$\Delta\phi_0 \neq 0$ the deviation from the circular path is therefore given by the following differential equation:

$$\sigma''+\sigma(1+y^2)=\tfrac{1}{2}(1+y)\Delta\phi_0/\phi_0. \quad (43)$$

The general solution of this equation is given by:

$$\sigma=a\sin(1+y^2)^{\frac{1}{2}}\theta+b\cos(1+y^2)^{\frac{1}{2}}\theta+\tfrac{1}{2}(1+y)\Delta\phi_0/\phi_0. \quad (44)$$

With the initial conditions:

$$\sigma=\sigma'=0 \text{ for } \theta=0, \quad (45)$$

we get:

$$a=0, \quad b=-\frac{1}{2}\frac{(1+y)}{(1+y^2)}\frac{\Delta\phi_0}{\phi_0}. \quad (46)$$

At $\theta=\pi/(1+y^2)^{\frac{1}{2}}$ we therefore have:

$$\sigma\left[\frac{\pi}{(1+y^2)^{\frac{1}{2}}}\right]=\frac{1+y}{1+y^2}\frac{\Delta\phi_0}{\phi_0}. \quad (47)$$

Since $(2e\phi_0/m)^{\frac{1}{2}}=v_0$ we have:

$$\frac{d\phi_0}{\phi_0}=2\frac{dv_0}{v_0}, \quad (48)$$

and since $\delta=\sigma\cdot r_0$, we get for the line width D:

$$D=2\frac{1+y}{(1+y^2)}r_0\frac{dv_0}{v_0}. \quad (49)$$

Since the velocity resolution is only noticeable if it causes the line width to be greater than that due to second-order aberrations, a quantity τ has been introduced called the reduced resolution. It is defined by:

$$\tau=|D/L|\alpha^2. \quad (50)$$

We get for τ:

$$\tau=2\left|\frac{1+y+y^2+y^3}{1+\frac{1}{3}y+y^2+3y^3}\right|. \quad (51)$$

PHYSICAL REVIEW VOLUME 67, NUMBERS 7 AND 8 APRIL 1 AND 15, 1945

On Permanent Charges in Solid Dielectrics

I. Dielectric Absorption and Temperature Effects in Carnauba Wax

B. Gross and L. Ferreira Denard
National Institute of Technology, Rio de Janeiro, Brazil
(Received February 6, 1945)

The influence of the temperature upon dielectric absorption is studied for carnauba wax. Isothermic and non-isothermic current-time curves are measured. It is shown that a considerable part of the absorbed charge can be "frozen in," if the temperature is reduced to a value sufficiently inferior to that prevailing during the charging period before the system is short-circuited. The "frozen" charge dissipates extremely slowly, if the temperature is kept low, but it is liberated rapidly if the temperature is raised again. The effect is explained by the increase of the charging and discharging rates with increasing temperature. It is closely related to the permanent moment of the electret.

I. INTRODUCTION

An electret is a dielectric body that retains an electric moment after the externally applied electric field has been reduced to 0. It was shown by Eguchi[1] that permanent electrets are obtained when certain waxes and resinous materials, mainly carnauba wax, previously melted, are allowed to solidify while exposed to strong electric fields. Eguchi's results were considered very startling ones because for a long time it was the general opinion that any self-maintained electric field in solid bodies would soon be neutralized in consequence of the movement of the free electric charges existing in all substances. But these results have been confirmed and completed by various authors.[2] While the behavior of the electret is now fairly well known, no generally accepted explanation of its

[1] M. Eguchi, Phil. Mag. **49**, 178 (1925).

[2] A. Gemant, Phil. Mag. **20**, 929 (1935); W. M. Good and J. D. Stranathan, Phys. Rev. **56**, 810 (1939).

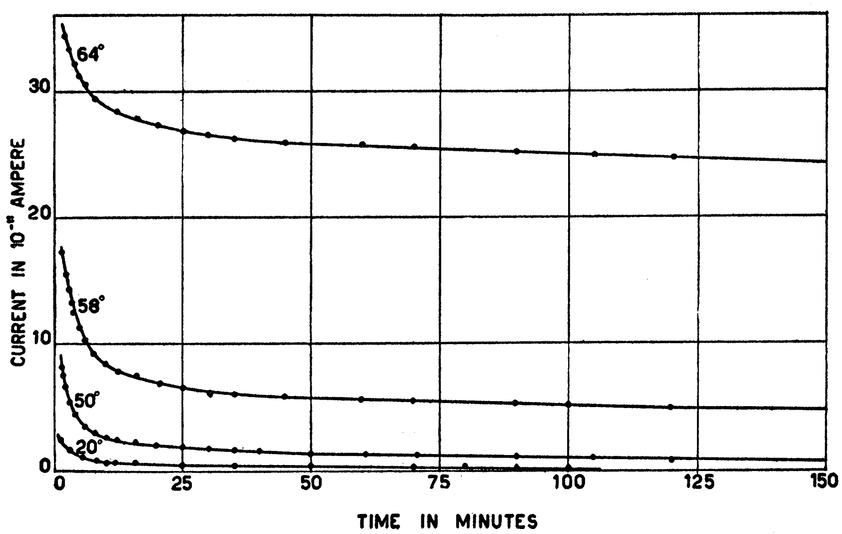

FIG. 1. Charging currents for different temperatures.

physical mechanism has been established so far. Formally, the existence of a permanent electric moment of a dielectric body must be considered as representing one more form of the "anomalous" behavior of solid dielectric. The fundamental form of anomalous behavior is dielectric absorption, which for solid dielectrics is characterized by the appearance of the reversible *absorption* or *anomalous charging* current. The condition of reversibility granted, other forms of anomalous behavior—variance of capacitance with time, dielectric loss, and residual charge—can be calculated quantitatively from the data for the absorption current.[3] This suggests the existence of a physical relationship between dielectric absorption and the permanent moment of the electret. And it can be expected that further information about the properties of electrets would derivate from the systematic study of the influence of temperature upon dielectric absorption for dielectrics which are submitted to a heat treatment similar to that of Eguchi's electret.

The influence of the temperature upon dielectric absorption has been treated in a general way by K. W. Wagner.[4] He showed that for heterogeneous dielectrics the total amount of absorption is nearly independent of the temperature, while the rate of absorption increases strongly with increasing temperature. Wagner was able to establish a simple relationship between the form of the absorption currents for different temperatures, which he exemplified by the results of many measurements performed with technical insulators. Many other measurements are due to J. B. Whitehead.[5] Non-isothermic current-time curves for quartz are reported by Altheim.[6] Groetzinger[7] observed considerable discharge currents when capacitors containing beeswax previously solidified under the influence of an electric field were reheated beyond the melting point of the wax.[7] Other authors who have studied the conductance of crystalline dielectrics occasionally also refer to non-isothermic effects.[8]

In this paper we relate a series of measurements of temperature effects for carnauba wax.

II. TECHNIQUE OF MEASUREMENT

Samples of carnauba wax, 1 mm in thickness and having an area of about 15 cm^2, were chemically silvered on both faces and put between

[3] E. v. Schweidler, "Die Anomalien der dielektrischen Erscheinungen," in L. Graetz, ed. *Handbuch d. Elektrizitaet u. d. Magnetismus* (Johann Ambrosius Barth, Leipzig, 1918), Vol. I, p. 232.

[4] K. W. Wagner, in H. Schering ed., *Die Isolierstoffe der Elektrotechnik* (Verlagsbuchhandlung Julius Springer, Berlin, 1924), p. 24.

[5] J. B. Whitehead, Physics **2**, 82 (1932).

[6] O. G. v. Altheim, Ann. d. Physik **35**, 417 (1939).

[7] H. Frei and G. Groetzinger, Physik. Zeits. **37**, 720 (1936).

[8] A. F. Joffé, *The Physics of Crystals* (McGraw-Hill Book Company, Inc., New York, 1928), p. 109; F. Quittner, Zeits. f. Physik **56**, 597 (1929).

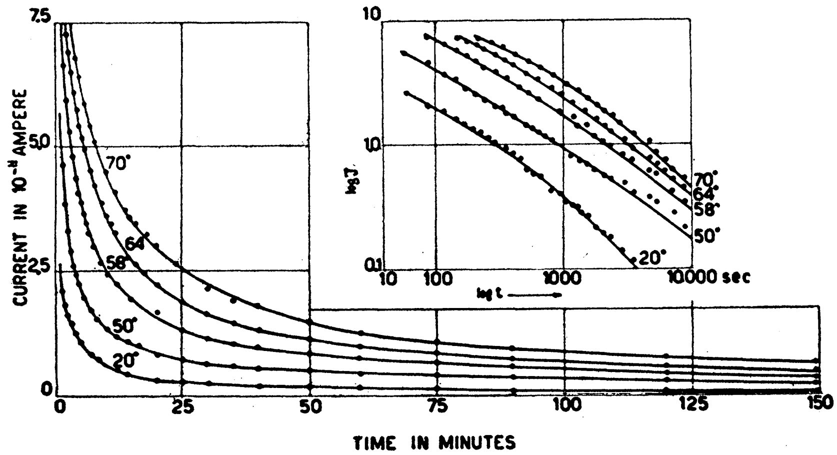

FIG. 2. Discharge currents for different temperatures.

plates in a small oven suitable for measurements up to 100°C. Readings of the temperature were taken with the aid of a mercury thermometer put closely at the side of the sample. The current was measured in most cases by the potential difference it produced across the terminals of a high-ohm resistor (10^{10}–10^{12} ohm) connected in series with the sample. But sometimes the current was measured by taking the charging time curve of an air capacitor (50 to 2.000 $\mu\mu$f) connected in place of the resistor. The potential difference in both cases was measured with a one-string fiber electrometer. The tension applied to the system was furnished by dry cells. In most measurements it was equal to 118 v.

III. ISOTHERMIC CURRENT-TIME CURVES

Figure 1 gives the charging currents for different temperatures between 20°C and 70°C. The currents at the higher temperatures are considerably stronger than those at the lower temperatures, but the main increase is obviously due to a rise of the steady state current. The influence of the temperature upon this latter

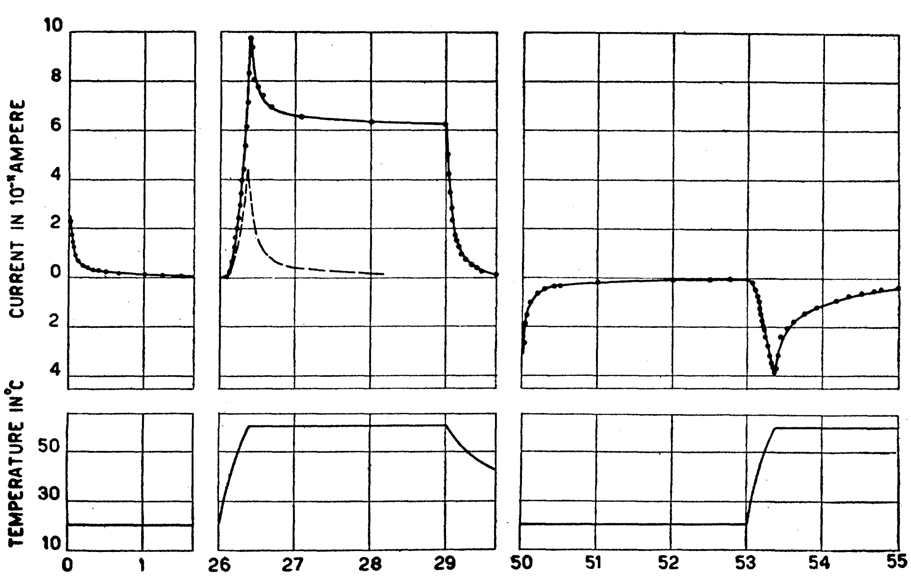

FIG. 3. Non-isothermic effect.

component of the current is known; here we are interested mainly in the behavior of the transient current component. This is shown in Fig. 2, where the discharge currents are indicated in an ordinary scale and a logarithmic scale. The charging time, in every case, was 20 hours; the temperature during the charge was the same as that indicated for the corresponding discharge. These currents rise with increasing temperature. Within the limits of the experiment, the discharged quantity of electricity and, therefore, the dielectric absorption, increase with increasing temperature. No saturation value and no intersection of curves belonging to different temperatures were observed. Yet an intersection of curves for different temperatures may still occur at times greater than those for which measurements could be taken.

IV. NON-ISOTHERMIC EFFECTS

And now we investigated the influence of temperature changes upon capacitors, which either were energized by a constant voltage source or were kept in short-circuit after having been subjected to a constant tension. The general aspect of the currents so produced is seen from Fig. 3. There are 5 phases of the experiment.

(1) *A constant potential difference is applied to the capacitor* at low temperature (20°C). The usual absorption current is observed. After one day, this current has decreased to a very low value. No measurable steady state current is observed at 20°C.

(2) *The temperature of the energized capacitor is rapidly heightened*, then maintained constant again. A sudden increase of the current is observed; it is due in part to the rise of the steady state current. But a transient also appears; it manifests itself by the peak in the current-time curve, the occurrence of which coincides with the moment when the temperature becomes constant. This transient is found to depend on the temperature and on the slope of the temperature-time curve; if the temperature rises rapidly, the current increase is stronger and the peak higher than if the temperature rises slowly.

The appearance of the transient can be predicted from the study of the isothermic curves of Figs. 1 and 2. If the capacitor is charged, for the same time, once at a low temperature and a second time at a high temperature, then according to the data of the isothermic curves, in the second case more electricity is stored up in the system than in the first one. Therefore, if the temperature of the same capacitor, while energized by a constant voltage source, is raised from a low to a high level, the system passes from a state of low absorption to a state of high absorption. This must have the same effect as a voltage jump. Accordingly, the increase in temperature is followed by a transient current. The current subsequent to a slow increase of the temperature is lower than the current subsequent to a rapid increase, just as it happens for variations of the applied potential difference.

The temperature is maintained high for a time sufficiently long to let the transient decay far below the level of the steady state current.

(3) *The temperature of the energized capacitor is reduced* to the initial low value. The current falls off very rapidly, but it depends now on the instantaneous values of the temperature only, not on the slope of the temperature-time curve. No transient is observed. We conclude that the current-temperature function obtained during the cooling period gives the relation between steady state current and temperature. The knowledge of this function enables us to evaluate what fraction of the current during the heating period is due to the steady state current and what is due to the transient. To obtain the latter, from every point of the current-time curve obtained during the heating period one must subtract the current value observed for the corresponding temperature during the cooling period. In this way, the dashed curve of Fig. 3 was obtained.

(4) *The capacitor is short-circuited* at low temperature (20°C). The usual discharge current is observed. Its magnitude at any instant is that of the corresponding value of the charging current belonging to the same temperature. This behavior shows that in spite of the additional absorption caused by the heating, the principle of superposition remains valid.

More generally, it could be established that the discharge current does not depend on the temperature at which the capacitor is charged, provided this temperature is not inferior to the temperature during the discharge. This condition

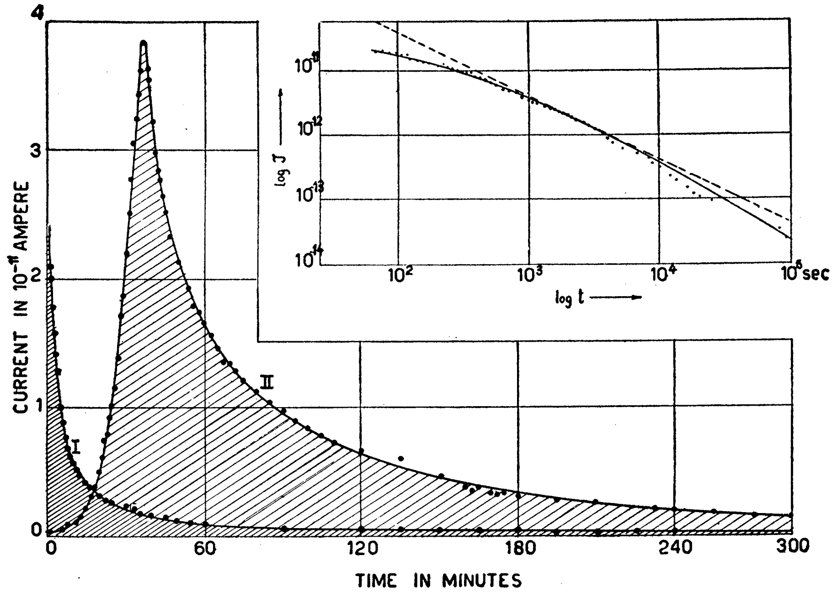

FIG. 4. I—Discharge current at 26°C. II—Discharge current raised in consequence of reheating of the dielectric to 70°C, 24 hours after short-circuiting. Inset—Absorption current at 26°C.

granted, the discharge current at any temperature has the same values which would be observed under the conditions of the isothermic experiment to which Figs. 1 and 2 refer.

(5) *The temperature of the shorted capacitor is raised* in the same way as before, then maintained constant. Again a transient is observed, similar to that subsequent to the first heating, but now in the direction of a discharge current. This behavior confirms our earlier conclusion that the first transient is a reversible absorption current, by which electric charge is stored up in the capacitor. During the cooling of the energized capacitor, no discharge takes place—this is testified by the absence of any transient during this stage of the experiment. After the short-circuit at low temperature, the charge stored up in the system is removed at the same slow rate as it was absorbed during the first stage of the experiment. The quantity of electricity absorbed during the heating period remains apparently "frozen" in the dielectric. It is liberated by the reheating of the capacitor.

The amount of liberated charge is independent of the rate of the previous cooling. It increases with increasing temperature and duration of the charging period; it decreases slowly when the interval of time between short-circuiting and reheating is lengthened. In one case, for example, an increase of this interval from 165 min. to 15 days resulted in a reduction of less than 20 percent of the liberated charge. This slowness of dissipation was confirmed by other measurements covering the period of 2 years.

With regard to the influence of the voltage, a linear relationship was found for values up to 10.000 v/cm.

V. THE PHENOMENON OF THE "FROZEN" CHARGE

There are two characteristic features of the effect: (1) No transient appears during the cooling of the energized capacitor. (2) The discharge current depends only on the temperature of the capacitor during the discharge. We conclude therefrom that the effect does not involve any variation with temperature of the total absorption capacitance (defined by the integral over the relaxation function), but that it must be explained by the variance of the charging and discharging rates. It follows that the absorption capacitance must be much higher than could have been inferred so far from measurements far below the melting point. At such temperatures, the rate of absorption is so low that it is practically impossible to charge the capacitor to any considerable degree. The charge, which is absorbed during weeks or even years, would be only a fraction of the saturation value. With increasing temperature, the rate of absorption increases; then, during the same time, more charge can be absorbed than before although saturation may still be far ahead. Conversely, if a charged capacitor is cooled and is shorted at a temperature far below that at which it was charged, the rate of discharge at the low temperature is so low that the quantity of electricity discharged during a long time represents only a small part of the quantity of electricity previously absorbed. The same reason which does not allow the capacitor to be completely charged at the low temperature, now prevents it from being completely discharged. And so, if one has succeeded in getting the capacitor strongly charged by charging it at a high temperature, one may trap the bulk of the absorbed charge by the cooling experiment.

Some numerical data may be obtained from Fig. 4. The capacitor, to which this figure refers, was charged with 118 v at 70°C during 24 hours. Then it was cooled to room temperature (26°C) and shorted; 24 hours after the sudden short-circuit it was heated again to 70°C and remained at this temperature for one day. Curve II gives the discharge current flowing during the reheating; the area under this curve gives the liberated charge. During the first 5 hours of discharge 1.3×10^{-7} coulomb are liberated. The absorption current at 26°C is given by Curve I in a simple and in a logarithmic scale (inset). An upper limit to the observed values of the current is represented by the dashed curve (inset), given by $J=4\times10^{-9}/t$ (J in amperes, t in seconds). An extrapolation of this function to greater values of t permits an evaluation of the rate of dissipation of the frozen charge; according to this equation, 100,000 years after the sudden short-circuit there would still be left in the capacitor almost half the charge, which at 70°C is absorbed within a few hours. A lower limit for the total amount of the absorbed charge of the capacitor can be calculated from the areas under Curves I and II; one obtains 1.6×10^{-7} coulomb. If one takes into account the value of the applied potential difference and the dimensions of the sample, there results for the static dielectric constant a lower limit of 135. In consequence of the extrapolations involved, these calculations have only a purely qualitative value. But they show at least that in the low temperature range one has to count with relaxation times of the order of thousands of years. This order of magnitude is at first sight surprising. But it may be remembered that similar values occur for the elastic after-effect, the relation of which to the electric effect has been observed repeatedly.[9] The discharge current curves for different temperatures must overlap themselves mutually. But at low temperatures, the points of intersection are so far from origin that they are inaccessible to direct observation. They must approach the origin for higher temperatures and finally a state of saturation should be arrived at. But the corresponding temperatures are probably so near the melting point that observation again is made difficult.

The very nature of the phenomena here described as well as the references in the literature[6, 7] and my own observations made with other substances make it clear that this is an effect of a very general kind, not restricted to carnauba wax alone; this being so, the static dielectric constant of many solid dielectrics may be of an order of magnitude which hitherto has been considered as exceptional and the dielectric relaxation function must approach 0 still more slowly than is believed generally. The same opinion has been recently emphasized by Cole,[10] whose conclusions are entirely confirmed by the result of the measurements here reported.

VI. DIELECTRIC ABSORPTION AND THE FIELD OF THE ELECTRET

The phenomenon of the "frozen" charge shows that the charges associated with dielectric absorption can be preserved over very large periods of time. In this respect it meets the basical requirement to be fulfilled by any mechanism, which may be held responsible for the permanent charges of the electret. But, with regard to opinions occasionally expressed,[11] it may be

[9] R. Simha, J. App. Phys. **13**, 201 (1942); N. W. Taylor, J. Phys. Chem. **47**, 235 (1943).
[10] K. S. Cole and R. H. Cole, J. Chem. Phys. **10**, 98 (1942).
[11] G. Nadjakoff, Physik. Zeits. **39**, 226 (1938).

mentioned that a dielectric containing a "frozen" charge is not necessarily an electret, i.e. it may or may not be found to produce an electric field when the plates are detached. It must also be pointed out that in Eguchi's heat treatment the melting point of the substance is exceeded, while in our measurements we have confined ourselves to the range of temperatures between room temperature and melting point. But the difference between the two cases is apparently a purely qualitative one. According to our measurements covering so far a period of nearly 2 years, disks of carnauba wax polarized below the melting point produce electric fields which are very enduring although somewhat smaller than those reported by Eguchi.

Reversible dielectric absorption in homogeneous substances, according to present theories, may be caused by an anomaly either of displacement or of conduction. In the first case, referring to polar substances, the dielectric polarization lags behind the externally applied electric field in consequence of hindered dipole rotation. In the second case, ions free to move within the dielectric but unable to discharge freely at the electrodes, built up slowly appearing and slowly disappearing space charges. Both effects lead to the formation of an electric moment of the dielectric body, which persists for a certain time after the externally applied field has been reduced to zero. The side of the dielectric, which is adjacent to the positive polarizing electrode, takes a negative charge; the side, which is adjacent to the negative polarizing electrode, takes a positive charge. The field of the charges residing in the dielectric induces charges on the plates of the shorted capacitor. The value of the charge of either electrode, at any moment t after the sudden short-circuit, is given by $q=\int_t^\infty J(\tau)d\tau$, where $J(t)$ is the anomalous discharge current associated with dielectric absorption. The formula is exact for the dipolar effect and approximately valid for the ionic effect, in the presence of which the true value of q may be somewhat greater than the value given by the integral, because after the short-circuit, some of the ions which constitute the space charge eventually do not return to within the dielectric, but are lost by discharge at the electrodes. The value of the induced charge of the electrodes is taken as a measure of what has been called the "free surface charge" of the electret. A heat treatment perpetuates the existence of the charges associated with dielectric absorption. The electret behavior of strongly absorptive dielectrics cannot therefore be a surprise. For example, with the data of Fig. 4, a surface charge of the order of 10^{-8} coul/cm^2 and field strength of the order of 10^5 v/cm are calculated. Still higher values would result if a higher voltage had been applied to the dielectric. Nevertheless, dielectric absorption alone is insufficient to account for the electret effect. Experiments with electrets indicate not only surface charges and fields many times lower than those here obtained, but a polarity of the charges, which is contrary to that expected, when the polar moment of the electret is produced exclusively by one of the mechanisms just discussed. And indeed, there exists another mechanism—leakage of charge from the plates to the surface of the dielectric—which yields the accumulation, on the dielectric, of "compensation" charges of the contrary polarity, the field of which neutralizes and partially overcomes the field of the "frozen" charge. The most direct evidence for the working of this third mechanism is given by Franklin's experiment of the dissectible Leyden jar, which proves that at high tensions the charge of the electrodes is transferred to the dielectric itself.[12] A tentative theory of the electret on this basis was given in a preliminary note.[13] A more complete discussion shall be given in the second part of this paper.

We express our gratitude to the Director of the National Institute of Technology, Professor E. L. da Fonseca Costa, who made this study possible.

[12] B. Gross, Am. J. Phys., in press.
[13] B. Gross, Phys. Rev. 66, 26 (1944).