

(3) Another debatable point in Penndorf's work is the assumption that the oxygen atoms recombine in three-body processes. The relative importance of two-body and three-body processes has been discussed in Appendix 5 above. It may perhaps be mentioned here that since no provision is made for the emission of radiation in Penndorf's theory, the oxygen will keep on transforming solar radiation into the kinetic energy of the atoms and molecules, with a consequent continual rise in the temperature of the atmosphere; for at the low pressure and low values of the d^2T/dh^2 in this part of the atmosphere, the loss of heat by conduction is very slow.

(4) The result given in Table VII for the time of "half-recombination" in the absence of solar radiations does not seem right. One certainly expects the time taken for "half-recombination" to be shorter the greater the value of the coefficient of recombination k_1 . The reverse, however, is shown in Table VII.

B. Consider now Rakshit's work.³ As Rakshit's work is a refinement of, and supersedes, the earlier work of Majumdar,² it will be sufficient to confine our discussions to Rakshit's paper.

(1) Rakshit also assumes a given temperature distribution $T(h)$ and the proportion (7). From $T(h)$ and the total pressure P at 80 km, the total pressure and the partial pressure p of oxygen before dissociation are calculated for other heights. Here, as in Penndorf's work, the assumption (P-9) is also made, with the same consequent difficulty with the pressure. Thus at 115 km, the assumed $T=300^\circ\text{K}$ and $P=1.50\times 10^{-4}$ mm of mercury lead to the partial pressure p of oxygen $p=3.00\times 10^{-5}$ mm as given in Table II. On the other hand, from Table III, one finds for the partial pressure p_d after dissociation the value 5.4×10^{-5} mm, contradicting the original total pressure assumed.

(2) Rakshit calculates the total number N_2 of oxygen molecules in a column of unit cross section above the height h by means of the relation $N_2=pNH$, where p is the partial pressure of oxygen

before dissociation, H the height of the homogeneous atmosphere for O_2 , and N the number of molecules of a gas per cc at standard temperature and pressure. It is not clear how H has been obtained, but the use of the partial pressure of oxygen molecules before dissociation instead of that of the existing molecules is obviously unjustified. Thus, Rakshit's calculation is open to the same objections discussed in A, (1) and (2), above.

(3) Rakshit assumes that the recombination process is simply the reverse of the dissociation process—namely, (1a). The distribution of oxygen atoms in the 3P and 1D states is assumed to be given by the Boltzmann theorem. Now for $T=300^\circ\text{K}$, the Boltzmann factor is $\exp(-77)$ so that the concentration of 1D atoms will be extremely small and the dissociation process becomes practically unidirectional. For this reason, recombinations involving two 3P atoms, even though very improbable, have to be considered. Failure to consider these would lead to too high an estimate for the degree of dissociation.

That the calculated values for the degree of dissociation x are not too high is due to an error in the calculation. The ratio $n_A'n_B/n_{AB}$ should have been $4Nx^2 \exp(-E/kT)/(1-x)$ instead of the expression $Nx^2/(1-x)$ given by Rakshit, since $n_A' = n_B \exp(-E/kT)$ and hence $n_A' \ll n_B$. E is the energy difference between the 1D and the 3P states of oxygen. When this correction is made, Eqs. (12), (14), and (15) in Rakshit's paper should all be multiplied by the factor $\frac{1}{2} \exp(E/kT) \cong \frac{1}{2} \exp(77)$ on the right-hand side. It is seen that Rakshit's theory, when correctly calculated, would have led to too high values for x for all heights.

(4) The relation between the absorption coefficient ψ_ν ($\psi_\nu = \sigma_\nu$ in the present paper) and the recombination cross section β_ν of the reverse process as obtained by Rakshit depends on the temperature of the gas. This cannot be correct, the correct relation being (43) given in Appendix 1 above.

On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audiofrequencies

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Semiconducting $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$, prepared in different ways, has been investigated. It appeared that the ac resistivity and the apparent dielectric constant of the material show a dispersion which can be explained satisfactorily with the help of a simple model of the solid: there should be well-conducting grains separated by layers of lower conductivity. Dispersion formulas are given. There is good agreement between experiment and theory.

I. INTRODUCTION

MEASUREMENTS by Blechstein¹ in 1938 showed that certain manganese ferrites have an astonishingly high apparent dielectric constant. Brockman, Dowling, and Steneck² also found such high dielectric constants in ferromagnetic cores made of ferrites which had been developed in this laboratory.³ This property was, in fact, essential in the theory for the dimensional

resonance effects in these cores investigated by these authors.

In order to obtain more quantitative information about the behavior of the ferrites, precise impedance measurements were carried out with disks and rods of several compositions. In the present paper the measurements at room temperature and a phenomenological theory of the impedance of NiZn ferrite and its dispersion are given.

II. EXPERIMENTAL DETAILS

A new alternating current bridge constructed and already described by Köhler and Koops⁴ was used. The

* This paper has been written by Dr. J. Volger of this laboratory from observations and calculations left by the late Ir. Koops (deceased October 22, 1950).

¹ E. Blechstein, *Physik. Z.* **39**, 212 (1938).

² Brockman, Dowling, and Steneck, *Phys. Rev.* **77**, 85 (1950).

³ J. L. Snoek, *New Developments in Ferromagnetic Materials* (Elsevier Company, New York, 1947).

⁴ J. W. L. Köhler and C. G. Koops, *Philips Research Repts.* **1**, 419 (1946).

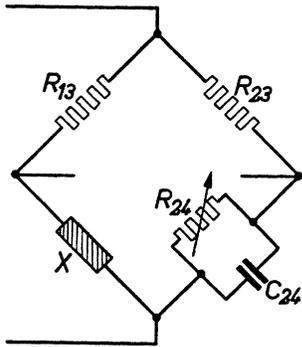


FIG. 1. Principle of bridge.

principle of the measurement is shown in Fig. 1. The sample X was compared with a resistance R_{24} shunted by a capacitance C_{24} . R_{24} had a sufficiently low self-inductance, C_{24} a sufficiently small loss angle. R_{23} and R_{13} were standard resistances of 1000Ω and 10000Ω , respectively, with very small time constants. The way in which certain errors, possibly introduced by the geometry of the bridge network, were almost completely reduced is discussed by Köhler and Koops.

After the bridge and the Wagner earth connections have been balanced, the impedance X of the sample can be calculated in the usual way. In fact, the parallel resistance R_p and the parallel capacitance C_p of the sample are determined:

$$X^{-1} = R_p^{-1} + j\omega C_p. \quad (1)$$

From R_p and C_p the apparent resistivity ρ_p and the apparent relative dielectric constant ϵ_p of the material were calculated with the help of

$$R_p = \rho_p d / O, \quad (2)$$

$$C_p = \epsilon_0 \epsilon_p O / d, \quad (3)$$

O and d being the cross section and height of the cylindrical sample. (Giorgi units are used.) Also the loss angle δ can be calculated:

$$\tan \delta = (R_p \omega C_p)^{-1} = (\rho_p \omega \epsilon_0 \epsilon_p)^{-1}. \quad (4)$$

III. RESULTS AND DISCUSSION

The results given below were obtained on a ceramic disk of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$. This spinel had been prepared

TABLE I. Room temperature data of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ fired in air at 1280°C and cooled slowly in air.

ν (c/s)	$10^{-2}\rho_p$ (Ωm)	ϵ_p	$\tan \delta$
0	202	—	—
160	187	1980	3.05
250	175	1870	2.20
500	143	1520	1.66
1000	104	1090	1.59
2000	74	610	2.00
4000	58	256	3.03
8000	52	93	4.7
16000	50	37	6.1
32000	49	22	5.2
64000	48	17	3.4
100000	47	16	2.4

by milling together the constituent oxides, prefiring at 1000°C , milling again, molding the disk, and firing it at 1280°C , after which the sample was slowly cooled in air. No second phase was detected by x-ray analysis. Mr. Gorter of this laboratory was entrusted with the preparing of the materials.

The disk had a diameter of 36 mm. First, a series of measurements were made with the disk at a thickness of 6 mm. Afterwards the thickness was reduced to 1.1 mm by grinding. It appeared, however, that the calculated ρ_p and ϵ_p of the ferrite were not at all affected by this change of thickness.

Electrodes were deposited on both sides of the disk by evaporating silver in vacuum. The sample was then clamped between two suitable copper plates, which formed sufficiently short leads to the bridge itself.

Table I gives the results obtained. See also Figs. 2 and 3.

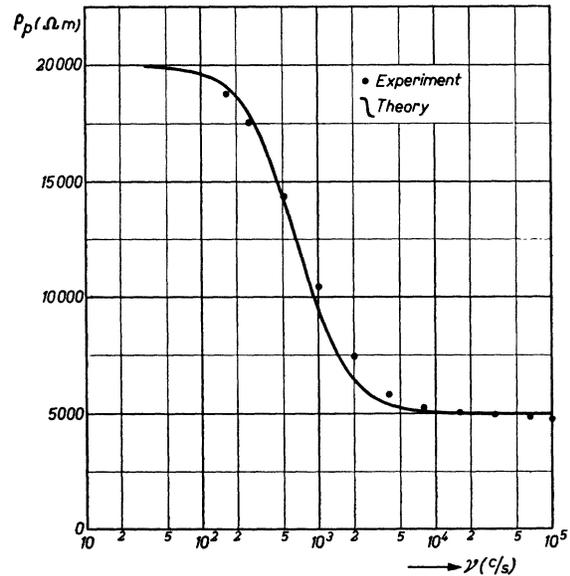


FIG. 2. Dispersion of resistivity.

What can be the quantitative explanation of this remarkable dispersion of both ρ_p and ϵ_p ? It is clear that neither dimensional effects as found by Brockman *et al.*² nor skin effect play a part here. The material being an electronic semiconductor, it is also very unlikely that an intrinsic dispersion of the conduction mechanism itself would exist at such very low frequencies, as is the case here.

A good phenomenological theory of the dispersion can be based, however, upon the assumption that R_p and C_p result from an equivalent circuit as shown in Fig. 4, in which R_1 , R_2 , C_1 , and C_2 are constants. It is well known from ac theory that R_p and C_p then obey dispersion formulas. From a purely circuit-theoretical point of view it can be proved that two capacitors and two resistors are needed in order to build up a two-pole having a finite value of dc resistance and showing the

typical $\tan\delta$ vs ω curve with one hump which have been found with the material. Self-inductance has been omitted. In any real model obviously only resistors with parallel capacitors may be assumed, and therefore the circuit shown in Fig. 4 is chosen.

The model indicated might be justified by taking into account the barrier layers which may be present between the material and the electrodes (caused by impurities). With the sample under investigation, however, the electrodes proved to have no influence upon the

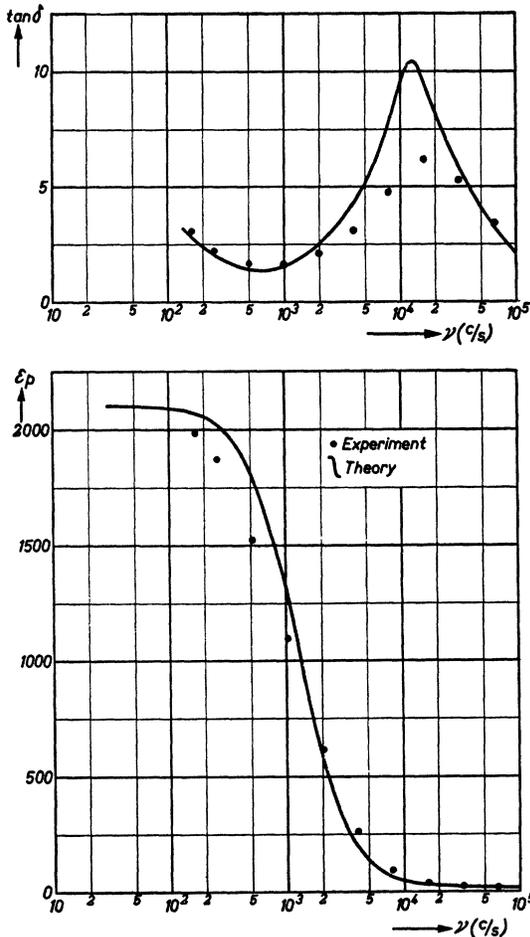


FIG. 3. Dispersion of dielectric constant and $\tan\delta$.

measurements of ρ_p and ϵ_p , since ρ_p and ϵ_p were quite the same with a thick disk and a thin one.

It is very probable, therefore, that layers of lower conductivity must be assumed to be present in the solid itself.

It must be noted here that an inhomogeneity model has already been proposed as a means of explaining certain characteristics of the $\tan\delta$ vs ω curves of dielectrics.^{5,6} See also the paper by Blechstein,¹ who, by mixing

⁵ J. C. Maxwell, *Electricity and Magnetism* (Oxford University Press, London, 1873), Vol. I, Sec. 328.

⁶ K. W. Wagner, *Ann. Physik* 40, 817 (1913); *Arch. Electrotech.* 2, 371 (1914).

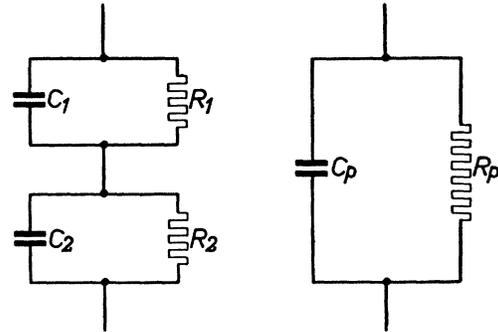


FIG. 4. If the right-hand circuit is equivalent to the left-hand one, with C_1 , C_2 , R_1 , and R_2 constants, then C_p and R_p are not constants with respect to the frequency but obey dispersion formulas.

graphite or metal powder and paraffin wax, prepared artificial samples which showed the same high apparent dielectric constant as found in his ferrites.

One thus arrives at the model shown in Fig. 5. The solid is imagined to consist of well-conducting grains separated by poorly conducting layers, while the current is assumed to flow along parallel alignments of grains, as has been drawn.

Let x be the ratio of the thickness of the layers to the thickness of the grains, and let ρ_1 , ρ_2 , ϵ_1 , and ϵ_2 denote the resistivity and the relative dielectric constant of the layers (1) and grains (2), respectively. Suppose $x \ll 1$. If, moreover, sideways admittances between the grains are omitted, one easily computes with the help of common ac calculus

$$\rho_p = \rho_p^\infty + \frac{\rho_p^0 - \rho_p^\infty}{1 + \tau_p^2 \omega^2} \quad (5)$$

with

$$\left. \begin{aligned} \rho_p^\infty &= \frac{\rho_1 \rho_2 (\epsilon_1 + x \epsilon_2)^2}{\rho_1 \epsilon_1^2 + x \rho_2 \epsilon_2^2}, \\ \rho_p^0 &= x \rho_1 + \rho_2, \\ \tau_p &= \epsilon_0 \left(\frac{\rho_1 \rho_2 (\rho_1 \epsilon_1^2 + x \rho_2 \epsilon_2^2)}{x \rho_1 + \rho_2} \right)^{\frac{1}{2}}. \end{aligned} \right\} \quad (6)$$

Likewise,

$$\epsilon_p = \epsilon_p^\infty + \frac{\epsilon_p^0 - \epsilon_p^\infty}{1 + \tau_\epsilon^2 \omega^2} \quad (7)$$

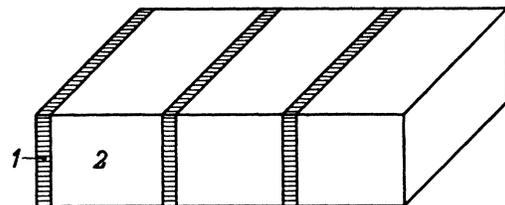


FIG. 5. Model of a grain-structured conductor. Layers of poorly conducting material separate the grains.

TABLE II. Room temperature properties of 4 samples of $\text{Ni}_{1.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$, fired at 1300°C in oxygen or air and cooled slowly or rapidly.

$\nu(c/s)$	1a sintered in O_2 , cooled slowly in O_2 , 0.10% FeO		1b sintered in O_2 , cooled rapidly in air, 0.38% FeO		2a Sintered in air, cooled slowly in air, 0.07% FeO		2b sintered in air, cooled rapidly in air, 0.42% FeO	
	$\rho_p(\Omega m)$	ϵ_p	$\rho_p(\Omega m)$	ϵ_p	$\rho_p(\Omega m)$	ϵ_p	$\rho_p(\Omega m)$	ϵ_p
1×10^3	5400	1710	12.80	28200	1360	4300	10.8	39000
8×10^3	2700	218	12.00	14000	702	1280	10.3	21500
1×10^6	2300	32	11.11	716	495	66	8.9	1320
1×10^6	1295	18.1	8.65	97	463	30.7	6.78	147.5
6×10^6	790	15.9	8.15	51.6	403	26.0	5.66	82.1
35×10^6	704	13.8	5.95	42.1	290	22.4	4.43	68.5

with

$$\left. \begin{aligned} \epsilon_p^\infty &= \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + x \epsilon_2}, \\ \epsilon_p^0 &= \frac{x \rho_1^2 \epsilon_1 + \rho_2^2 \epsilon_2}{(x \rho_1 + \rho_2)^2}, \\ \tau_\epsilon &= \epsilon_0 \frac{\rho_1 \rho_2 (\epsilon_1 + x \epsilon_2)}{x \rho_1 + \rho_2}. \end{aligned} \right\} (8)$$

Thus,

$$\tau_\epsilon = (\rho_p^\infty / \rho_p^0)^{1/2} \tau_p. \quad (9)$$

If the measured ρ_p and ϵ_p are to fit the dispersion equations (5) and (6), it is impossible to obtain more than 4 independent quantities from experiment. In the phenomenological theory, presented here, however, there are 5 quantities, and in order to calculate these from the data it is necessary to make one more assumption. Let this assumption be

$$\epsilon_1 = \epsilon_2, \quad (10)$$

which is quite reasonable.⁷ Since $x \ll 1$ and $\rho_1 \gg \rho_2$, formulas (6) and (8) are reduced to

$$\left. \begin{aligned} \rho_p^\infty &= \rho_2, \\ \rho_p^0 &= x \rho_1 + \rho_2, \\ \tau_p &= \epsilon_0 \epsilon_2 [\rho_1^2 \rho_2 / (x \rho_1 + \rho_2)]^{1/2}, \end{aligned} \right\} (11)$$

$$\left. \begin{aligned} \epsilon_p^\infty &= \epsilon_2, \\ \epsilon_p^0 &= \epsilon_2 \cdot \frac{x \rho_1^2 + \rho_2^2}{(x \rho_1 + \rho_2)^2}, \\ \tau_\epsilon &= \epsilon_0 \epsilon_2 \frac{\rho_1 \rho_2}{x \rho_1 + \rho_2}. \end{aligned} \right\} (12)$$

⁷ This assumption is based upon the knowledge that the true dielectric constant of various oxides is almost the same. Moreover, only small local deviations from stoichiometry might be the reason for the large differences of ρ_1 and ρ_2 which appear here, and such deviations will probably not affect the true dielectric constant. (See also reference 8.)

It is possible to fit experimental and theoretical values of ρ_p and ϵ_p quite well if one takes:

$$\begin{aligned} \rho_1 &= 3.3 \times 10^6 \Omega m, & \epsilon_1 &= 17, \\ \rho_2 &= 5.0 \times 10^3 \Omega m, & \epsilon_2 &= 17, \\ x &= 0.45 \times 10^{-2}. \end{aligned}$$

The theoretical curves in Figs. 2 and 3 have been calculated on the basis of these values. Rather good agreement can also be obtained with values of these parameters differing by 10 or 20 percent from the given values. It is a very interesting fact that the experimental data in Table I agrees satisfactorily with dispersion formulas with only two relaxation constants.

The sample investigated belonged to a series of samples of NiZn ferrite all of the same composition as regards the amount of constituent metal oxides from which they had been prepared. Owing to their being fired and cooled in different ways, however, they differ in Fe^{2+} content and therefore also in specific resistance.⁸ All samples showed the same sort of dependency of ρ and ϵ on frequency. Table II gives a survey of some room temperature measurements.

The measurements at 1, 6, and 35 Mc/sec have been carried out by Dr. Gevers of this laboratory. Dr. Gevers determined ρ_p and ϵ_p of the sample by tuning an LC-circuit, the capacitor of which was shunted by the sample. The dispersion interval of these samples does not lie in the audiofrequency range. The phenomenological theory given above does not apply in every respect to the data in Table II; e.g., ϵ_p happens to fall off at lower frequencies than does ρ_p , which is not in accordance with (9). Possibly the existence of more than two relaxation constants τ , or even quite a range of them, plays a part here.

A number of measurements on other semiconducting materials will be published in the near future.

⁸ Verwey, Haayman, Romeyn, and v. Oosterhout, Philips Research Repts. 5, 173 (1950).