Section 3.4 has not as yet been carried out in satisfactory manner, if indeed it is possible to do so. The only conclusion drawn at the moment is that it is possible to obtain dramatic changes in the variation of μ and C with biasing fields with the proper choice of cations and firing conditions.

4.5 Structure and Properties of Ni₁₋ₓZnₓFe₂O₄

There is a thermal anomaly at about 9.5⁰K in ZnFe₂O₄. This is carried over to specimens containing some nickel. It is believed that this is due to a transition from the paramagnetic to the antiferromagnetic state as the temperature decreases. Just what type of ferromagnetic ordering is involved is not understood at present.

Magnetic moment measurements and the statistical model of the variation of the local fields indicates that the concept of Curie Temperatures loses significance as the percentage of nickel decreases. Instead there would be localized regions carrying aligned magnetic moments. The size and number of these regions decreases as the temperature increases.

No indication of a Yafet and Kittel type transition in a nickel zinc
ferrite was found. Because of the small percentages of nickel present when the result was predicted it is believed that localized variations would cause differing temperatures at which these changes in magnetization would occur. The result would, therefore, be spread out and probably not observable.

5. PROGRAM FOR THE NEXT INTERVAL

5.1 Q-Meter Measurements

It is hoped that curves showing the variation in permeability with the size of the $\Delta H$ field as a function of frequency can be obtained during the next period.

5.2 Iron-Rich Nickel Zinc Ferrites

The future program here has not been decided at present, and will be held pending until the forthcoming technical report is completed.

5.3 Effect of Grain Size on Magnetic Properties

It is expected that four batches of cores will be made, with two different mean permeabilities. For each permeability, one batch will be treated by a fairly high firing temperature and a short firing time—the other by a long firing time and a lower temperature. (Both times and temperatures to be long enough for the spinel formation to be completed.) The grain sizes in these mixtures will be determined.

The material is purposefully not prefired and ground to a specified grain size since maximum intergranular contact is to be desired.

5.4 Effect of Fluxes

It is expected that the effect of differing quantities of $V_2O_5$ will be determined. An effort will be made to understand the role of the flux.


5.5 Cobalt, Nickel, Iron, Zinc Ferrites

The type of data presented in Section 3.1 will be obtained at higher frequencies. Parallel field data at 500 kc will also be obtained. Further manufacture awaits these results. A theoretical interpretation of the variation of $\mu$, $Q$ with the internal magnetization values will be attempted.

5.6 Magnetization Mechanisms

The precise conditions under which magnetization by wall movement, and magnetization by rotation, occurs have never been shown. The question is whether or not magnetization occurs by rotation when the material has been initially fired, then gradually shades to wall movement as the firing time or temperature increase and the resulting grain size increases. In order to study the question, a detailed analysis of the frequency spectra of nickel-zinc ferrites fired various lengths of time will be made. This is currently well underway but it is too early to quote results. If the spectra seems similar for all cores such that one could conclude magnetization by rotation in the manner shown by Park, then it is planned to study material with a higher anisotropy constant, i.e., either a magnesium or a cobalt series.
REFERENCES


28. University of Michigan, EDG, Quarterly Progress Report No. 8, Task 6, Sec. 3.6, September, 1954.
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