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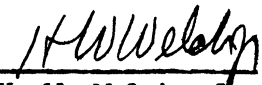
STUDY, DEVELOPMENT, AND PRODUCTION OF FERROSPINELS

APPLICABLE TO TUNING OF SEARCH RECEIVERS

QUARTERLY PROGRESS REPORT NO. 7, TASK ORDER NO. EDG-6
Period Covering April 1, 1954 to June 30, 1954

Electronic Defense Group
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TABLES

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 cry-
stallite with the various measured magnetic parameters;

e. Theoretical explanations, where possible, for the relation-
ships 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 investi-
gations 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.

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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.

ABSTRACT

        The problem of reproducibility in the properties
of ferrite cores is discussed. Probable causes of observed
deviations between supposedly identical specimens are exam-
ined and related to experimental circumstances. Methods of
planned improvement in both manufacturing and measurement
controls are discussed. A rough quantitative evaluation of
the reproducibility obtained by present methods is included.

        Correlations of permeability and density with the
extent of compacting of the material before firing are
examined.

        Preliminary results of Firing Series IV are pre-
sented, in which univalent ions are added to prevent the
reduction of excess iron to the ferrous state. Extent of the
completeness of the spinel formation with firing time and
temperature is presented. Initial mixing of the ingredients
by coprecipitation is further examined.

        The problems of resistivity measurements are dis-
cussed and some preliminary results are given. Plans for
theoretical calculations on the frequency spectrum of the
permeability of polycrystalline material are discussed.

        The status of the specific heat measurements is
presented.

STUDY, DEVELOPMENT, AND PRODUCTION OF FERROSPINELS

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QUARTERLY PROGRESS REPORT NO. 7, TASK ORDER NO. EDG-6
Period Covering April 1, 1954 to June 30, 1954

1. PURPOSE

The purpose of this report is to summarize the progress made by Task Group 6 of the Electronic Defense Group from April 1, 1954 to June 30, 1954 on the Signal Corps Contract Nos. DA-36-039 sc-15358 and 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 Group 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

Two technical reports were issued during the quarter:

Technical Report No. 24 Reversible Susceptibility in Ferrimagnetic Materials

D. M. Grimes and D. W. Martin

Technical Report No. 35 Toroidal Sample Holder for Measuring VHF Permeability and Losses

R. E. Nace

Mr. Grimes attended the annual Washington meeting of the American Physical Society on 29 and 30 April and 1 May.

3. FACTUAL DATA

3.1.1 The General Program - Manufacture

Section 3.2.1 of QPR No. 6 discusses the problems involved when attempting to produce specific magnetic properties. It is well known that measurement of X_o is a sensitive test for determining structural changes in a material. Therefore, the reproduction of given susceptibility and losses for all values of biasing field requires extremely delicate control of the structure.

Groups of specimens of our own manufacture, pressed in the same way from the same mix and fired together, often show widely divergent values of μ_1 and μ_2. A general evaluation of the reproducibility we have obtained in higher frequency properties will be found in Sec. 3.2. For the present discussion, some results at 2 mc/sec. are given in Table I. The manufacturing parameters of the samples are given in Table II.

TABLE I

SPREAD OF COMPLEX PERMEABILITY VALUES

Type	No. of Samples	μ_1 Ave.	μ_1 Std. Dev.	μ_1 ± %	μ_2 Ave.	μ_2 Std. Dev.	μ_2 ± %
A-231	25	886	61.2	6.9	264	61.1	23.1
A-303	8	1025	60.3	5.9	542	216	39.9
A-304	8	1092	67.6	6.2	785	270	34.2
A-305	8	530	36.5	6.9	30.2	8.59	28.4
A-88	8	850	105.9	12.5	261	88.7	34.0
A-88	13	846	115.5	13.6	266	104.8	39.4

TABLE II

MANUFACTURING DATA

Type	Ball Mill Time, Hrs.	Pressing Force, tons	Firing Temp. $^\circ$C.	Time on Temp., Hrs.
A-231	24	1.5	1200	4
A-303	6	3	1150	63
A-304	6	3	1150	168
A-305	6	3	1100	63
A-88	6	1.5	1200	4

All these cores contain 20 mole % NiO, 30 mole % ZnO and 50 mole % Fe_2O_3, and were cooled at approximately 60°C/hr to 400°C, from there to room temperature at the normal cooling rate of the oven.

Of the two rows for A-88 in Table I, the top eight were manufactured together, the other 13 were fired at four different times from four different mixes. It is to be noted that standard deviation in the latter case is only slightly higher than in the former. It is evident that control of the chemical composition and the mixing, pressing, and firing procedure is not alone adequate to assure uniform magnetic properties.

The arguments of Sec. 3.1.1 of QPR No. 5 would indicate that to date either or both (a) the slope of the quasireversible energy curve and (b) the total number of potential holes are not sufficiently controlled. If the material has been well annealed, one can identify (a) with grain size and relative grain orientations, (b) with crystallographic imperfections.

In well-annealed specimens, crystallographic imperfections should be statistically the same between samples. Certainly the probability of any specific

relative orientation between neighboring grains would also be the same. There then remains the grains size as at least a likely cause of the permeability differences.

For separate particles, it is well known that the grain size and shape play a major role in determining the permeability. In ferrites one is dealing with a continuous distribution of grain sizes. However, at least for low ratios of M/M_s the permeability must lie between that of a conglameration of many small uniform single crystals and that of a homogeneous structure.

The distribution function giving the number of grains per unit volume with individual volumes in the range V to $V + dV$ may be expected to display a maximum at some value V_o, and to be characterized by a half-width δV_o. To achieve a substantial reduction in the permeability deviations one must achieve finer control over at least these two features of the distribution.

The volume V_o will increase with increased firing time and temperature. (This is, of course, to be expected and has been observed with surface photomicrographs.) To control the final firing time and temperature more accurately we have ordered a G. E. saturable reactor, and will equip our controller with a motor-driven control of the temperature pointer allowing more accurate reproduction of the firing cycles.

The presence of certain added fluxes such as V_2O_5, or of trace impurities which act as fluxes, can greatly increase the rate of grain growth. The concentration of such constituents might vary between samples of a single batch and cause a spread in V_o. There might also be unequal distributions of such traces within one sample, producing an effect on V_o. A desirable way to reduce these affects would be the use of very pure materials. This would involve

considerable experimental difficulty and at this time does not seem to be com-
pletely justifiable. We are and intend to continue to rely upon prolonged mixing
to distribute thoroughly any fluxes present. (Compare A-88 and A-231 of Table I).

In principle δV_0 should be quite small if one uses a firing tempera-
ture either (a) sufficiently low that there is little grain growth or (b) suffi-
ciently high that all grains are large. An example of a high temperature core
would be our type A-135. (20m % NiO, 24m % ZnO, 56m % Fe_2O_3; firing temperature
1350°C.)

TABLE III

CORE TYPE A-135

No. of Samples	Average μ_1	Std. Dev.	$\pm$ %
9	230	7.7	3.4

Here the observed deviations approach the limit of accuracy of our experiment for
μ_1; μ_2 was too small to be measured. Unfortunately, this material showed con-
siderable drift - possibly due to the high Fe^{+2} content.

Pressing may affect grain growth during firing and hence affect δV_0.
We observed large differences in grain size between the interior and the surface
of our pressed specimens.

It therefore would seem that for material fired at a moderate tempera-
ture some method of formation of the original pill which eliminates internal
stresses or at least produces more uniform stresses from sample to sample might
be desirable. Three alternatives to the separate pressing of each core are
extrusion, formation of the material in a mold, as with the clay ceramics, and
cutting of the toroid from a rolled sheet of the material with a sharp "cookie
cutter." These methods would require the use of a binder and would necessitate

finer control and a slower change of temperature in the region of core shrinkage and binder burn-off. The last two methods are being investigated, the latter one at this writing shows considerable promise. Details will be found in Section 3.6.

To evaluate these procedures it is most desirable to have an independent means of measuring the grain size distribution. The standard methods are either to (a) take photomicrographs of several typical cross sections, count and measure the grains, or to (b) take an X-ray diffraction pattern and measure the sizes of the resulting spots. Method (a) is long and laborious, but can yield accurate results. Method (b) does not yield as good results due to the small coverage of the beam. Both methods have been tested, and it is expected that both will be used.

If there is any difference in characteristic grain shape between different treatments, as has been observed in some ceramets, the surface photomicrographs will show them but X-ray might not.

3.1.2 The General Program - Measurement. Some of the variations between samples as listed in Table I may be due to nonsimilar magnetic history of the specimens or to other external effects, rather than to real magnetic differences. The measured permeability will depend strongly on the state of remanence. It has also been reported that some magnetic properties are affected by the moisture content of the core. We have always taken care that our samples are exposed to no magnetic fields other than that of the earth before measurement. However, we have not so far attempted any moisture controls. The influence of moisture and the feasability of control are being investigated.

Table IV lists pairs of observations of μ_1 and μ_2 made several months apart on a group of samples. The observed changes over this time interval are seen to be much less than the deviations of Table I. Clearly the greatest part of the differences in Table I are real. All values in Table IV are at 2 Mc/sec.

TABLE IV

CHANGES WITH TIME

Core	μ_1		% difference	μ_2		% difference
A-144-1	507	494	2.6	187	161	14
A-145-1	562	551	2.0	262	233	11
A-146-1	538	537	-	239	217	9
A-147-1	504	516	2.4	204	196	3.9
A-230-1	224	223	.5	26.6	24.6	7.5
A-231-1	674	650	3.6	79.8	77	2.5
A-79-1	262	259	1.1	14.1	9.7	31
A-80-1	209	203	2.9	8.4	4.3	49
A-89-1	734	512	3.0	342	301	12
A-93-1	632	630	.3	280	265	5.4
A-94-1	669	626	6.4	312	236	25

It is planned to extend all the complex permeability measurements to include the presence of a bias field. At the high frequencies this will require passing a large dc current through the coaxial inductor. At the medium frequencies, a Q-meter can be used. These modifications are being considered.

Three of our cores are being tested by the CGS Laboratories for the variation with biasing field of the resonant frequency of a circuit containing the core as its inductive element.

3.2 Reproducibility (P. E. Nace)

The data on the values of μ_1 and μ_2 at 50 and 200 mc of a large number of our cores has been analyzed to attempt to evaluate the reproducibility obtained under our existing manufacturing controls.

The nature of the sampling requires special mention. The data cover 171 samples representing 78 different core types. For most of these types there were only two samples, and in most cases these two were manufactured at different times under as identical conditions as possible. Therefore, the analysis applies mostly to batch to batch reproducibility, rather than to in-batch reproducibility.

With only two samples to represent a given type, the question arises as to what shall constitute the norm for that type from which deviations are to be measured. One might assume the first sample to define the norm and compute the deviation of the second sample from it. This type calculation actually adopts the following point of view. One makes a core and subsequently attempts to reproduce it and considers the deviation of the second sample from the first as a measure of reproducibility. Alternatively, one might take the average of the two as the norm and consider the two samples to be examples of plus and minus deviations from it. The first procedure will lead to a deviation about twice as large as will the second.

In the next report we shall establish that the use of the average of two samples as the norm gives the lower limit of the expected deviation of existing data. In addition we shall consider the significance of the former method of computation.

In what follows the second alternative has been used. We computed the average of the several (two or more) readings of μ_1 at 50 mc, and at 200 mc, and the same two averages for μ_2. The percentage deviations of the individual readings from the four norms of each core type were calculated, and the results from

all types were assembled to obtain four distribution curves (number of cases versus per cent deviation). It was found that, although the μ_1 and μ_2 distributions differed significantly from each other, the μ_1 and μ_2 distributions at 50 mc were respectively identical to those at 200 mc. Therefore, the data at the two frequencies were combined to give a single curve for μ_1 and another for μ_2. These curves are shown in Figs. 1 and 2.

The percentage deviations were generally greater for μ_2, but they were not functions of the size of μ_1 and μ_2. In other words attempts to reproduce low permeability or low loss cores were percentage wise no less nor no more successful than attempts to reproduce high permeability or high loss cores at these frequencies. So one is justified in grouping all these data into two groups and proceeding to compute a quantitative measure of reproducibility.

The average deviations and mean square deviations were computed by the following formulae:

$$d_{avg} = \frac{\sum\limits_i N_i \, d_i}{\sum\limits_i N_i} \qquad\qquad d_{mean\ sq} = \left[\frac{\sum\limits_i N_i (d_i)^2}{\sum\limits_i N_i} \right]^{\frac{1}{2}}$$

where N_i = the number of data with the deviation d_i.

In the computations for the mean square deviation larger values of deviation are strongly weighted. A small error in reading the scale on the bridge, or in computing μ_1 and μ_2, or in the manufacturing procedure can easily lead to a value that is far out of line. We suspect that at least some of the large deviations are human non-random errors, so certain of them were discarded. The criterion was to use all of the data in computing a provisional value of mean
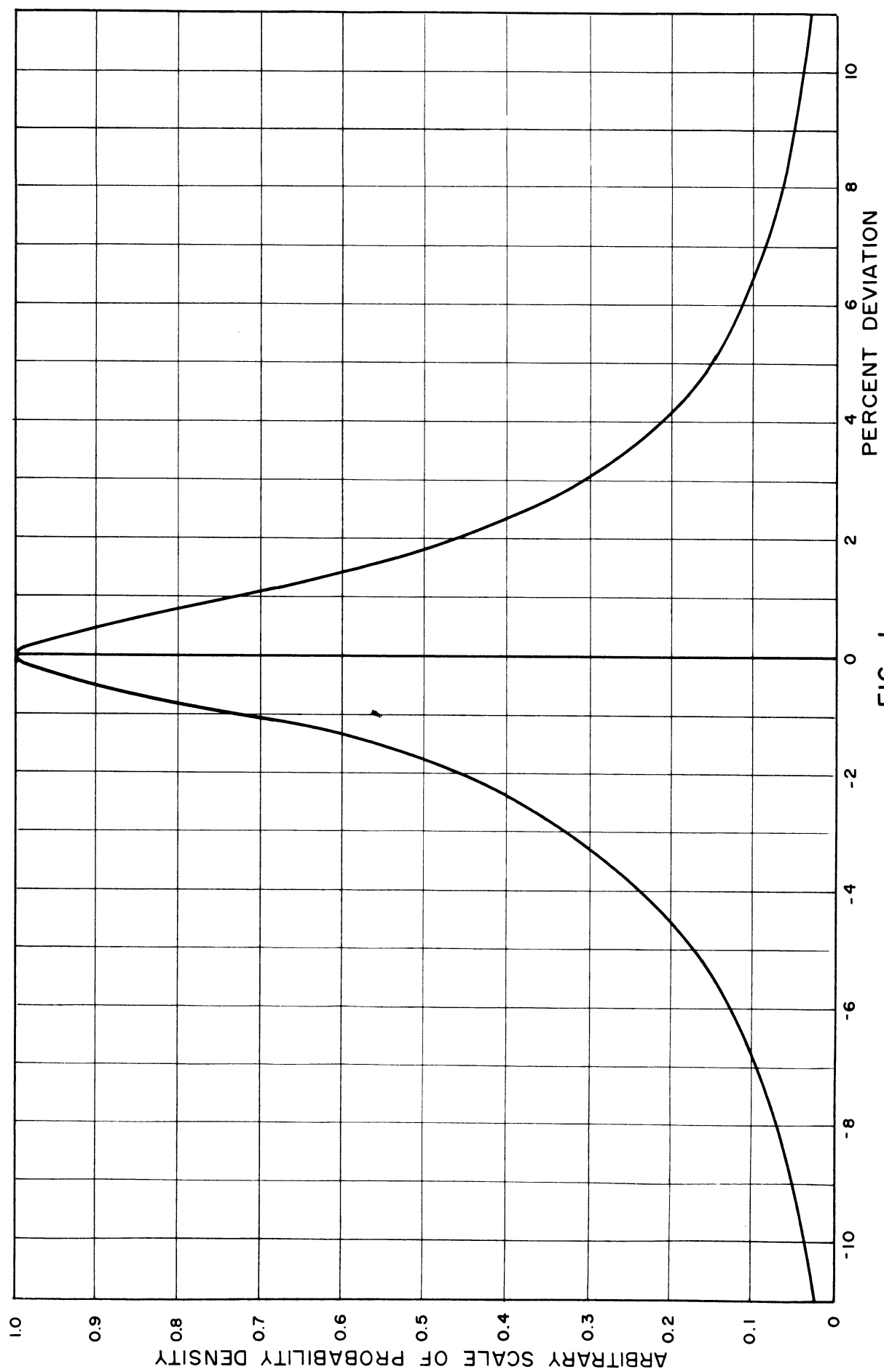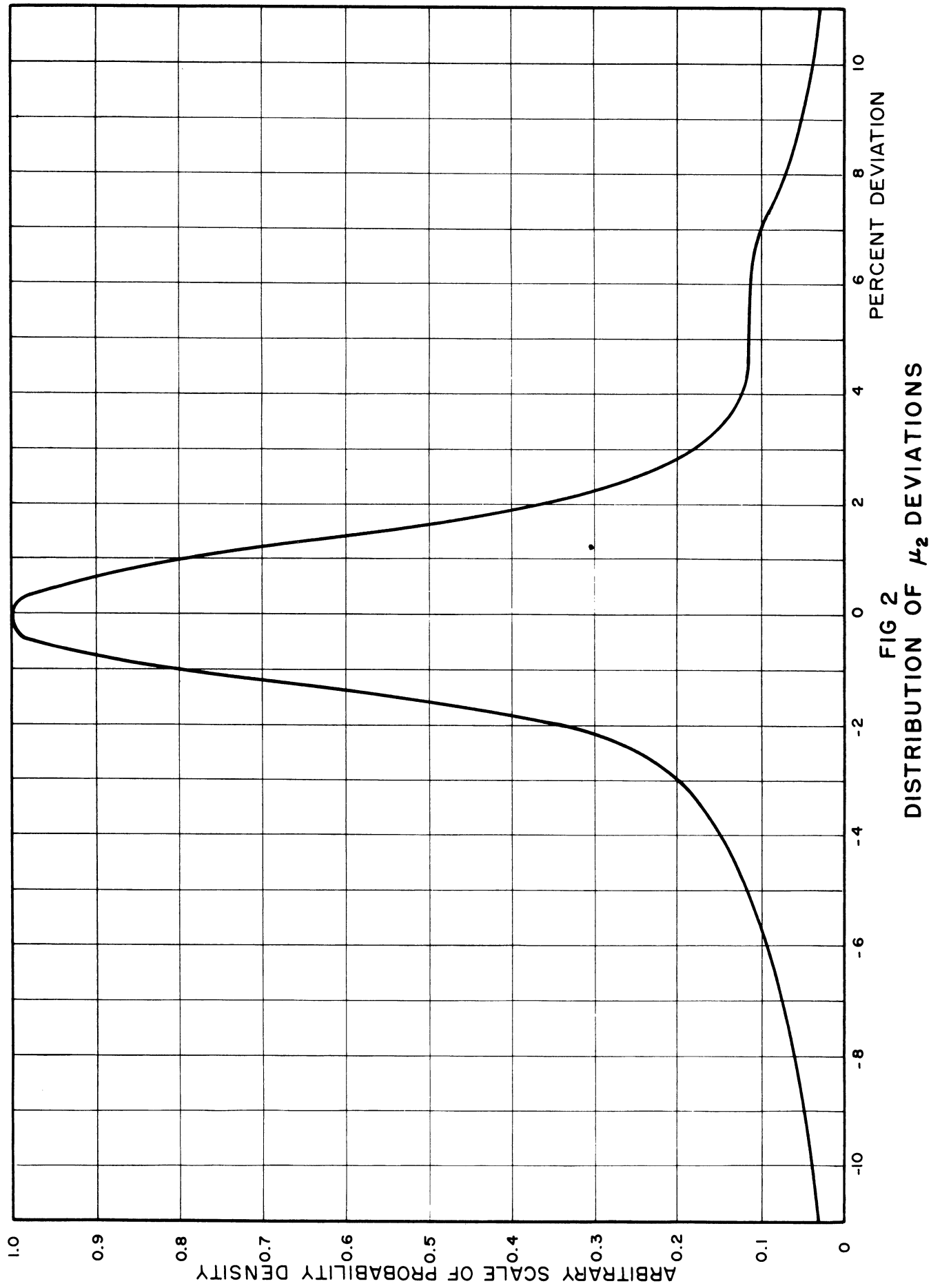
FIG I
DISTRIBUTION OF μ_i DEVIATIONS

PERCENT DEVIATION

ARBITRARY SCALE OF PROBABILITY DENSITY

FIG 2
DISTRIBUTION OF μ_2 DEVIATIONS

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square deviation. Then all values of deviation greater than 3.4 $d_{mean\ square}$ were discarded and a new value of mean square deviation was calculated. The process was repeated until no data were retained whose deviation exceeded 3.4 times the final value of mean square deviation. If our distribution were Gaussian, this would correspond to discarding data whose probability of occurence was less than one in one thousand trials. As the figures show, the distribution of our data is, in fact, better than a Gaussian. It was found that 5.2% and 7.9% of the μ_1 and μ_2 data respectively could be discarded according to the above scheme. Seventy-one percent of the data lie within the mean square deviation for both μ_1 and μ_2.

As noted earlier, the figures obtained must represent a lower limit to what would have been obtained if we had had enough samples of each type to determine a reliable norm for that type. Repeating the whole calculation by the other scheme (in which the percentage deviations are arbitrarily measured from the first sample of every type) gave figures roughly twice those calculated by the former procedure. The significance of the latter calculation is as yet in doubt. Perhaps it more closely approximates the correct values of reproducibility. The data are still undergoing analysis. Table V gives the results of the former calculation. Multiply by two to obtain the results of the latter calculation.

TABLE V

LOWER LIMITS OF AVERAGE AND MEAN SQUARE DEVIATION

	μ_1	μ_2
Average Deviation	2.9%	3.2%
Mean Square Deviation	4.0%	4.9%

3.3 The Effect of the Green Density on Core Properties (C.F.Jefferson)

Part of the objective of firing series III (QPR No. 6, p. 10) was

to evaluate the effects of various forming pressures on the properties of

pressed toroids. It was soon found that the total force exerted on the

die was not a good criterion of the degree of compacting of the material.

Because of friction in the die, raw compacts made with the same pressure showed

a considerable spread in density. Therefore the "green density" of the

unfired toroids is itself used as the measure of compacting.

The cores for this investigation were made as follows. The oxides

were ball-milled for 6 hours in water, then the water was removed by evapo-

ration. The dried material was crushed and passed through a 200-mesh seive.

Cores were pressed with forces ranging from 250 to 6,000 pounds. Green densi-

ties were determined by measuring and weighing. Then the cores were fired

at various temperatures in the range 1000° to 1200°C for 4 hours and cooled

at 60°C/hour in oxygen.

3.3.1 The Final Density

The final density was determined by weighing the cores in air and

in water. The more porous specimens were coated with paraffin wax to prevent

absorption of water.

For sufficiently high firing temperature, it is to be expected

that the final density will approach the X-ray density for any reasonable

value of green density. Similarly, at sufficiently low firing temperatures

there will be no reaction at all, and the final density should equal the

green density. If the difference δd between the final and green densities

is plotted against the green density, g (each normalized by division by the

X-ray density), these two limits would be represented by the two solid lines

in Fig. 3.

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δd

FIG 3

EXPECTED BEHAVIOR OF
DENSITY CHANGE UPON FIRING

HI TEMP

LO TEMP

o   I   g
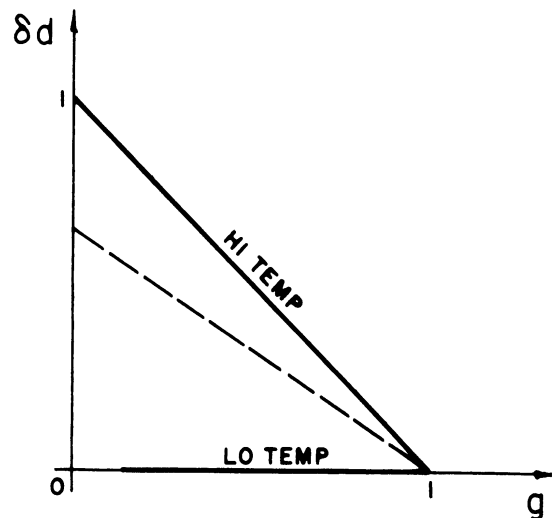
At an intermediate temperature the relationship might still be linear as represented by the dashed line in Fig. 3. Such a line would be given by

$$\delta d = -f_1(T) \cdot g + f_2(T) \tag{1}$$

where the slope $-f_1$ and the intercept f_2 are functions of the firing temperature T. It is required that $f_1 = f_2 = 0$ at low temperature, and that $f_1 = f_2 = 1$ at high temperature. If the lines actually do pass through the point $(1,0)$ as in Fig. 3, this implies that $f_1(T) = f_2(T)$.

In Fig. 4 the experimental values of δd vs. g (not normalized) are shown. It is seen that points for the various firing temperatures do cluster about a series of straight lines, although there is considerable scatter, particularly at the middle temperatures. At 1000° the increase in density is small and constant. At 1200° the increase in density plus the green density is almost constant.

The lines shown in Fig. 4 were fitted to the experimental points, and used to compute values of f_1 and f_2 of Eq. 1. These are plotted against temperature in Fig. 5. Note that f_1 and f_2 are almost equal throughout the temperature range, indicating that all the lines of Fig. 4 would very nearly pass through a common point if extended.
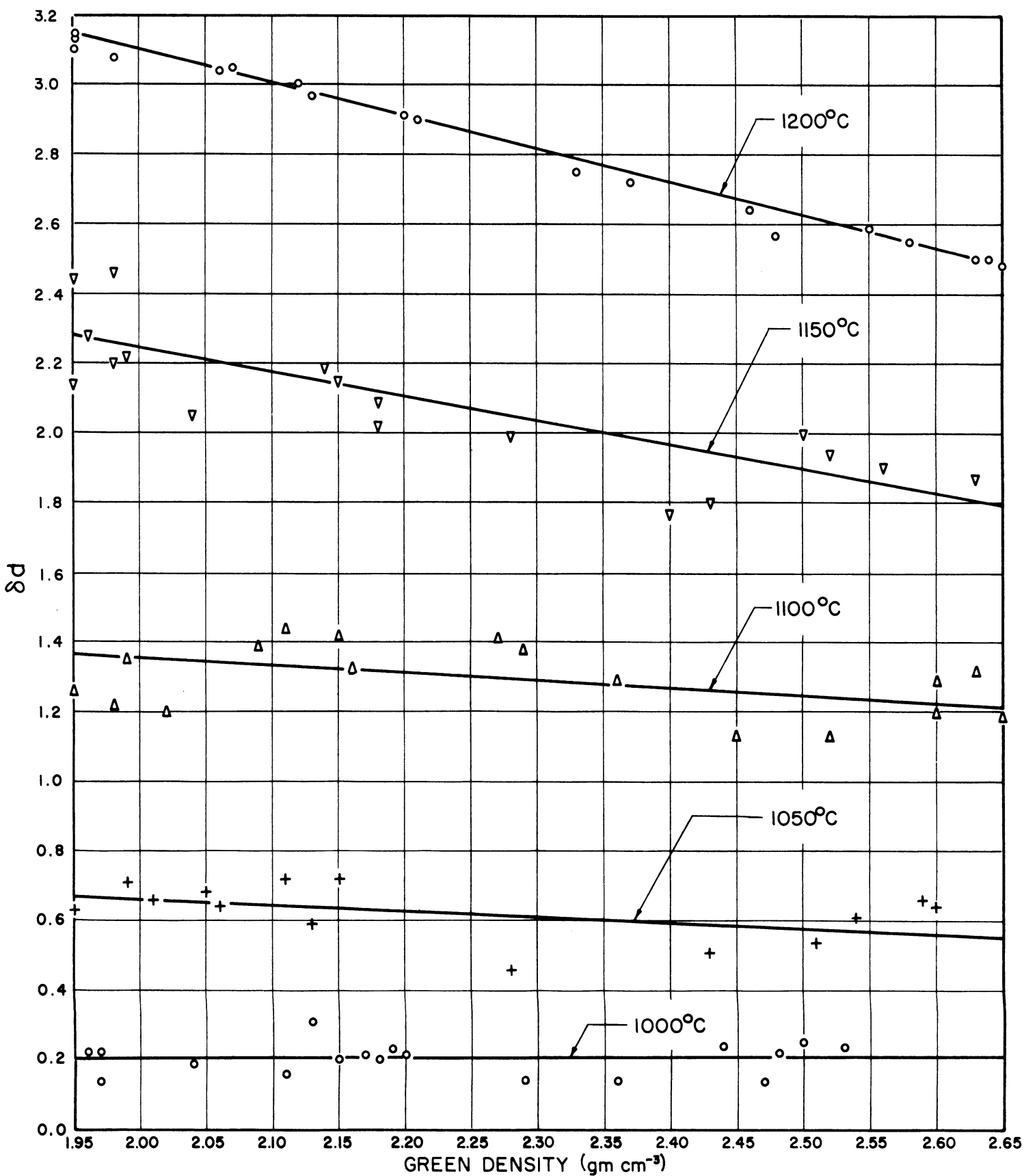
FIG 4

CHANGE IN DENSITY VS GREEN DENSITY FOR
SEVERAL FIRING TEMPERATURES

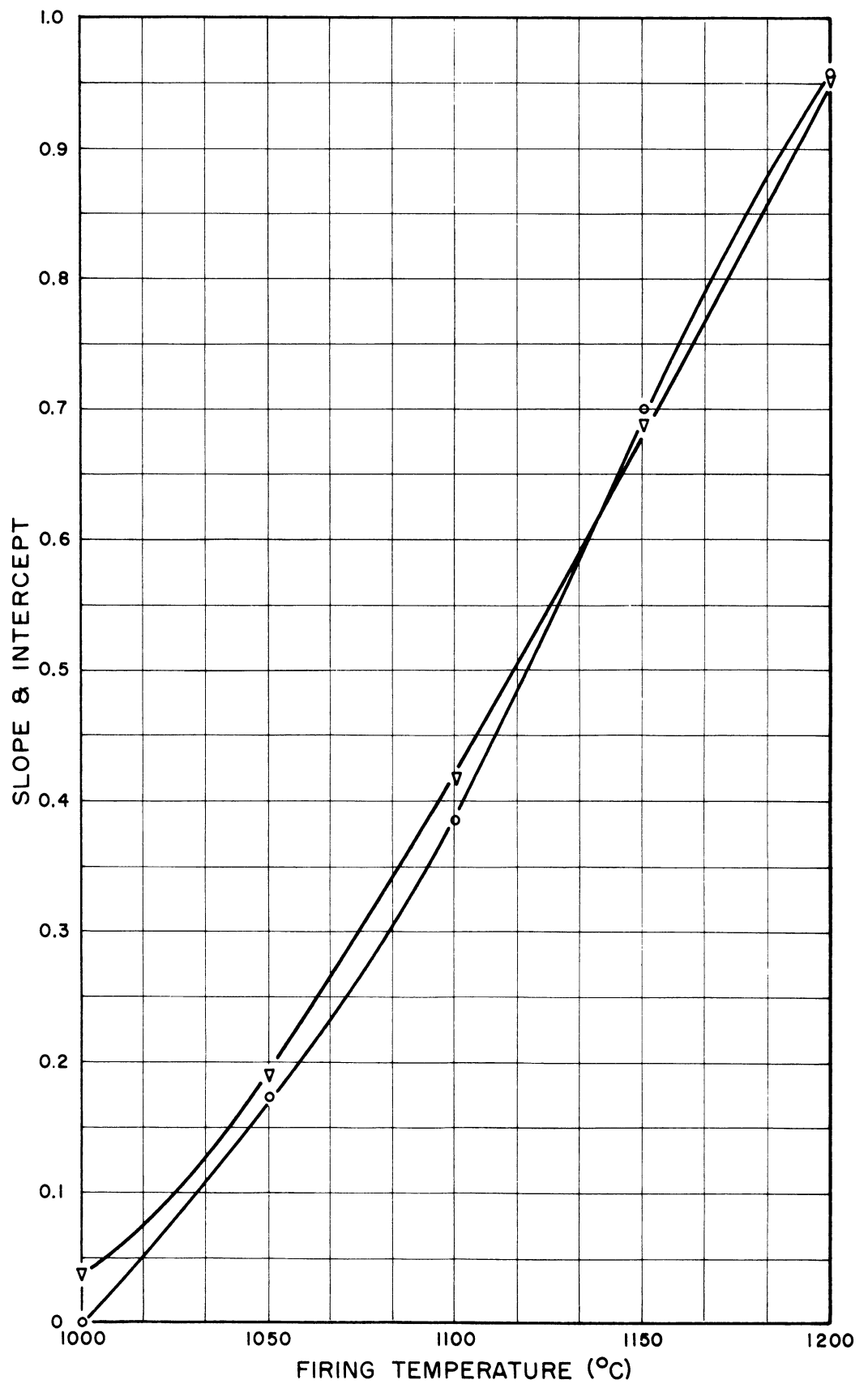δd = FINAL DENSITY - GREEN DENSITY

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FIG 5
$f_1(T)$ AND $f_2(T)$ OF EQUATION I

o   SLOPE, $f_1(T)$
▽   INTERCEPT, $f_2(T)$

<u>3.3.2 Permeability</u>. The permeability of a ferrite generally tends to increase with the density. Two obvious reasons are that the denser material is less magnetically dilute, and that the elimination of voids removes obstructions to the motion of domain walls. Naturally, the permeability will also increase with firing temperature (up to a point) because the density and the temperature are correlated.

If one simply plots μ_1 against either density or firing temperature, however, the points will be found to scatter a great deal. No very effective control of μ_1 can be obtained by regulating only these variables.

We have measured μ_1 at 2 Mc/sec. for all the cores of Sec. 3.3.1 fired at 1100-1150-1200°C to see if the correlations can be improved by including considerations of the green density.

A simple plot of μ_1 against the green density contained no apparent correlation at all. However, if one notes the μ_1 values of the points of Fig. 4, one observes the following fact. For the points at 1100 and 1150°C, which show the greatest scatter in Fig. 4, the direction and magnitude of this scatter from the median line are decidedly correlated with the observed permeability. Fig. 6 is an enlarged view of part of Fig. 4, in which the μ_1 value is noted for each point. Instead of drawing a single straight line through all the points for a given temperature as in Fig. 4, one can draw a series of several parallel lines, each passing through points of constant permeability.

The isopermeability lines look like a series of isotherms for slightly different temperatures (note that they are drawn parallel in Fig. 6, but should converge slightly to the right if they are isotherms.) This suggests that the scatter of points of Fig. 4 is actually due only to temperature variations in the oven. However, it would require variations of at least ± 10°C to produce the
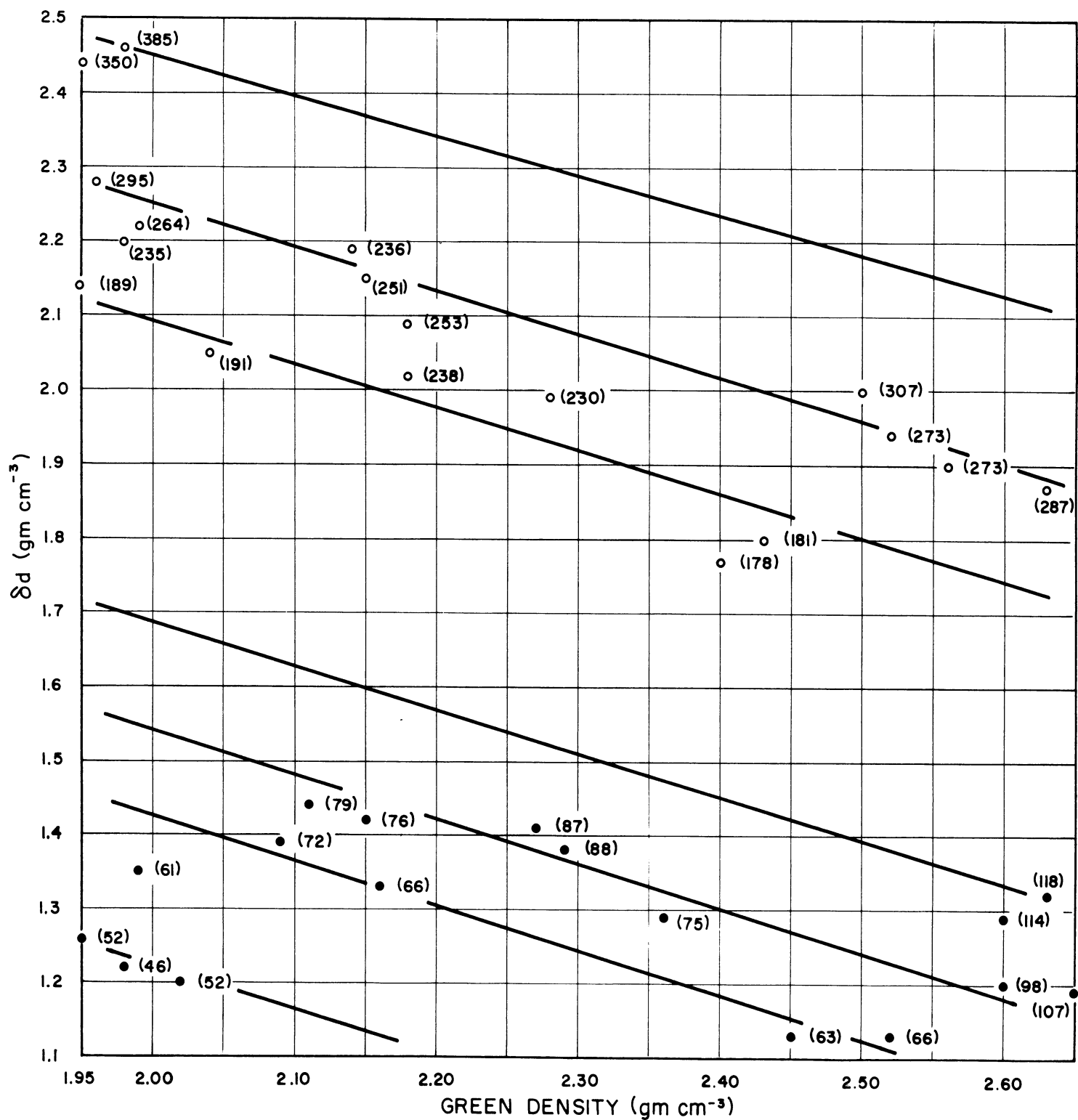
FIG 6
δd VS GREEN DENSITY

SHOWING (μ_1) AT f = 2 Mc
o T = 1150°C   • T = 1100°C

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observed scatter, and measurements show that the actual variations in our oven do not exceed $\pm$ 5°C. Some additional variable must be present that modifies both the permeability and the increase of density on firing just like a small change in firing temperature would.

Fig. 7 was prepared to emphasize the correlations of Fig. 6. Each point of Fig. 6 is projected parallel to the isopermeability lines to the vertical line, green density g = 2.0. In Fig. 7, μ_1 is plotted against this projected value of δd so obtained. The points define a curve with far less scatter than do plots of μ_1 against any other variables we have tried.

The above correlation breaks down for the samples fired at 1200°C. The points for 1200° show rather little scatter in Fig. 4, yet they have wide scatter in μ_1 values.

It is concluded that the forming pressure of the samples has no direct bearing on the permeability. However, we do have at least a handle on the problem of permeability control at the middle temperatures, in that whatever produces scatter in the values at a given temperature is the same factor that produces variation in the density change.

3.4 Analysis of Firing Series IV (B. Hershenov, B. T. Kimura)

In Section 3.3.2 of QPR No. 6, j' material was defined and some of its characteristics given. In an attempt to retain the reproducibility and fairly high Q of this material while at the same time eliminating the drift, univalent cations were introduced to reduce the quantity of ferrous iron present. Forty per cent of the amount of univalent cation necessary to completely eliminate the ferrous iron in a stochiometric composition was added, i. e.,
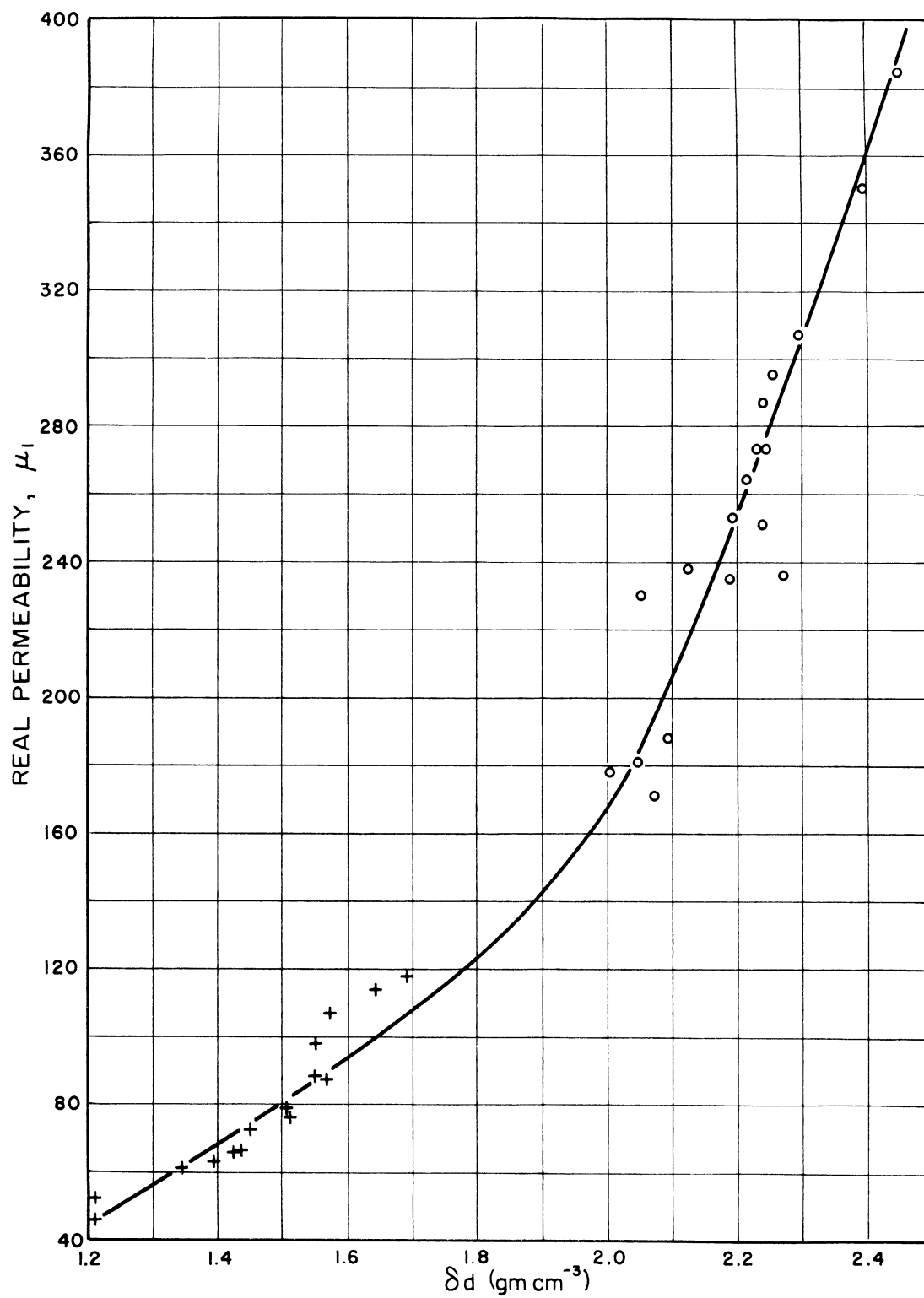
FIG 7

μ_1 VS δd

δd PROJECTED ONTO GREEN DENSITY = 2.00 gm cm^{-3}

f = 2 Mc   FIRING TEMPERATURE $\begin{cases} \circ & 1150°C \\ + & 1100°C \end{cases}$

$$\left[Li_2O\right] = \frac{1}{5}\left\{\left[Fe_2O_3\right] - .5\right\} \qquad (2)$$

while for **stochiometric composition:**

$$\left[Li_2O\right] = \frac{1}{2}\left\{\left[Fe_2O_3\right] - .5\right\} \qquad (3)$$

All cores were fired at 1375°C for four hours. The following code
designations apply:

TABLE VI

FIRING SERIES IV

Fe$_2$O$_3$	[NiO] / [ZnO]	Code Designation Li^{+1}	Na^{+1}
.56	.783	C-36	D-36
.56	.946	C-37	D-37
.56	.646	C-38	D-38
.54	.883	C-40	D-40
.58	.683	C-50	D-39
.59	.633	C-60	-
.60	.583	C-70	D-47
.62	.483	C-80	-
.56	.877	C-82	-
.58	.980	C-83	-
.60	1.111	C-84	-

The results were a shifting from a low Q at low iron content to a high Q at a high iron content as was found with the j' material. There is still drift present, as there was with the j' cores. To date no quantitative measurements on either drift or Fe^{+2} content has been made. The permeability measurements are shown in Figs. 8, 9, 10, 11, and 12 as a function of frequency for several samples. Several points can be noted from these figures:

(1) Increasing iron content decreases μ_2.

(2) Increasing the [NiO]/[ZnO] ratio generally increases the permeability.

(3) Increasing iron content decreases μ_1.

(4) The magnitude of the μ_1 peak usually associated with wall resonance decreases as the iron content increases.

(5) The peak μ_2 occurs at a higher frequency with increasing iron content.

(6) All the above effects except (2) are **more** pronounced for Na^{+1} than for Li^{+1}. The Na core D-39 resembles the Li core C-60 with higher iron content more closely than it does its matching sample C-50.

Fig. 13 summarizes some of these observations.

It is planned now to extend the series to include cores containing the stochiometric percentages of univalent cations, as given in Eq. (3).

3.5 Effect of Firing Time on Spinel Formation. (C. F. Jefferson)

Investigations of the time rate of spinel formations have been reported by several laboratories. Okamura[2] and co-workers report that the reaction proceeds rapidly to equilibrium at a given temperature, and that to continue the reaction further the temperature must be increased. Hopkins[3] states that the method of preparing the Fe_2O_3 influences the extent of reaction that takes place between NiO and Fe_2O_3 in a given time.
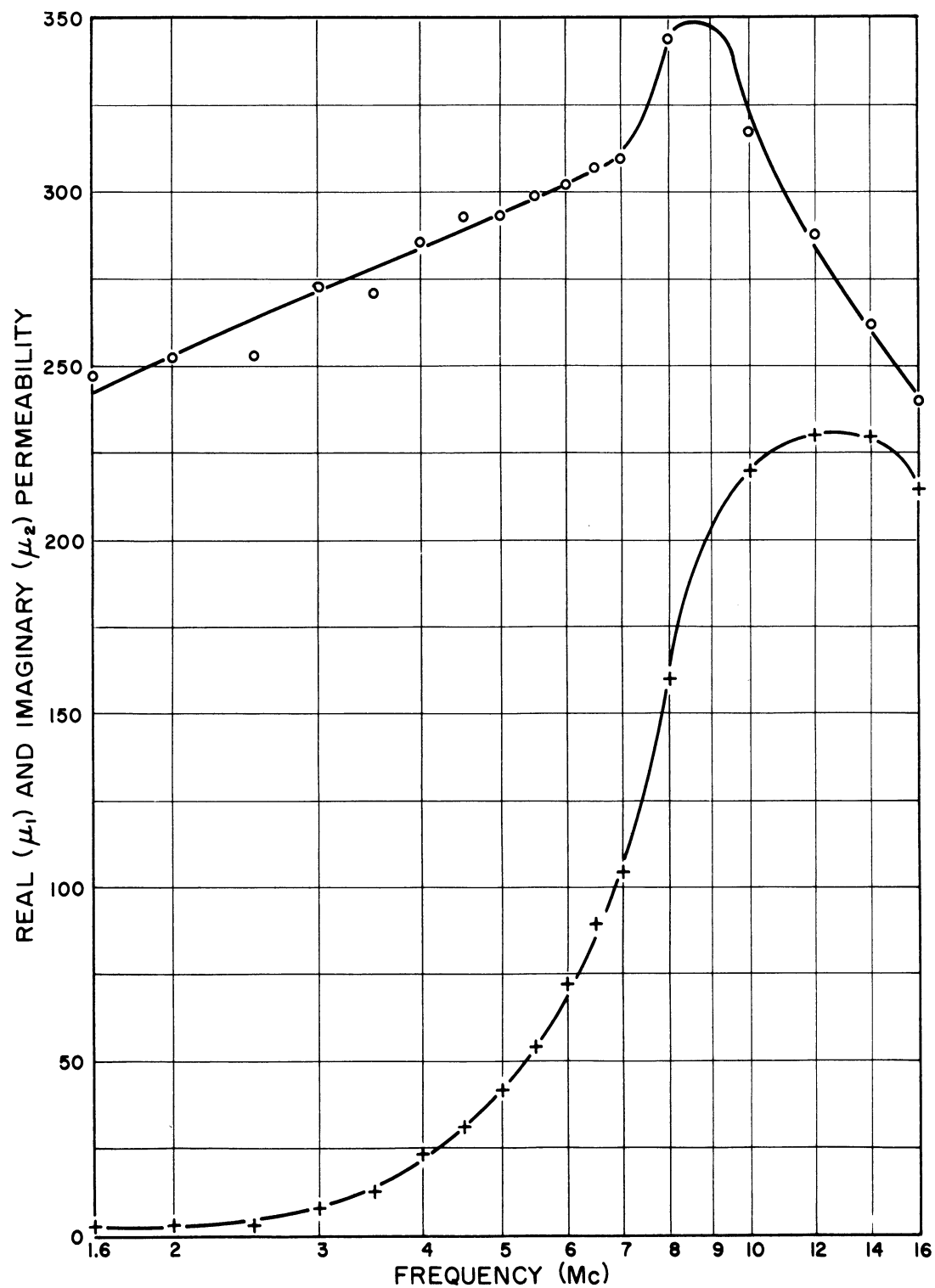
FIG 8
COMPLEX INITIAL PERMEABILITY VS FREQUENCY

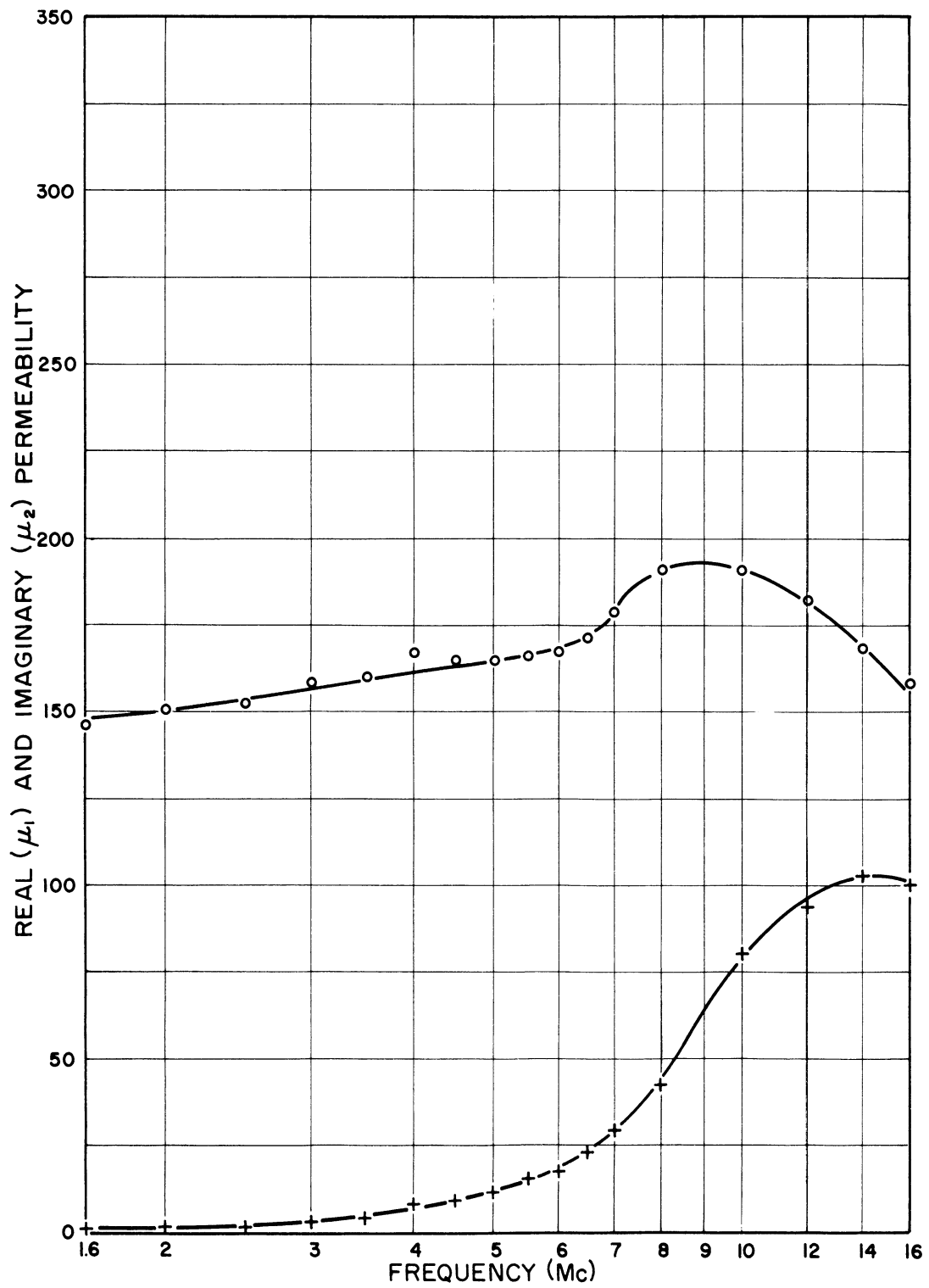CORE C-36-3 μ_1 o———o
                μ_2 +———+

FIG 9

COMPLEX INITIAL PERMEABILITY VS FREQUENCY

CORE C-50-1

μ_1 o————o
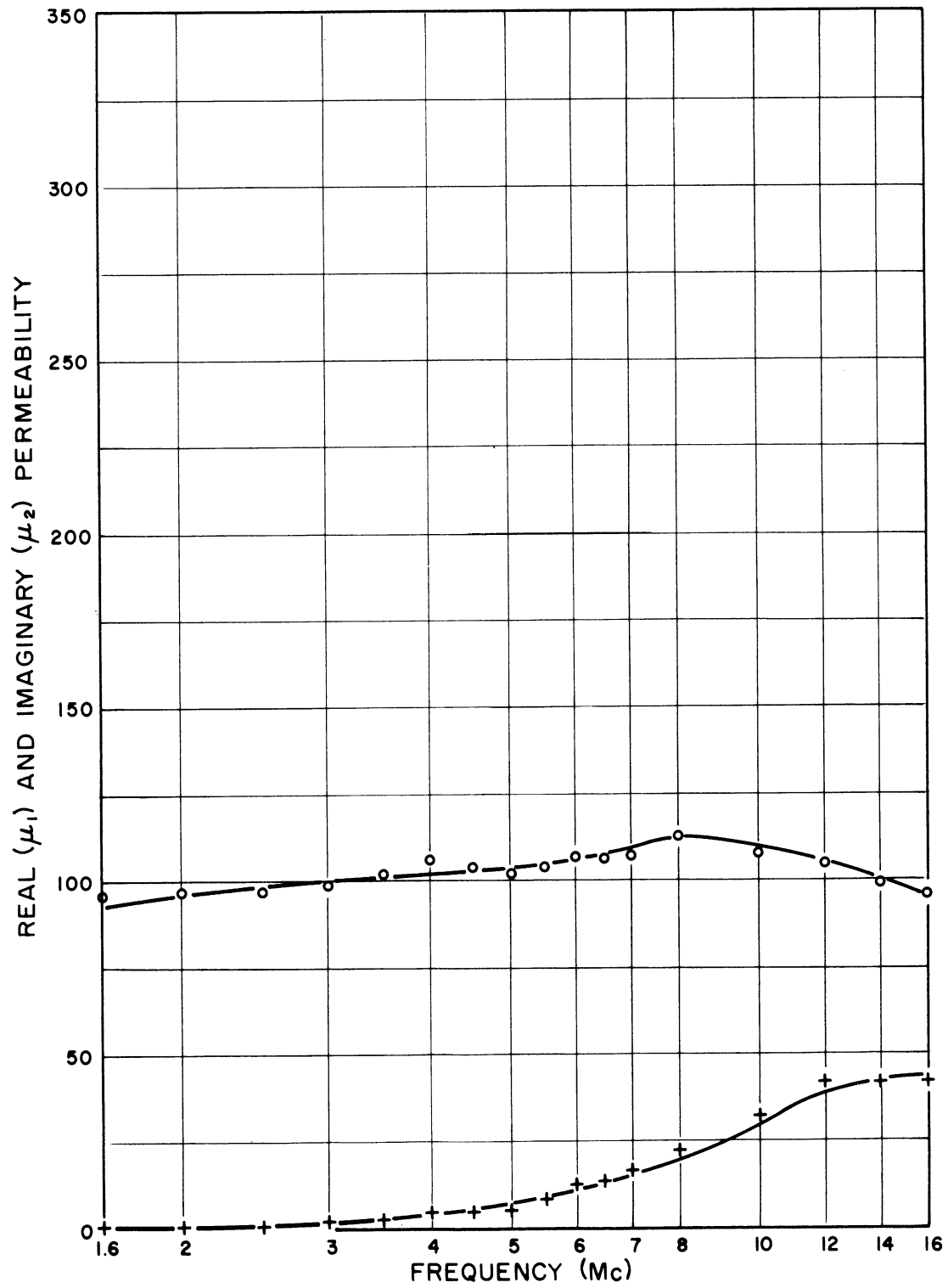μ_2 +————+

24

FIG 10
COMPLEX INITIAL PERMEABILITY VS FREQUENCY
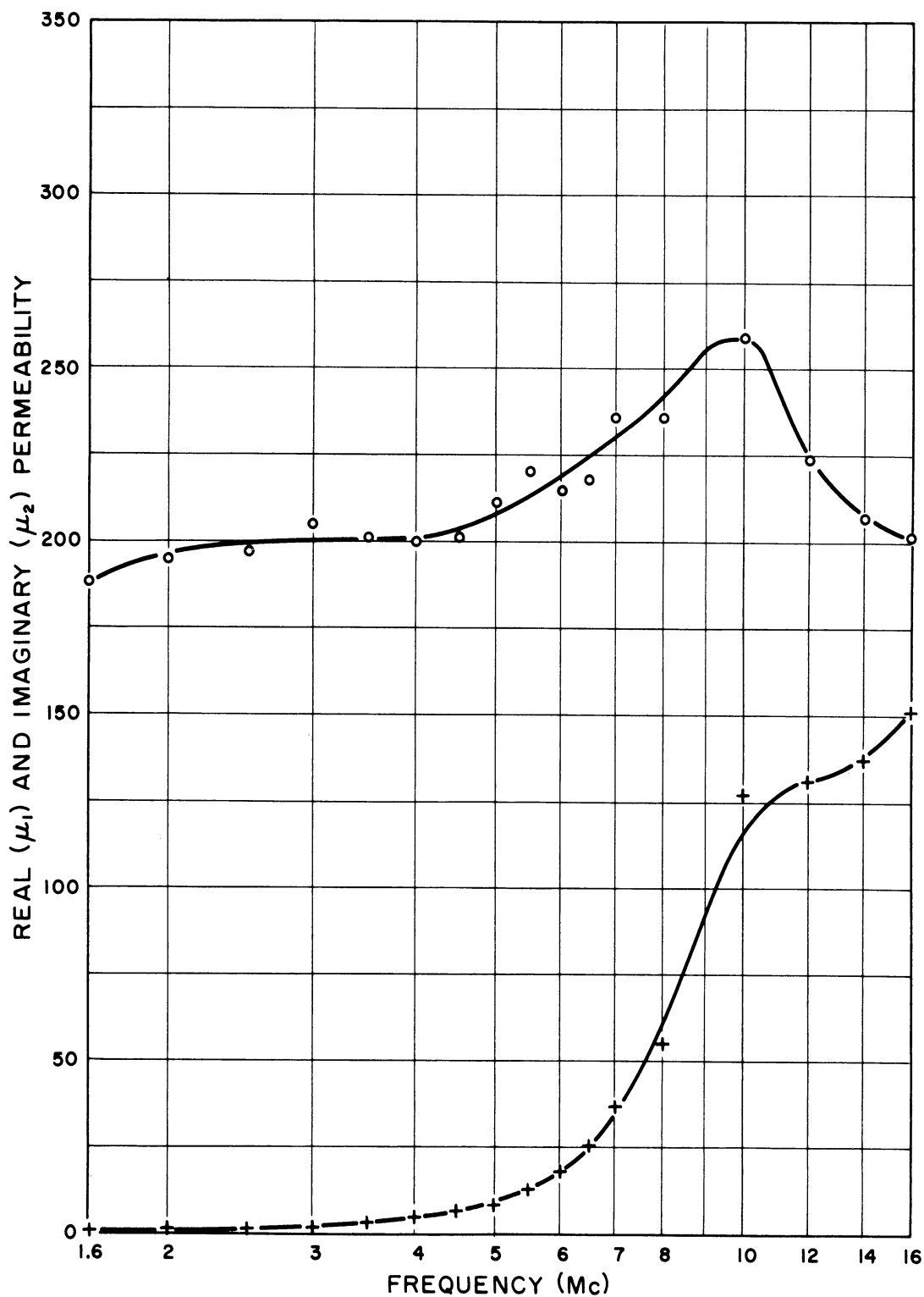
CORE C-60-1

μ_1 o————o
μ_2 +————+

FIG II

COMPLEX INITIAL PERMEABILITY VS FREQUENCY

CORE D-36-1

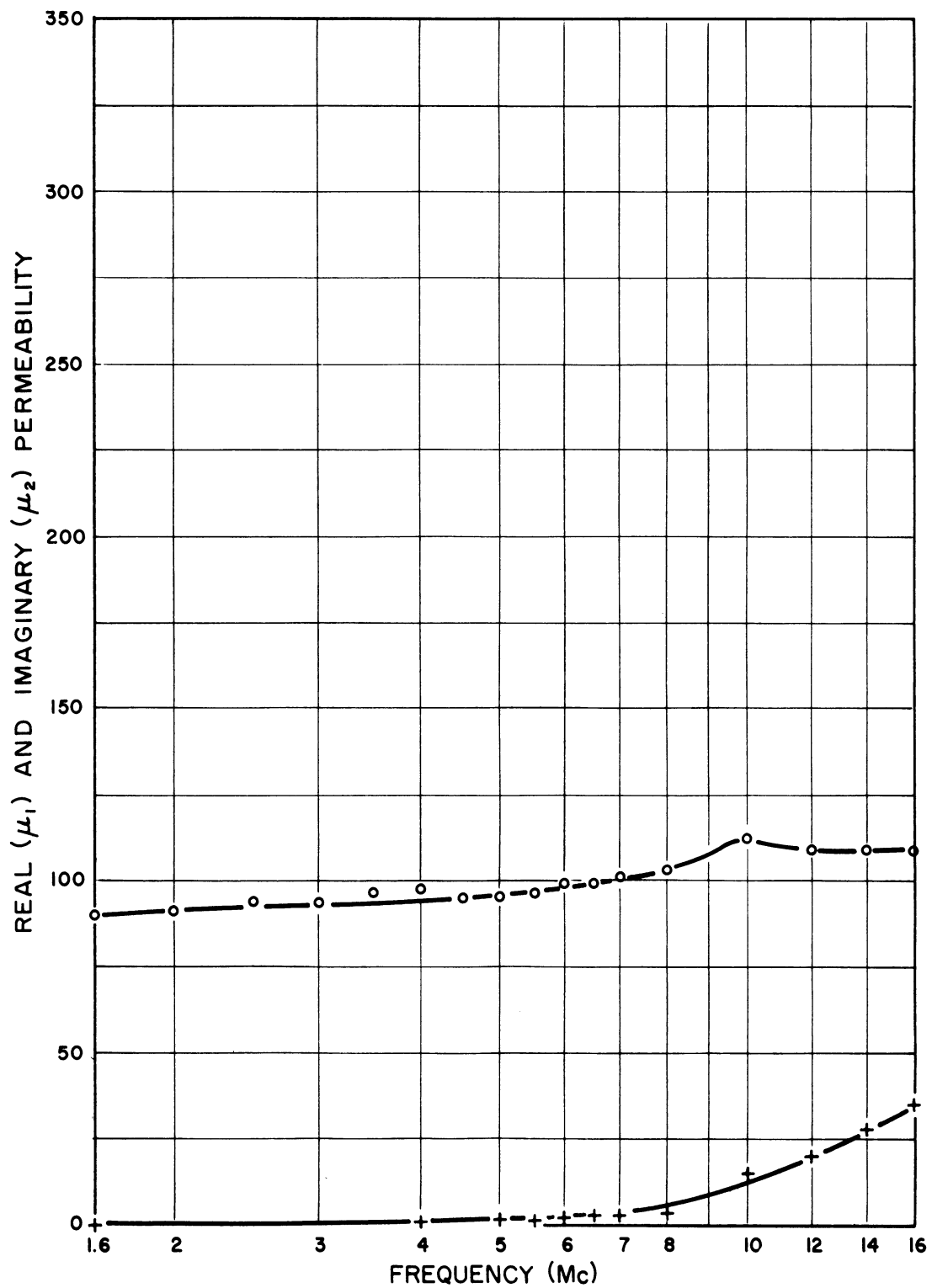μ_1 o———o
μ_2 +———+

FIG 12

COMPLEX INITIAL PERMEABILITY VS FREQUENCY

CORE D-39-1

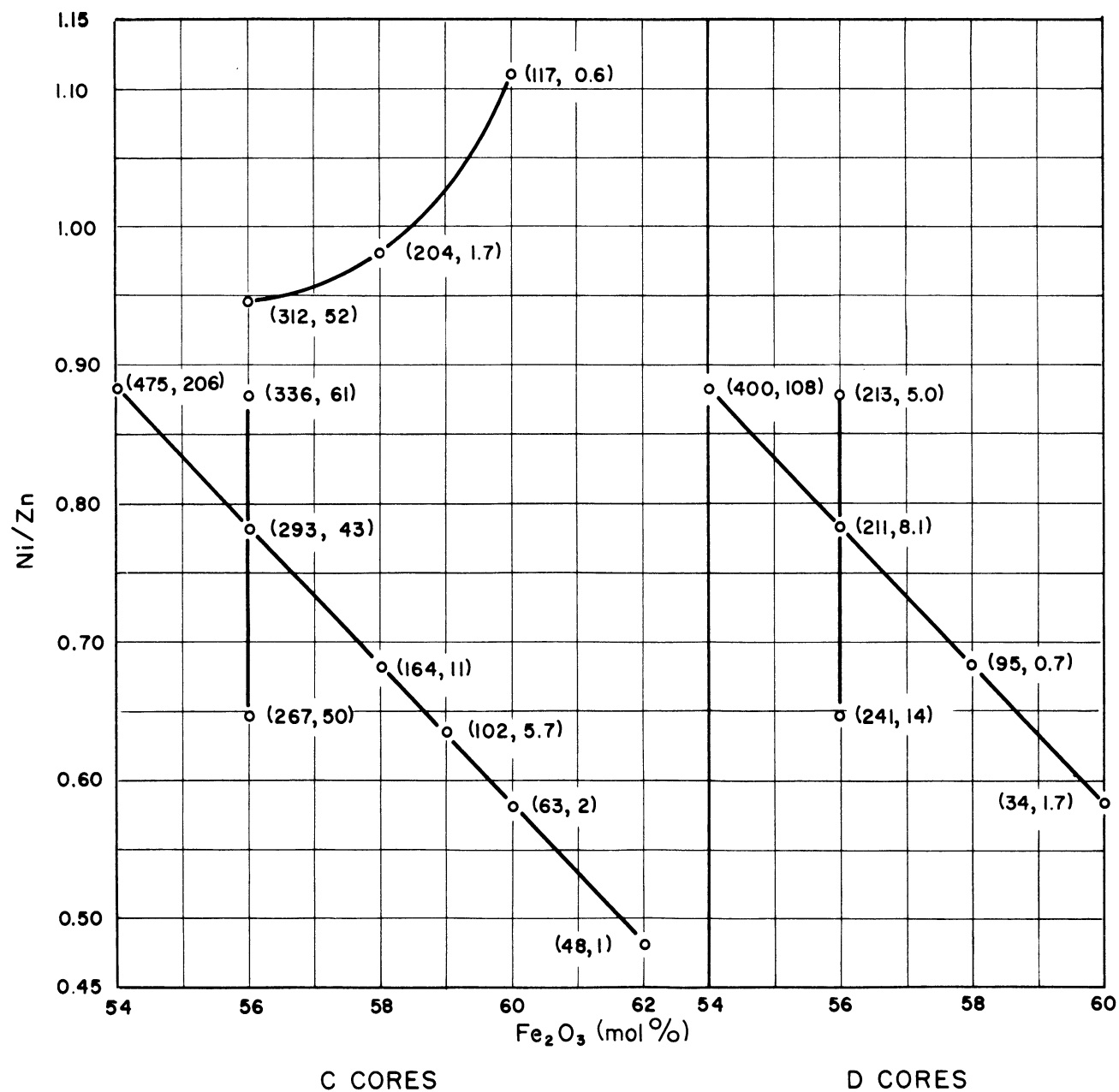μ_1 o————o

μ_2 +————+

FIG 13

COMPLEX PERMEABILITY FOR DIFFERENT COMPOSITIONS

5 Mc (μ_1, μ_2)

An extensive study of the effects of firing time has not been undertaken here, but it was thought desirable to make a preliminary investigation.

Material was prepared by ball-milling according to procedure standardized for this laboratory. The material was pressed into cores and fired for various lengths of time at temperatures between 1050° and $1200^{\circ}C$.

It was found that at temperatures of $1150^{\circ}C$ and below, the reaction did not reach equilibrium in 4 hrs. The density and permeability were both observed to increase on longer firing at the same temperature. At $1200^{\circ}C$ the density appears to have reached a constant value after 4 hrs. firing, but the permeability decreased on longer firing. The permeability is known to reach a maximum and then decrease as the firing temperature is increased, so this would indicate that the longer firing time at $1200^{\circ}C$ acted in the same direction. Tables VII and VIII present the data.

TABLE VII

FINAL DENSITY

Temp. $^{\circ}C$	Time: 4 hrs.	48 hrs.	63 hrs.
1050	2.90	-	3.34
1100	3.66	-	4.56
1150	4.3	-	5.08
1200	5.09	5.09	-

TABLE VIII

AVERAGE μ_1

Temp. $^{\circ}C$	Time: 4 hrs.	48 hrs.	63 hrs.	168 hrs.
1100	80	-	530	-
1150	238	-	1025	1092
1200	850	588	-	-

The reproducibility of cores fired for longer periods of time was investigated and found to be no better than can be obtained for shorter firing periods, provided that the oxides are adequately mixed. The results are shown in Tables I and II of Section 3.1.1.

3.6 Fabrication of Cores by Stamping. (B. T. Kimura)

In the conventional method of forming cores, the oxides are pressed in a die. It is found that this process does not lead to uniform packing of the material throughout the sample volume. A floating die whose outer ring moves freely with respect to the plungers which exert the force has been used in an attempt to counteract the tendency of the packing to be concentrated near the top surface. Even with the greatest care, however, the fired cores are found to be distorted. The radius and thickness are not uniform, and the supposedly rectangular cross section through the ring is found to be slightly trapezoidal with concave edges.

It is believed that these distortions must be accompanied by internal stresses which might affect the magnetic properties of the sample. Therefore we are investigating alternative methods of sample formation that do not involve packing by pressure.

We have attempted to form cores by simply pouring a water slurry of the oxides into a plaster-of-paris mold. However, the material shrinks a great deal on drying, and toroidal samples tend to crack radially because the center post of the mold cannot yield to the shrinkage. So the method is difficult for this sample shape. In addition, the material sticks to the mold and is very difficult to remove without further mechanical damage. No satisfactory samples have been made in this way.

Better results have been obtained by cutting toroids from a sheet of oxide "dough" with a sharp-edged stamp or "cookie cutter." Fig. 14 is a drawing of the stamp. The dough was prepared by moistening 35 gm. of well-mixed oxides with 20 cc. of a 1.5% solution of gum tragacanth. This mixture was worked until it was free of air and had the consistency of a thick paste. The paste was spread into a uniform sheet from which the cores were stamped. As Fig. 14 shows, the stamp is fitted with an air inlet on the back. Air pressure is used to force the core out of the stamp.

The cores were dried at $90^\circ C$ and prefired for one hour at $900^\circ C$. Then they were fired for four hours at the final temperature.

Evaluation of the magnetic properties of these cores has not yet been completed. However, it can be said that the cores produced seem to be satisfactory mechanically.

3.7 Coprecipitation from Solution as a Method of Mixing. (C. F. Jefferson)

It is supposed that the most intimate possible mixing of the oxides before firing would be achieved by coprecipitation of the oxides from solution. Cores have been prepared from coprecipitated material for comparison with cores made from the usual ball-milled mixtures.

The chloride salts of Ni, Zn, and Fe were dissolved in distilled water and coprecipitated with Na_2CO_3. The precipitate was filtered, washed free of chlorides and carbonates, and dried at $350^\circ C$. Cores were pressed from this material and fired at the temperatures 600°, 800°, 900°, and $1100^\circ C$.

Fig. 15 shows the permeabilities of these cores together with those of a group of similar cores prepared from ball-milled material. It is seen that at any given firing temperature the coprecipitated material always shows
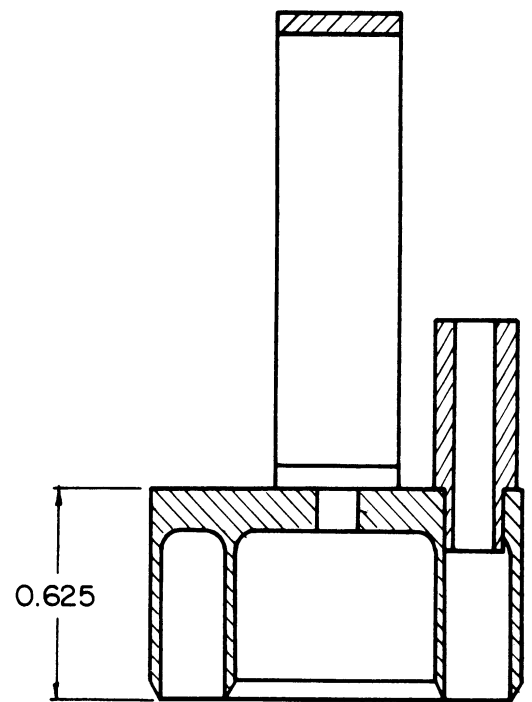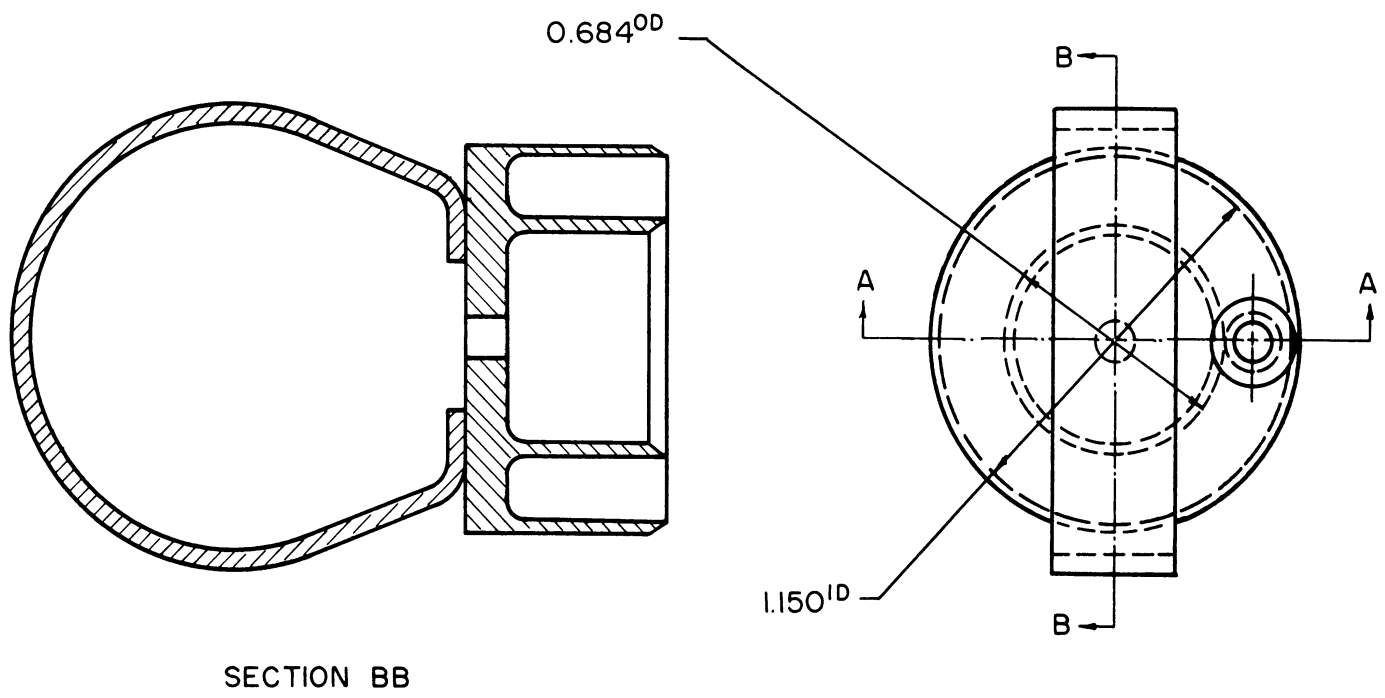
0.684^{OD}

SECTION BB

1.150^{ID}

0.625

FIG 14
STAMP FOR CUTTING SAMPLES

SECTION AA

FIG 15
EFFECT OF MIXING METHOD UPON REAL PERMEABILITY

MIXING METHOD:

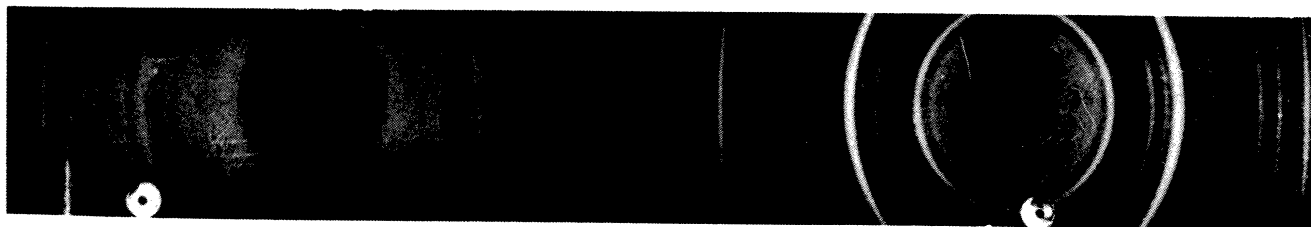COPRECIPITATION —— —— ——
BALL MILL ——·——·——

33

the higher permeability. If one compares the permeability spectra of two cores, formed from coprecipitated and ball-milled materials respectively, and fired together, the coprecipitated sample is seen to behave in every way like a ball-milled sample fired at a higher temperature. It can be assumed from this that the reaction proceeds farther at a given temperature for the coprecipitated material.

It is known that when a solution of $FeCl_2$ and $FeCl_3$, formed by dissolving magnetite in HCl, is precipitated as the hydrous oxides and dried at $100^\circ C$, that the precipitate is magnetic. Okamura, Simoizaka and Torizuka[2] report the formation of magnetic hydrous oxides by coprecipitation of ferrous and ferric ions, and of cobalt and ferric ions. They state that the reactions occur as as low a temperature as $100^\circ C$. Milligan and Holmes[4] have made a similar study of cupric ferrite.

The formation of magnetic ferrous ferrite has been repeated in this laboratory. It was found that the coprecipitated oxides were already magnetic at room temperature before drying. However, the magnetic properties were lost upon heating with a Bunsen burner.

Coprecipitated 20-30 Ni-Zn ferrite was found not to be magnetic at room temperature when first formed, but became so on standing for several hours. X-ray data shows that spinel formation begins at low temperatures. Figure 16 shows the powder patterns of material fired at 120°, 350°, and $1200^\circ C$. The pictures for $350^\circ C$ and higher show only the spinel lines, which are broad at 350° but become sharper at higher temperature.

The complete absence of the oxide lines seems to indicate that the reaction is complete even at 350°. However, this material still has the physical appearance of the unreacted oxides. It is red, not fused together, and soft. In addition, the permeability data indicates only that the reaction goes somewhat

FIRING TEMPERATURE: 120°C
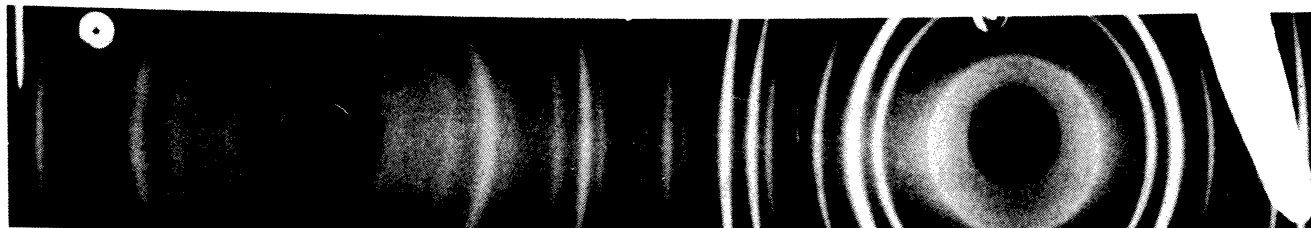
FIRING TEMPERATURE: 350°C
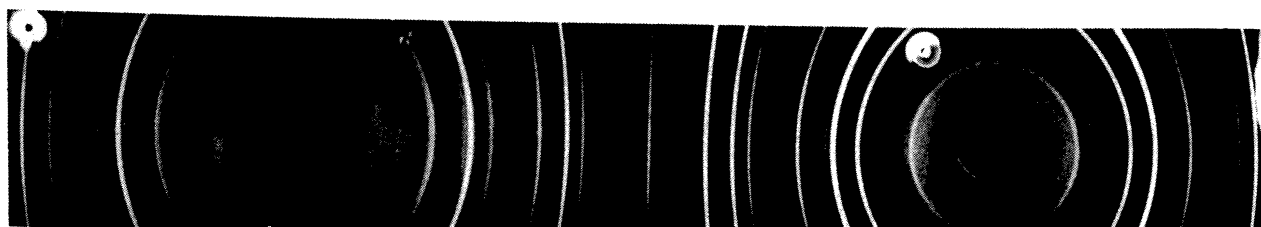
FIRING TEMPERATURE: 1200°C

FIG 16
X-RAY POWDER PHOTOGRAPHS
20-30 Ni-Zn; COPRECIPITATED

further at a given temperature than for ball-milled material, and does not indicate completion at these low temperatures.

The explanation of this discrepancy may lie with a phenomenon called mutual protective action. It is reported[5],[6] from X-ray diffraction studies of hydrous oxides systems that two regions of concentration are found in which the crystallization of one oxide is prevented by the other, and further, that the effect is sensitive to temperature. More study is needed to determine if such a phenomenon is occurring in this case.

3.8 Resistivity and Dielectric Constant. (P. E. Nace, B. Hershenov)

3.8.1 DC Resistivity. The resistivity of a ferrite is known to be a sensitive function of certain properties of the material. In particular, its value is greatly reduced by the presence of even a small amount of bivalent iron. It is hoped that resistivity measurements can be used as a qualitative check for ferrous iron. In any case, it is desired that resistivity be measured for its own sake.

Preliminary investigations have shown that there are considerable difficulties in making such measurements on ferrites. The value obtained is found to vary with the applied voltage (Fig. 17), the length of time the voltage is applied (Fig. 18), the temperature, and the mechanical pressure of the electrodes against the surface. When a sharp probe is used for one of the electrodes, the measured resistivity is found to vary by as much as a factor of 50 as the probe is moved from point to point on the surface. This variation shows some correlation with the physical appearance of the surface under a microscope; the values are typically lower in regions where the surface grains appear to be large. However, there is still considerable variation over regions that present
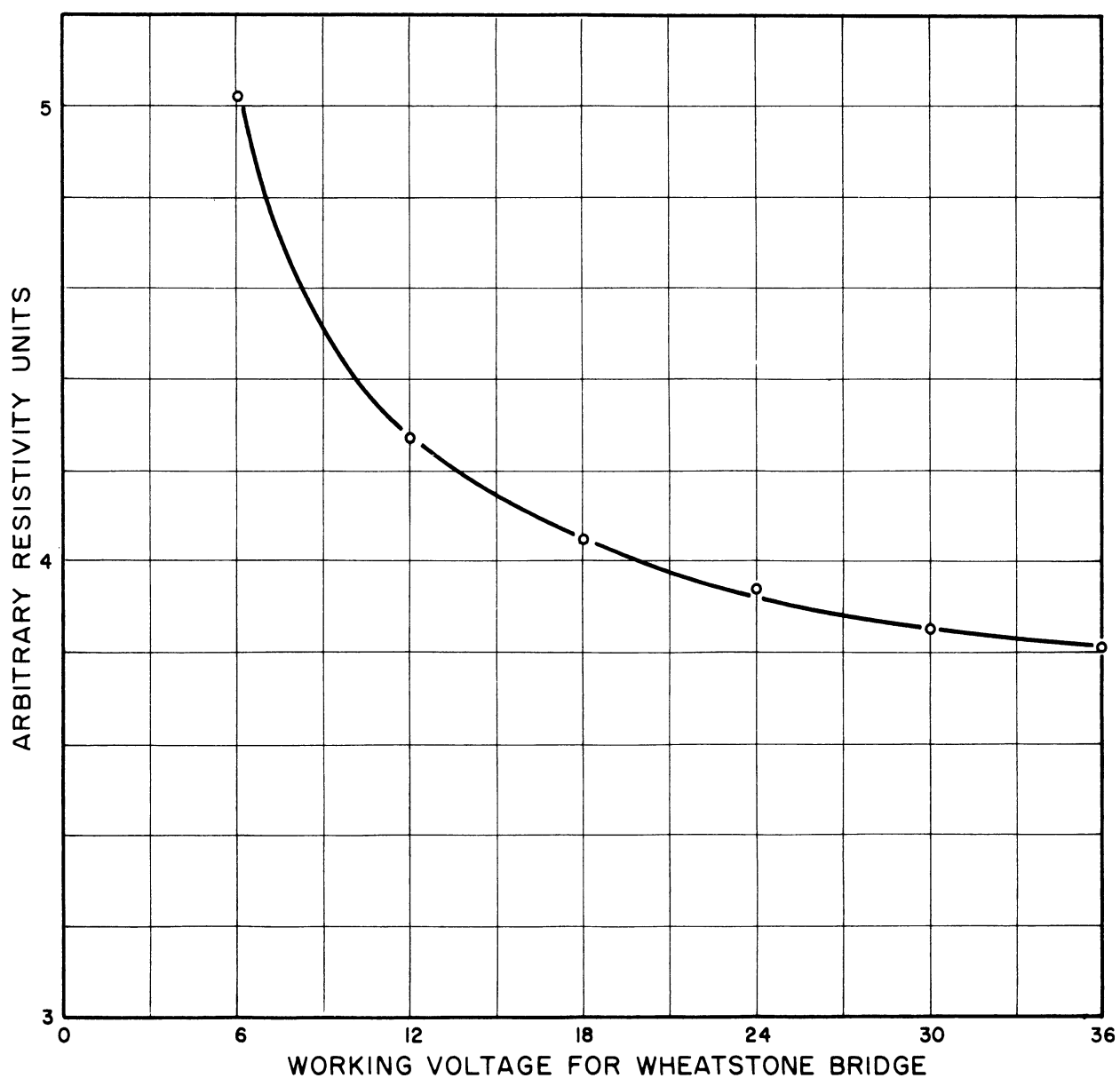
FIG 17

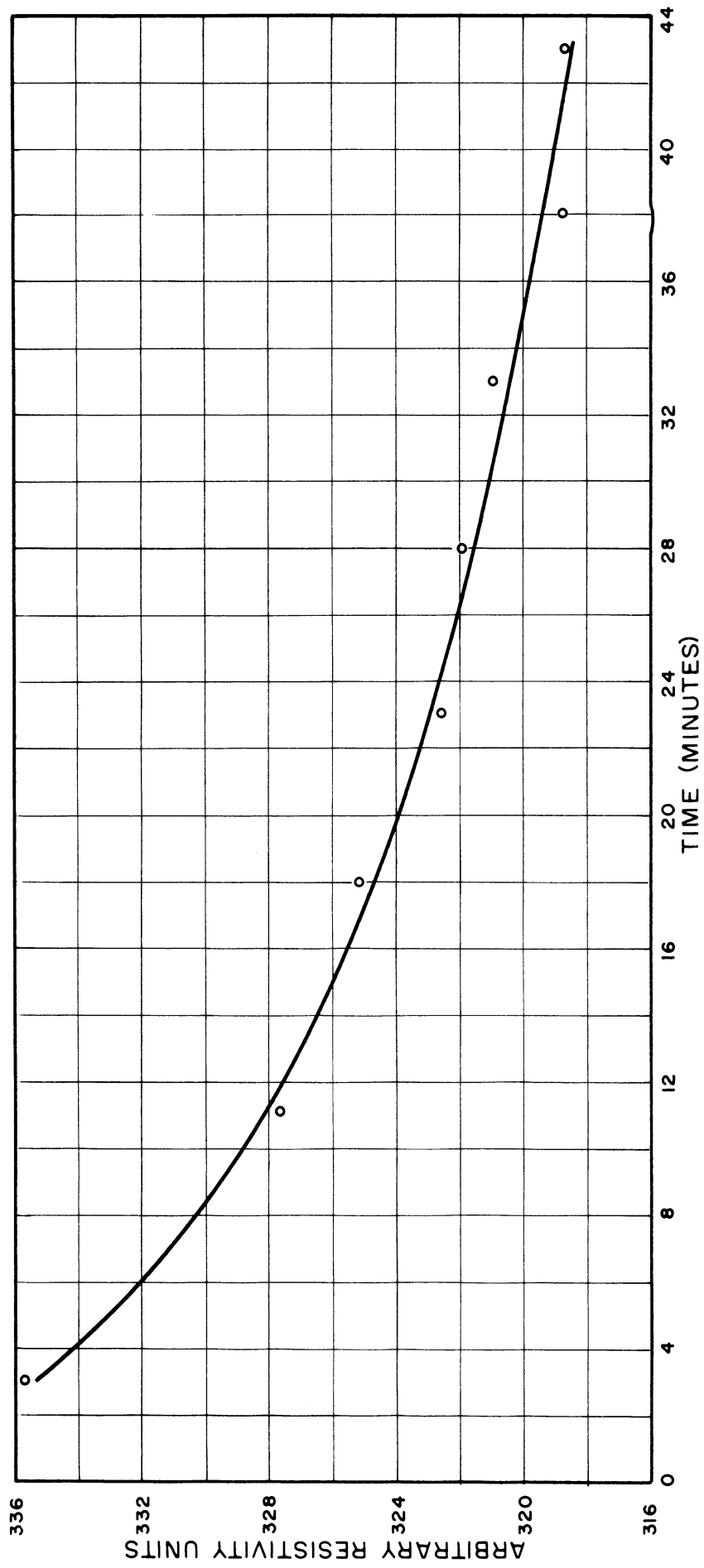RESISTIVITY AS A FUNCTION OF APPLIED VOLTAGE

FIG 18
RESISTIVITY AS A FUNCTION OF TIME
12V WORKING VOLTAGE FOR WHEATSTONE BRIDGE

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a uniform appearance. Generally, the measured resistance showed no correlation with the distance separating the electrodes. Abrading the ferrite surface before applying the electrodes was found to decrease the resistance by as much as a factor of 20. Similarly, abrading the surface under only one electrode was found to introduce a polarity dependence of the resistance as great as 40:1.

It is clear that many of the above observations are surface effects. Henisch[7] describes a number of them as properties of rectifying barrier layers on pp. 20-29 and 39 of his book. Such surface layers could take several forms. There could be a thin film of foreign matter such as grease. In addition, the surface may simply differ from the interior in density, grain size, composition, or in the type of impurity centers present (taken to include lattice vacancies and interstitial atoms as well as foreign atoms).

It is hoped that these surface effects can be averaged out to allow true measurements of the bulk resistivity by using electrodes that make intimate contact over a large surface area. To this end, three types of silver baking paint are being tested. If this effort proves successful, analysis can be made of the effects of other factors such as temperature and moisture content, to determine what degree of control will be required to obtain useful results.

3.8.2 RF Measurement of Dielectric Constant and Resistivity. Three samples have been measured at a frequency of 1 Mc/sec. using a General Radio Dielectric Sample Holder and a General Radio Twin-T Impedance Bridge. The samples were not polished or coated with silver paint to improve contact. The results are summarized in Table IX.

TABLE IX

RF DIELECTRIC CONSTANT AND RESISTIVITY

Sample	Calcining Temp., °C	Firing Temp., °C	Relative Dielec. Const.	Resistivity (ohm-meters)
A-40-1	-	900	3.2	10^5
A-105-2	800	1350	34	2900
A-108-4	950	1350	206	220

Some of the dc effects noted in Section 3.8.1 will effect measurements at rf frequencies as well. Henisch[7] describes rf measurements and gives the various equivalent circuits that have been used for rectifying junctions.

3.9 Theoretical Frequency Dependence of Complex Permeability. (B. Hershenov)

An attempt is being made to formulate semi-general expressions for the frequency dependence of μ_1 and μ_2 of polycrystalline material. The theoretical μ_1 of a single crystal has a zero and a change of sign at a frequency ω_0, and, in fact, displays considerable point symmetry about this zero. Experimental values do not display this effect, and in fact, remain usually positive.

Parks[8] has treated this matter for the case of rotational susceptibility. He assumes that the resonant frequencies of the individual crystallites have various values, and that the experimental features follow by averaging over many of them.

We hope to do the same thing for the case of domain-wall movement. The coefficients α, m, β of the equation of motion of the wall will be assumed to differ among the crystallites. A distribution function must be devised that is physically realizable and yet leads to integrable expressions. The work has not yet progressed far enough to warrant further details.

<u>3.10 Specific Heat Measurements.</u> (E. F. Westrum, Jr., D. M. Grimes)

Additional samples of $(NiO)_x \cdot (ZnO)_{1-x} \cdot Fe_2O_3$ ferrite have been made

for which x = 0.1 and x = 0.3. Specific heat measurements of these samples are

now nearing completion. It has proven to be difficult to separate the magnetic

contribution from the lattice contribution to specific heat. It is planned to

follow with measurements of simpler systems to clarify this point. Fe_3O_4,

α-Fe_2O_3 and γ-Fe_2O_3 have been ordered for this purpose. The final results should

provide information on the effects of different nickel-zinc ratios.

The chemical analysis of Ferramic E reported on p. 24 of QPR No. 2 is

now believed to be in error. Corrected values will be given later.

<u>4. CONCLUSIONS</u>

It is concluded that better control of ferrite properties and improve-

ment of reproducibility will require better control of the grain size and the

porosity of the material. Necessary refinements of manufacturing procedure

include more intimate mixing of ingredients and greater homogeneity of com-

paction and stresses in the samples before firing.

Certain magnetic properties are optimized by lower firing tempera-

tures and shorter firing times. Mixing of constituents by coprecipitation is

found to make this possible.

It was found possible to correlate the permeabilities of samples with

the "projected" value of the density change on firing much better than with

other manufacturing parameters.

The elimination of ferrous iron from excess-iron ferrites by the use

of univalent cations appears promising. Some improvement in properties has

been achieved.

Stamping of cores as an alternative to pressing was found able to produce mechanically satisfactory samples. It is yet to be determined if significant gains in magnetic properties are achieved.

Separation of the magnetic and the lattice contributions to the specific heat has proven to be difficult. Measurements will have to be made on simpler systems to clarify this point.

5. PROGRAM FOR THE NEXT INTERVAL

A. Manufacturing Procedures - The attempt to produce better ferrites by varying the iron content while controlling the ferrous iron by means of univalent cations will be continued. Attempts to control the grain size and porosity will follow two lines: (1) lowering of firing times and temperatures through the use of fluxing agents and better mixing methods, and (2) the control of stresses in sample formation. In the latter regard, the possibilities of the stamping method will be pursued.

B. Measurements - More sensitive determination of losses at the medium frequencies may be sought. Complex permeability measurements will be extended to lower frequencies, and means of incorporating a bias field at all frequencies are being investigated. Eventually these measurements will be extended to temperatures both above and below room temperature.

Specific heat measurements on simpler systems to aid in analyzing the present data will be made as soon as samples arrive. Investigations of the drift phenomenon, of the effects of moisture and other external factors on permeability measurements, and of the problems of resistivity measurement will continue.

Selection of apparatus for measurement of irreversible Barkhausen magnetization will be considered in this period.

C. Theoretical - The effort to derive an expression for the wall-movement permeability spectrum of polycrystalline material will continue. Attempts are being made to understand better the whole subject of the micro-scopic origins of losses.

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