ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

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

QUARTERLY PROGRESS REPORT NO. 9, TASK ORDER NO. EDG-6
Period Covering October 1, 1954 to December 31, 1954

Electronic Defense Group
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Project 2262

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TASK ORDER

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

Purpose of Task:

To further the development of ferrospinels 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. Grimes

Countermeasures Branch, Evans Signal Laboratory:

Project Engineer: Mr. Leon I. Mond

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.

I. O. MYERS
Contracting Officer's Technical
Representative

ABSTRACT

An investigation of the magnetic properties of basically nickel-zinc ferrites with the addition of excess iron and the addition of different weight univalent materials is described. The univalent materials described are potassium, sodium, lithium and nothing. It is found that Q values considerably higher than for plain nickel-zinc ferrites can be obtained in this manner. The study of the correlation between grain size and magnetic properties is continued. A recheck of mean grain size using improved experimental techniques is reported. The temperature dependence of the magnetic Q is reported.

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

QUARTERLY PROGRESS REPORT NO. 9, TASK ORDER NO. EDG-6
Period Covering October 1, 1954 to December 31, 1954

1. PURPOSE

The purpose of this report is to summarize the progress made by Task 6 of the Electronic Defense Group from October 1, 1954 to December 31, 1954 on Signal Corps Contract No. DA-36-039 sc-63203.

The purpose of the task is to further the development of ferrospinels of different incremental permeabilities and low losses, with reference to specific applications of interest to the Signal Corps such as r-f 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

Professor E. F. Westrum, Jr., and Mr. D. M. Grimes attended the Conference of Ferrimagnetism held at the Naval Ordnance Laboratory, White Oak, Maryland, October 11 and 12, where they read a paper entitled "Low Temperature Heat Capacity Anomaly in Nickel Zinc Ferrite."

On November 9, Mr. D. M. Grimes visited the Carboloy Corp., Detroit, Michigan, for an inspection of their hot pressing and extruding apparatus used in the manufacture of carbides.

3. FACTUAL DATA

3.1 Specific Heats

It is expected that a technical report will be written during the coming quarter describing the work on specific heat in detail. Therefore, it will not be discussed here.

3.2 The Effect of Univalent Cations

The study of the effect of greater than 50 mole % Fe_2O_3 and added univalent cations to a nickel zinc ferrite was continued. The series of measurements designated as firing series 5 was designed to find, for the firing procedure used:

(a) The effect of additional iron oxide together with additional univalent oxides, computed according to

$$\left[R_2O\right] = \frac{1}{2}\left\{\left[Fe_2O_3\right] - 0.5\right\} .$$

(b) The effect of a differing $\left[NiO/ZnO\right]$ ratio for different values of $\left[Fe_2O_3\right]$.

(c) The effect of substituting nothing, Li, Na or K for R in (a) above.

The series was fired at 1375°C for four hours, then cooled at 60°C/hr. in an oxygen atmosphere. The results are given in Table I.

The μQ product for the E type core increases to the maximum value obtained in the upper left corner (see Table I). For type D the maximum is for $\left[Fe_2O_3\right] = .585$, and $\left[\frac{NiO}{ZnO}\right] = 1.1$ or 0.9.

Frequency spectra were run using the permeameter for several of the interesting cores. Data are given in Table II for several cores.

Two items are worth pointing out: 1)in the type A core, μ_2 drops after passing through a peak of the order of five, 2) the frequency of rapid increase in μ_2 is higher than for a 50 mole % Fe_2O_3 nickel zinc ferrite. To determine the

TABLE I

2 MC DATA ON UNIVALENT SUBSTITUTED,

EXCESS IRON, NICKEL ZINC FERRITE

Code	μ_1	Q	μQ	Code	μ_1	Q	μQ	Code	μ_1	Q	μQ
$\left[\frac{NiO}{ZnO}\right]$ = 1.1, $[Fe_2O_3]$ = 0.550				$\left[\frac{NiO}{ZnO}\right]$ = 1.1, $[Fe_2O_3]$ = 0.585				$\left[\frac{NiO}{ZnO}\right]$ = 1.1, $[Fe_2O_3]$ = 0.620			
-101	197	--	--	C-107	110	--	--	C-104	30	--	--
-101	243	57	13,850	D-107	101	176*	17,800	D-104	47	98	4,600
					104	154*	16,000				
-101	226	94	21,200	E-107	78	113	8,800	E-104	8.7	48	420
$\left[\frac{NiO}{ZnO}\right]$ = 0.9, $[Fe_2O_3]$ = 0.550				$\left[\frac{NiO}{ZnO}\right]$ = 0.9, $[Fe_2O_3]$ = 0.585				$\left[\frac{NiO}{ZnO}\right]$ = 0.9, $[Fe_2O_3]$ = 0.620			
-324	270	40	10,800	A-325	50	50	2,500	A-326	48	170	8,160
-102	233	30*	6,990	C-108	116	58*	6,700	C-105	41	70*	2,870
-102	261	47	12,300	D-108	98	145*	14,200	D-105	46	65	2,990
					100	165	16,500				
-102	223	70	15,600	E-108	82	118	9,700	E-105	11	38	418
$\left[\frac{NiO}{ZnO}\right]$ = 0.7, $[Fe_2O_3]$ = 0.550				$\left[\frac{NiO}{ZnO}\right]$ = 0.7, $[Fe_2O_3]$ = 0.585				$\left[\frac{NiO}{ZnO}\right]$ = 0.7, $[Fe_2O_3]$ = 0.620			
-103	234	30	7,000	C-109	100	57*	5,700	C-106	51	73*	3,700
-103	275	40*	11,000	D-109	118	94	11,100	D-106	46	63	2,900
-103	270	51	13,800					E-106	11.5	35	403

Note: μ_1 was measured on the permeameter, and the Q was measured on a Q meter.
* Showed a drift in Q values.

Code: Type A - no univalent cation;
Type C - Lithium added;
Type D - Sodium added;
Type E - Potassium added.

TABLE II

MAGNETIC SPECTRA FOR FOUR UNIVALENT SUBSTITUTED FERRITES

Type	Frequency	μ_1	μ_2
A-326-1	0.9	46.0	----
	2.0	48.5	.29*
	5.0	49.4	.95
	10.0	53.1	4.8
	18.0	11.2	1.1
D-108-2	2.0	100.0	.56*
	5.0	99.7	..76
	10.0	99.0	3.6
	18.0	18.1	6.7
E-101-1	0.9	199.5	----
	2.0	266.5	2.5*
	5.0	245.5	6.1
	10.0	312.7	118.0
	18.0	296.6	299.0
E-104-1	0.9	8.2	----
	2.0	8.7	.18*
	5.0	8.9	.14
	10.0	8.6	.37
	18.0	8.9	.61

* Q-meter readings.

extent to which these effects can be attributed to the excess Fe cations, and how much to the univalent materials, a series of six core types were made around the composition of D-108. The composition is 58.5 m% Fe_2O_3, 4.25 m% Na_2O, 17.65 m% NiO, 19.61 m% ZnO. Sodium variations ranging from none to twice the amount of D-108 were taken. The resulting frequency specrta are shown in Fig. 1. Note that for the D-108 composition, the μ_2 rise occurs at the highest frequency, and that also for this value the lowest low-frequency μ_1 occurs.

To determine the effect of excess iron, samples containing different amounts were made. Table III shows the results.

TABLE III

MAGNETIC SPECTRA FOR EXCESS IRON FERRITES

Type	m%Fe_2O_3	Sample No. 1 μ_1	Q	μ_1Q	Sample No. 2 μ_1	Q	μ_1Q
A-322	50.	386	4.1	1580	386	4.1	1580
A-323	52.25	521	12	6250	564	11	6200
A-324	55.0	269	40*	10760	287	76*	21800
A-325	58.5	50.1	50*	2500	---	---	----
A-326	62	48.5	168*	8150	47.2	175*	8260

Note: The other data were taken from permeameter. Asterisk indicates data from Q-meter.

Firing T = 1375°C

Cool 60°C/hr. in O_2

$\left[\frac{NiO}{ZnO}\right] = 0.9$

Table IV shows a frequency spectrum for the two A-326.

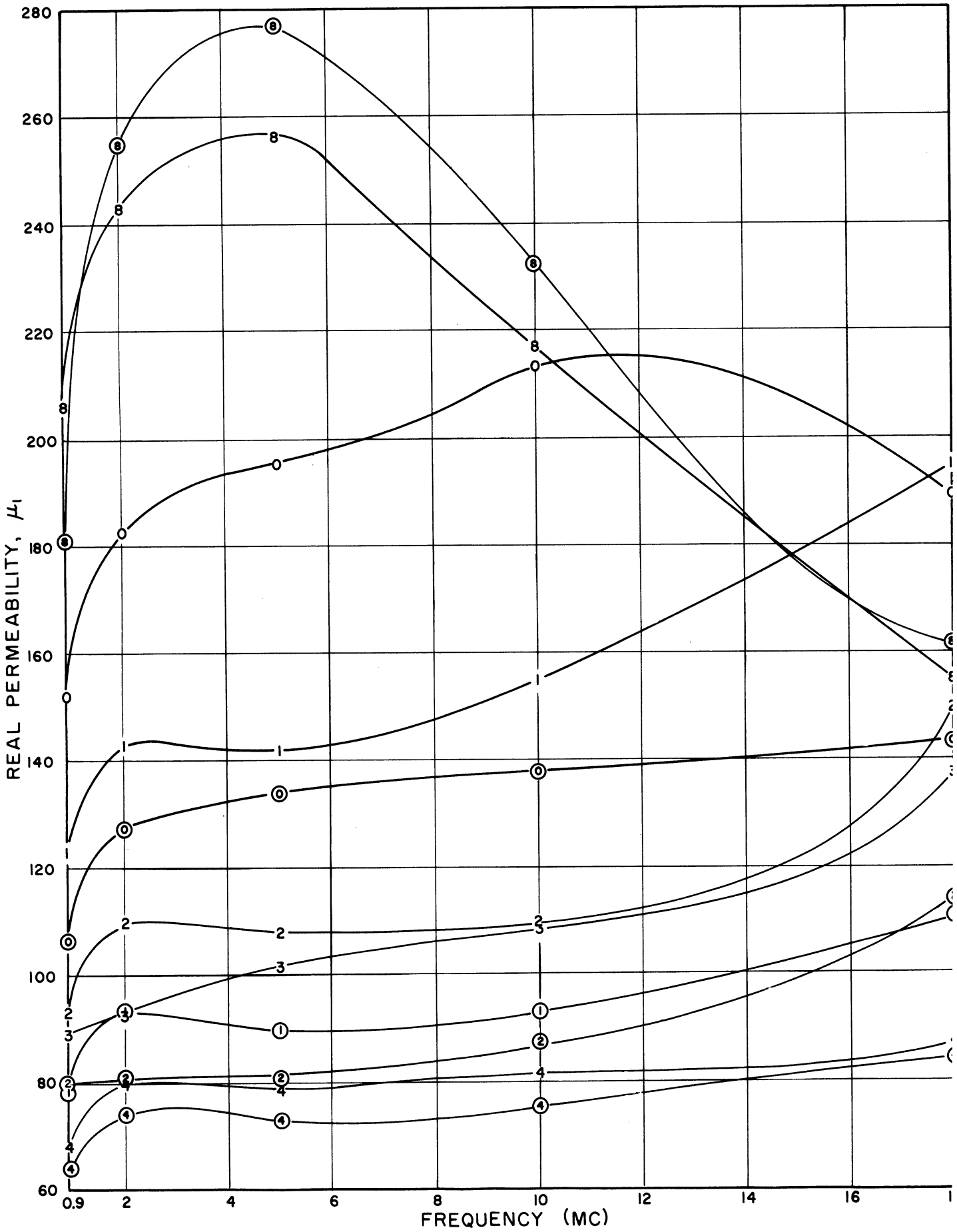

FIG 1a

MAGNETIC SPECTRA OF Na-Ni-Zn-Fe^{++}-FERRITES AS A FUNCTION OF Na-CONTENT

CURVES NO 4 REPRESENT D-108. i-TH CURVE HAS i/4 TIMES THAT Na CONTENT

FIG 1b
MAGNETIC SPECTRA OF Na-Ni-Zn-Fe^{++}-FERRITES
AS A FUNCTION OF Na-CONTENT

CURVES NO 4 REPRESENT D-108. i-TH CURVE
HAS i/4 TIMES THAT Na CONTENT

TABLE IV

COMPARISON OF FREQUENCY SPECTRA ON TWO SIMILAR CASES

Core	Frequency	μ_1	Q
A-326-1	2.0	48.5	168*
	5.0	49.4	52
	10.0	53.1	11
	18.0	11.2	10
A-326-2	2.0	47.2	175*
	5.0	48.5	47
	10.0	51.7	12
	18.0	12.6	13

Note: Asterisk indicates data taken from Q-meter.
The other data were taken from the permeameter.

Tests of the sodium-containing cores indicate that firing at a lower temperature of 1150°C, followed by slow cooling, yields results nearly the same as for the 20-30 nickel zinc ferrites (see dashed lines of Fig. 2).

A series of Na cores were made by placing them in a furnace at a specified temperature, holding that temperature for one hour, then air quenching. The high frequency characteristics of some of these cores are particularly interesting. An especially interesting example is core D-150-1. The VHF measurements on this core are shown in Fig. 2. The solid curves represent D-150-1, the dashed curves are data on 20-30 Ni-Zn cores.

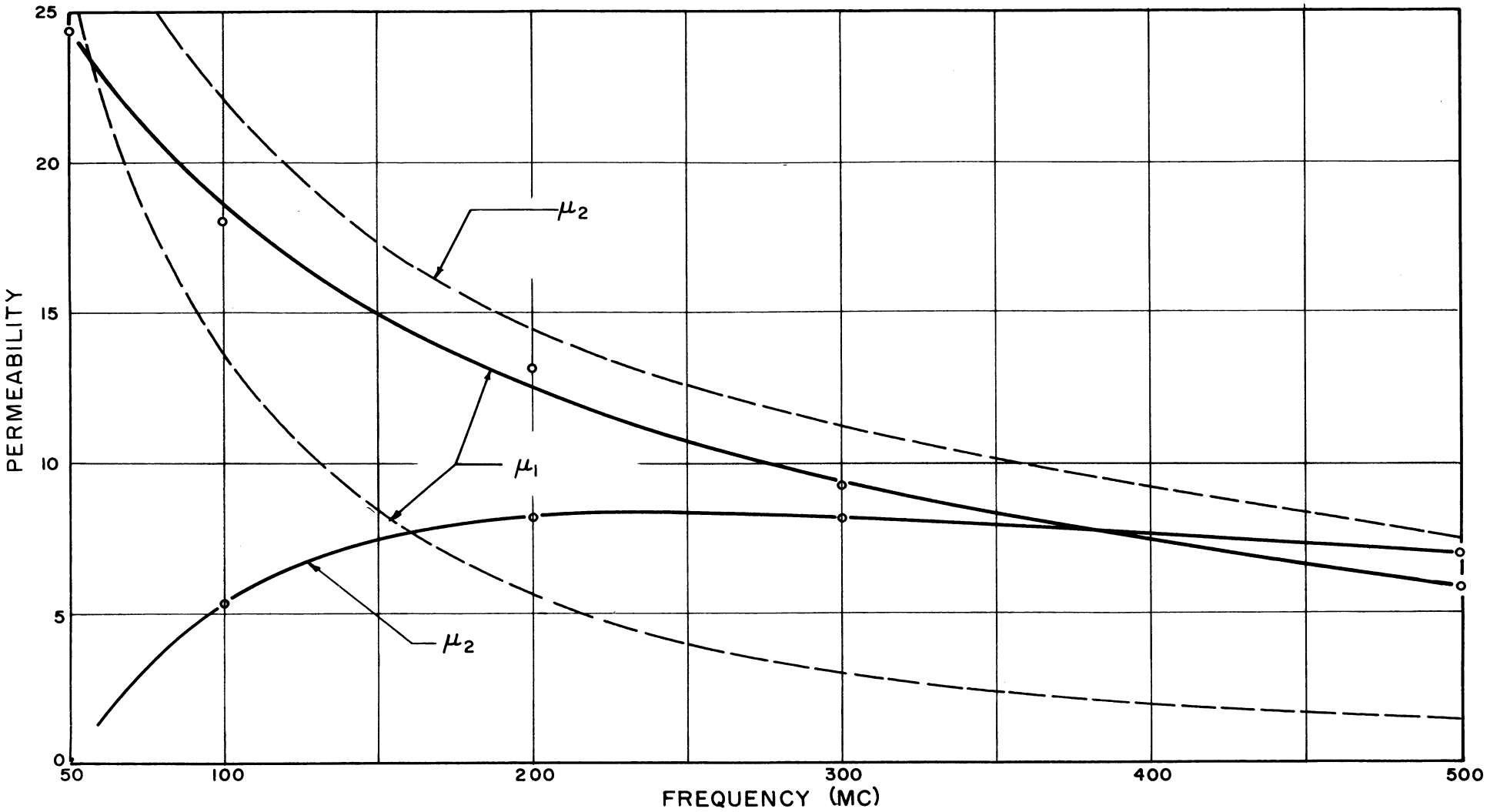

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FIG 2
PERMEABILITY SPECTRA OF AN EXCESS Fe
Ni-Zn-FERRITE WITH ADDED Na

DASHED LINES REPRESENT AVERAGE FOR TYPE A CORES

3.3 The System $\left[Ni_xZn_yFe_zFe_2O_4\right]$

The following study is being undertaken to investigate the effects of excess iron. Materials with a fixed $\left[\frac{Ni}{Zn}\right]$ ratio of 0.9 and differing iron content were made as shown in Table V.

TABLE V

MOLE FRACTION OF CONSTUIENT OXIDES BY TYPE DESIGNATION

Type	Mole Fractions		
	NiO	ZnO	Fe_2O_3
I	.2337	.2663	.5000
II	.2219	.2465	.5316
III	.2065	.2294	.5641
IV	.1842	.2048	.6110
V	.1613	.1791	.6596

This investigation is incomplete. The present trend is described here and a technical report will be issued when the study has been completed.

The cores (Types A-327 to A-350) were placed in the furnace and held at a fixed firing temperature. They were left for four hours then air quenched. Figure 3 shows the resulting μ_1 and Q at 2 mc as measured on a Q-meter. The optimum values of μ_1 and Q are seen to occur in the neighborhood of 1200°C. These samples were analyzed for Fe^{++} content. Fe^{++} and Q are shown in Fig. 4 for Type V. Note that the change in Fe^{++} with T is very rapid and thus shows considerable scatter. The limiting parameter is the temperature control. If the Q is a function of Fe^{++} only, a plot of Q vs. Fe^{++} should not show this scatter. Such a plot is shown in Fig. 5.

FIG 3

MAGNETIC PROPERTIES OF Ni-Zn-FERRITES VS FIRING TEMPERATURE

$[Fe_2O_3]$ AS MOLE FRACTION:

- ○ [.5641] —— μ_1
- + [.6110]
- ▵ [.6596] ---- Q

$\therefore \frac{[Ni]}{[Zn]} = 0.9$

FIG 4

MAGNETIC Q AND Fe^{++} CONTENT VS FIRING TEMPERATURE

FIG 5
MAGNETIC Q VS Fe^{++} CONTENT

3.3.1 Investigation of Reaction Rate. In order to follow the progress of the solid state reaction as a function of time, the cores were fired by varying the length of time at a given temperature.

Figure 6 shows the change in μ_1 with time on Composition V at two temperatures. It appears that at higher temperatures the Q reaches a maximum very rapidly and then falls off. At sufficiently high temperatures only the fall off can be observed. This is seen in Fig. 6 where Composition I was fired at 1212° and 1262°C. At 1212°C, Q is constant for a short time and then decreases. At 1262°C, only the decrease in Q is observed.

The change in % Fe^{++} with time is shown for Composition V at 1212°C in Fig. 7. Determinations for other temperatures are in progress.

3.4 The Effect of Grain Size on Magnetic Properties.

An initial investigation of possible statistical correlation of magnetic permeability with grain size was reported in Quarterly Progress Report No. 8. It was stated that although the results looked promising enough to warrant further effort, the percentage of the grains pulled out during the polishing technique was quite large. The percentage of grains pulled out was so large that the reliability of the value of mean grain volume obtained was questioned. During the past quarter a study of polishing techniques has been made. The percentage of the material consisting of voids has been drastically reduced. About 50 linear percent of the material consisted of voids under the original polishing technique. This percentage has been reduced to about 25 under the present polishing technique.

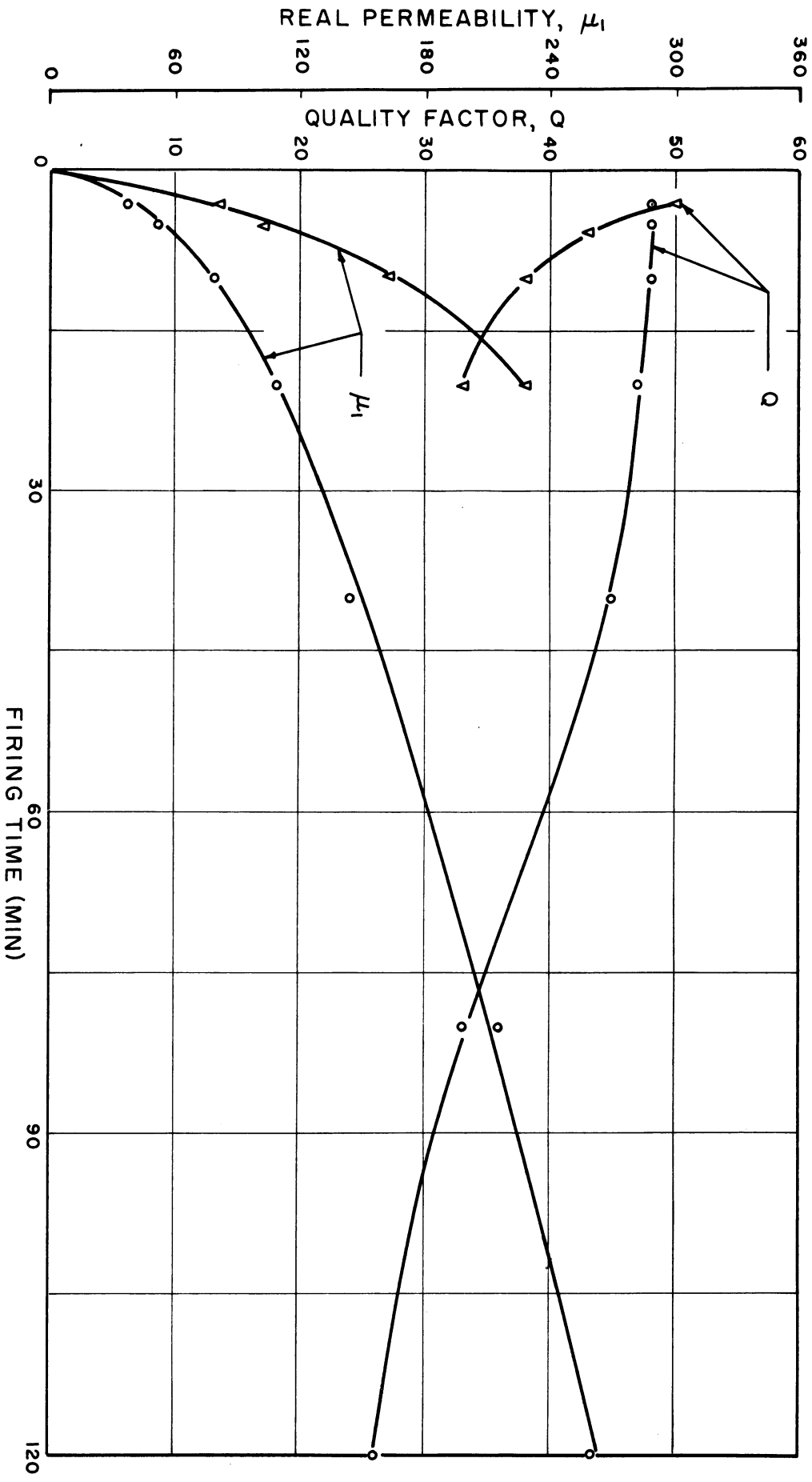

FIG 6

μ_1 AND Q VS FIRING TIME

○ 1212°C

▽ 1262°

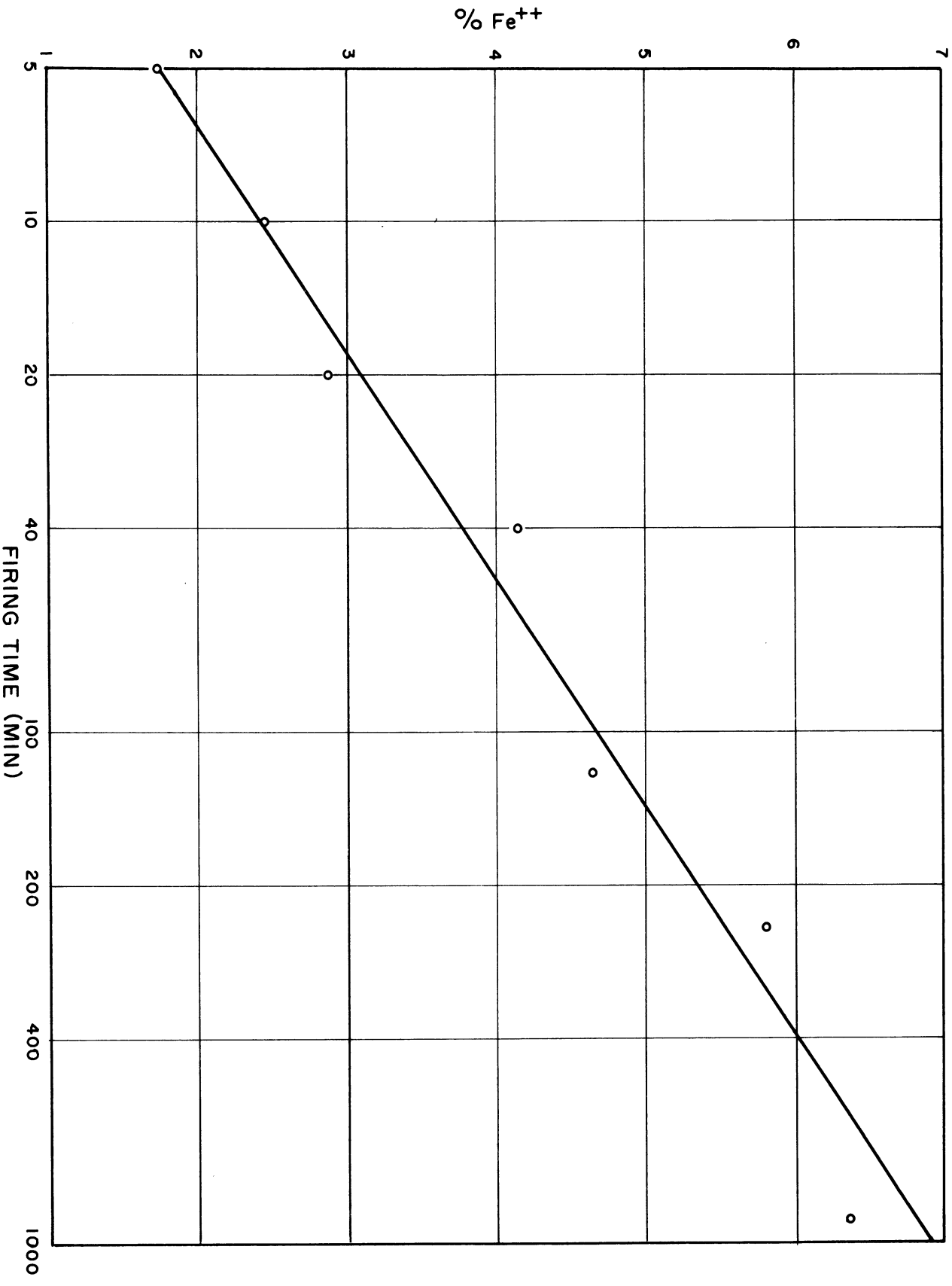

FIG 7
Fe^{++} CONTENT VS FIRING TIME

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An attempt was made to fill up the voids in the specimen (which were present after polishing through 4/0 paper) with some thermoplastic material so that grains could not be pulled out so easily. This was tried in two ways. In one case the specimen was subjected to a partial vacuum and was then covered with fluid thermoplastic material which was allowed to set. In another case the specimen was remounted with a layer of lucite powder below the specimen. Neither method gave an appreciable reduction in the amount of voids.

Next, a polishing cloth with practically no nap was used, together with several different abrasives, in an attempt to reduce the pulling out of grains. The investigations showed that Bursil and gamal cloths, with diamond paste and gamal abrasives, respectively, gave the best results. The new polishing procedure consists of polishing with light pressure through 340A, 1, 0, 2/0, 3/0 and 4/0 papers.

The initial polishing on wheels was done with 6-diamond paste on Bursil cloth at 600 rpm, and the final polishing with gamal abrasive on gamal polishing cloth at 600 rpm. It was found that continued polishing with gamal abrasive helped reduce voids up to a certain minimum limit after which no appreciable effect was observed.

The specimens of the Type A-231 core were polished with diamond paste and gamal abrasives, and were then etched with a mixture of HCl and $SnCl_2$. A photograph of a specimen polished according to the new method, and then etched, is shown in Fig. 8. Table VI gives the difference in mean grain length for each specimen using different polishing procedures. $\bar{\ell}_n$ is the one-dimensional mean grain radius after polishing according to the new technique. $\bar{\ell}_o$ is the same quantity, using the old polishing technique. Note that with the exception of

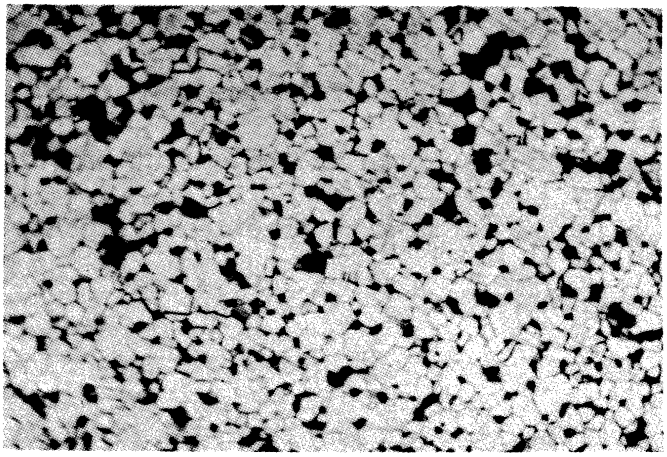

FIG 8

MICROPHOTOGRAPH OF POLISHED AND ETCHED SURFACE

A-231-14 X1000

Numbers 5 and 14, all of the mean grain lengths have decreased very slightly. Numbers 5 and 14 show quite radical differences. These differences[1] put core No. 14 second in mean grain volume and therefore, increases the correlation between permeability and grain volume. However, core No. 5 is correspondingly moved out of position. In the detailed breakdown of counting procedure, the reason for the increase in grain size in both Numbers 5 and 14 is the occurrence of a much larger number of the very large size grains.

3.5 Effect of Temperature on Complex Permeability

In making the Q-meter measurements as a function of frequency, the cores were wound by hand and immediately measured at a 1 mc check point. Then after a few minutes to allow the core to reach room temperature, the core was remeasured. In every case the check point fell high on the curve—roughly, 4 to 7 percent high. Apparently the core was heated to almost body temperature during the hand winding process. To determine the effect of temperature, the following measurement procedure was established. Initially, the core was measured in air. It was then immersed in oil (at room temperature) and remeasured. No change in μ_1 or Q resulted. The oil was then heated. Figure 9 shows the results of the three runs.

TABLE VI

DIFFERENCE IN MEAN GRAIN LENGTH USING DIFFERENT POLISHING PROCEDURES

Core No.	$\bar{\ell}_n - \bar{\ell}_o$ *	$\bar{\ell}_n$
3	-0.0114	1.0074
5	+0.2026	1.0596
13	-0.0455	1.0232
14	+0.1433	1.1633
18	-0.0390	0.8793
19	-0.0374	0.9226
25	-0.0857	1.1846

* The unit of linear measurement used is 2.1 microns.

FIG 9
CORE PROPERTIES VS TEMPERATURE
MEASURED ON Q-METER
CORE NO A-324-2

μ_1 increases almost linearly with temperature. This agrees with the findings of Harvey, et al.[1] This curve is explained as follows. For iron and nickel, anisotropy constant decreases rapidly to zero as the temperature increases. The magnetostriction constant also decreases with temperature, but more slowly.[2] These energies oppose the orientation of the magnetic dipoles away from the zero signal directions. As these energies decrease with temperature, the dipoles are reoriented more easily and the result is a higher permeability. Of course, μ_1 is proportional to the saturation magnetization which decreases with temperature, with increasing rapidity, as the Curie point is neared. The net result is a rising permeability as temperature increases until the neighborhood of the Curie point is attained. μ_1 then decreases rapidly. The rapid decrease in μ_1 was not observed because the cores were not raised to temperatures approaching the Curie point.

4. CONCLUSIONS

The study of the effective addition of univalent cations along with excess iron oxides, shows that the resonant frequency of the material can be materially raised in this way. The permeability spectrum shows that the rapid rise in loss-per-cycle occurs at a frequency at least ten times as high as materials made previously. The question as to whether this is due to the univalent material or the excess iron is partially answered in Section 3.3. A very definite improvement in magnetic properties in the higher frequencies can be obtained by introducing ferrous iron. Apparently the increased eddy current

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1 Harvey, Heggi, and Leverenz, RCA Review, XI, 1950, p 359.

2 Zener, Phys. Rev., 96, Dec. 1954, p 1335.

losses are more than offset by the decrease in other losses. A check on the grain size distribution reported in Quarterly Progress Report No. 8 has been made. The general agreement is quite satisfactory. The polishing procedure has decreased the linear percentage of voids by at least a factor of 2.

5. PROGRAM FOR THE NEXT INTERVAL

It is hoped that the specific heat work can be completed during the next quarter. Whether or not the work can be completed will depend upon the difficulty involved in the manufacture of a zinc ferrite with at least nearly all of its Zn^{++} located in tetrahedral sites and, at the same time, has suffered no appreciable loss of either zinc or oxygen during the firing process.

The study of the effect of ferrous iron on the spinel formation will be continued. An attempt will be made to establish the rate determining reaction of the spinel formation. Is it the compound formation, or is it grain growth? This study will require the use of more precise X-ray measurements. The study of statistical correlation of grain size and grain size distribution with magnetic properties is to be continued. The effects of wire size, the number of turns of wire, and the size of the incremental field measured on the Q-meter is currently being investigated.

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