The Response of a Poor Conductor to Alternating Electric Fields

BY B. M. JAFFE AND H. P. KALLMANN

The theory of the a.c. impedance or of the apparent dielectric constant of poor conductors has been revised, taking also into account the diffusion of the charges inside the poor conductor. The equation for the capacity of the whole system is augmented by terms which contain the effective penetration depths of the field into the conductor, which is closely connected to the Debye lengths. Because of this length, the saturation capacity is different for various excitations, whereas the usual theory gives the same saturation capacity for all excitations if the frequencies are only low enough. Further, it was shown that not only the free carriers contribute to the penetration depth but also those trapped electrons and positive charges which establish the equilibrium between conduction electrons and traps and positive charges during the period of the external field. Thus the existence of such trap levels reduces the penetration depth. Mostly, even at very low excitation levels, there are enough trapped electrons which are in equilibrium with the conduction electrons to make the penetration depth rather small so that it does not influence the saturation capacity very much.

If a good conductor is placed in an alternating electric field, it behaves like a material with an infinite dielectric constant, in which the polarization follows the alternating field almost immediately. Poor conductors behave quite differently under such conditions, not only is their apparent dielectric constant finite; but the polarization displays a phase difference with the external field, which may not be determined by the conductivity of the sample alone. These effects are due to the diffusion of free charges and to the interaction of trapped and bound charges with the conduction band. The diffusion effects can be essentially described by the Debye length.[1]

In this paper we will give an improved theory of these effects. We shall especially consider mixed systems consisting of poor conductors (or photoconductors) and insulating materials, which enclose the conductors, and we shall calculate the total impedance. We shall correlate this with the free and quasi-bound charges in the material. The impedance can be obtained by applying the Maxwell-Wagner theory[2] or by assuming that the systems consist of alternating conductive and nonconductive layers.[3] In first approximation the conductive portions were considered as capacitors with parallel resistors.

The measurement of such an impedance is often the only way to get some information about the free and trapped charges in the conductor. It is noteworthy that such an approach has been rather successful in giving at least qualitative results. Even for single crystals, the method has been applied successfully and allows the separation of surface and electrode effects from the bulk characteristics.[4] In the case of single crystals, the experiments have been done either with the crystals in direct contact with the electrode or with an insulating layer separating crystal and electrode.

It is, however, obvious that this was only a first approximation neglecting diffusion effects which are most important in materials with small conductivity.

The theory presented here also holds when the material has a rather low conductivity, since it takes into account the diffusion of free charges and since it considers that the density of free charges may be too low

for screening the interior from the external field. Then not only the free charges but also the evaporation of charges from localized sites may bring about the screening. For materials with resistivities of about 10^{11} ohm cm. and a mobility of 1 cm.^{2}/v.-sec. these effects may become rather small; for such poor conductors the screening of the sample from the external field becomes too small even when the evaporation of trapped charges is considered because the time for such evaporation may become unreasonably long.

The following simplified model will be treated. A poor conductive crystal is in series with highly insulating layers. Their thicknesses are d_c and d_i, respectively, and their true dielectric constants, not due to charges, are ϵ_c and ϵ_i. Assuming first that the crystal can be represented by a capacity C_c per unit area $= \epsilon_c/4\pi d_c$ and a parallel resistor corresponding to a uniform conductivity σ_c in the interior of the crystal and the insulator by a capacitor C_i one obtains for the measured series capacity C_m of the total system (for derivation of these formulas see Kallman, et al.[3])

$$C_m = \frac{C_i}{1 + \dfrac{\epsilon d_c}{d_i\left(1 + \left(\dfrac{\sigma_c}{\epsilon_c\omega}\right)^2\right)}}; \quad \epsilon = \frac{\epsilon_i}{\epsilon_c} \quad (1)$$

where ω is the angular frequency of the external field, and the dissipation factor D of the system is

$$D = \frac{\sigma_c}{\epsilon_c\omega}\frac{1}{1 + \dfrac{d_i}{\epsilon d_c}\left(1 + \left(\dfrac{\sigma_c}{\epsilon_c\omega}\right)^2\right)} \quad (2)$$

$\sigma_c = en_c 300\mu$, n_c is the density of conduction electrons, and μ is the mobility. For large σ_c or small ω, C_m approaches C_i which is the saturation value of the total capacity. D is small for small σ_c or large ω, goes through a maximum, and becomes small again for large σ_o and small ω.

These formulas fail for small σ_c and n_c for the following two reasons. The poor conductor is not completely screened even for d.c. fields for small n_c; rather, the field penetrates into the conductor by a finite distance λ_{eff} and the potential V_c across the crystal is $E_{cs}\cdot\lambda_{eff}$, where E_{cs}, the surface field strength in the crystal, $= (\epsilon_i/\epsilon_c)E_i$ (E_i is the field strength in the insulator). λ_{eff} is closely connected with the Debye

(1) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923).
(2) P. Mark and H. P. Kallmann, *J. Phys. Chem. Solids*, **23**, 1067 (1961).
(3) H. Kallmann, B. Kramer, and A. Perlmutter, *Phys. Rev.*, **89**, 700 (1953).
(4) H. Kallmann, B. Kramer, and G. M. Spruch, *ibid.*, **116**, 628 (1959).

screening length. It is dependent on V_c and on the free and "mobile" charges in the poor conductor. One must discriminate here between free charges, which are those which are in the conduction and valence bands, and "mobile" charges, which are those in electron and hole traps; the latter may, however, evaporate into the conduction or valence band when the external field drives free charges toward the crystal boundaries thus decreasing the densities of free charges in the interior. Then some of the originally trapped charges evaporate and are also swept toward the boundary, where they are retrapped and contribute to the screening of the interior from the external field. This is, of course, only important when n_c is so small that $n_c d_c$ is not sufficient to supply enough charges for screening.

With an external potential V_0 one has: $V_0 = E_i(d_i + \epsilon\lambda_{eff})$. The condition necessary to obtain a complete screening of the interior is

$$\frac{\epsilon\lambda_{eff}}{d_i} \ll 1 \qquad (3)$$

This means that λ_{eff} must be rather small when the insulating layers are small. For $V_c < kT/e$

$$\lambda_{eff} = \lambda_0 = \sqrt{\frac{\epsilon_c kT}{8\pi e^2 n}}$$

where n is the density of free and "mobile" charges in the poor conductor, which follow the field during the period of its application because of evaporation. A calculation of λ_{eff} will be given later for all situations.

For ϵ_c of the order of 4

$$\lambda_0 \sim \frac{1.5 \times 10^2}{n^{1/2}}$$

$$\sim 1.5 \times 10^{-3} \text{ for } n = 10^{10}/\text{cm.}^3$$

In most cases the thicknesses of these insulating layers are of the order 10^{-3} cm. and smaller. Thus, to fulfill (3), one must have $n > 10^{12}$. This is a rather high density which would correspond to a resistivity of $\sim 10^5$ ohm cm. (mobility ~ 100) if n were the density of free electrons. Only in rare cases do poor conductors or photoconductors under usual illumination have such high conductivities.

In order to determine the necessary supply of charges from localized sites, we calculate first the charge σ near the surface, $\sigma = en_s\lambda_{eff}$, which is necessary to screen the interior of the crystal, taking into account the external voltage

$$\sigma = e(n_s\lambda_{eff}) = \frac{V_0\epsilon_i}{300(d_i + \epsilon\lambda_{eff})4\pi} \qquad (4a)$$

where V_0 is in volts and n_s is the density near the surface. This gives as the condition necessary for screening $(n_c d_c) > (n_s\lambda_{eff})$; for a potential of 0.1 v. across 10^{-3} cm. of insulator we obtain

$$(n_c d_c) > (n_s\lambda_{eff}) \sim 5 \times 10^7 \text{ charges} \qquad (4b)$$

This means that an internal density of about $10^{10}/$cm.^{3} carriers is necessary to supply complete screening of a crystal of $d_c = 10^{-2}$ cm. For small values of V_0/d_i this condition is satisfied for densities below that required by (3). For large voltages this may be dif-

ferent since λ_{eff} decreases with increasing V_c under certain conditions even for the same n. Thus it may happen that (3) is fulfilled but (4a) is not. This would mean that the sweeping of charges to the surface diminishes the density in the interior considerably. This may be avoided by the evaporation of charges from localized sites.

Now the condition which makes $C_m \to C_{ms}$ in an alternating field of angular frequency ω will be investigated. This condition is

$$\frac{en_c 300\mu}{\epsilon_c\omega} \gg 1; \quad \frac{\epsilon_c}{en_c 300\mu} \qquad (5)$$

is the relaxation time due to the conduction electrons, and n_c their density.

This condition actually states that the charge accumulation at the surface is practically terminated in a fraction of the period. In (5), n_c is the density of free (conduction) electrons. In (3) and (4), however, n need not be the density of free electrons. It will be shown that n can equal $(n_c + n_t)$ under certain conditions ($n_t =$ the density of trapped electrons). For a frequency of 10^3 c.p.s., $n_c > 10^9/$cm.^{3} fulfills condition (5). With the parameters used above ($V_0 = 0.1$ v., $d_i = 10^{-3}$ cm.) the 2×10^7 charges required at the surface would cause a marked decrease of the density 10^9 in the interior since such a density means only 10^7 electrons in the sample of 10^{-2}-cm. thickness. This means that the conductivity is also reduced. In such a case the crystal cannot be screened completely in any period of time if there is not a supply of free charges from other sources. For instance, charges may be released from occupied traps or from the valence band either by light or by thermal action. In such a situation, however, the time to complete screening is not given by $\epsilon_c/en_c 300\mu$ but rather by a time τ which also depends on the rate of supply of charges from other sources. From traps, for instance, this rate would be $n_t d_c S e^{-E_t/kT}$, where S is a collision factor of the order of 10^{10} to 10^{12} sec.$^{-1}$ and E_t is the trap level energy below the conduction band. For light excitation this rate is $\alpha I d_c$ where αI is the number of electrons produced per cm.^{3} and sec.

In those cases where $n_c d_c$ is not sufficient to supply the screening, one has to replace the relaxation time of the free charges by the supply time of bound charges. Thus one has

$$\left(\frac{1}{\tau\omega}\right) \gg 1 \qquad (6)$$

instead of (5).

Equation 1 will now be modified by taking care of the finite penetration depth λ_{eff}. Therefore, $d_i + \epsilon\lambda_{eff}$ is substituted for d_i and $d_c - \lambda_{eff}$ for d. $\epsilon_i/4\pi \cdot (d_c + \epsilon\lambda_{eff})$ is now the capacity when the crystal is screened and $\epsilon_c/4\pi(d_c - \lambda_{eff})$ is the capacity which can be screened. Of course, the last expression only holds when $d_c > \lambda_{eff}$. We assume that only this latter capacity is shunted by a resistor and replace the shunting factor $[1 + (\sigma_c/\epsilon_c\omega)^2]$ in (1) by the factor $[1 + (1/\tau\omega)^2]$ introducing in this way the time necessary for supply. This last assumption is, of course, only a first approximation. Equation 7 is a better approximation than eq. 1 since it takes care of the diffusion effects inside the conductor through λ_{eff}. The latter

$$\gamma C_{\mathrm{m}} = \frac{C_{\mathrm{i}} \dfrac{d_{\mathrm{i}}}{d_{\mathrm{i}} + \epsilon\lambda_{\mathrm{eff}}}}{1 + \dfrac{\epsilon(d_{\mathrm{i}} - \lambda_{\mathrm{eff}})}{(d_{\mathrm{i}} + \epsilon\lambda_{\mathrm{eff}})(1 + 1/(\tau\omega)^2)}} \qquad (7)$$

is determined in the usual way from Poisson's equation and a Boltzmann equation for n.

$$\frac{\mathrm{d}^2 V}{\mathrm{d}x^2} = -\frac{4\pi C}{\epsilon_{\mathrm{c}}}(n^+ - n^-) \qquad (8)$$

n is the density of all possible charge carriers, $n^- = n_{\mathrm{c}}^- + n_{\mathrm{t}}^-$, n_{c}^- is the density of conduction electrons, and n_{t}^- that of trapped electrons. The positive charges $n^+ = n_{\mathrm{c}}^- + n_{\mathrm{t}}^-$ when no field is applied. If during the field application, equilibrium is established between n_{c}^- and n^+, one has the relationship $n_{\mathrm{c}}^- n^+ = N_0^+ \cdot N_0^- e^{-E_{\mathrm{gap}}/kT}$ for thermal excitation and under light excitation $n_{\mathrm{c}}^- n^+ = \alpha I/\beta = \delta$, where β is the recombination factor between electrons and holes. N_0^+, N_0^- are the densities of states in the valence and conduction band

$$n_{\mathrm{c}}^- = \frac{N_0^- e^{-E_{\mathrm{t}}/kT}}{n_0} n_{\mathrm{t}} \qquad (9)$$

when $n_{\mathrm{t}} \ll n_0$, n_0 is the number of electron traps available and E_{t} is their energy difference from the conduction band. Using

$$\nu = N_0^- e^{-E_{\mathrm{t}}/kT} \qquad (10)$$

Poisson's equation reads

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = -\frac{4\pi e^2}{\epsilon kT}\left(\frac{\delta}{n_{\mathrm{c}}} - n_{\mathrm{c}}^-\left(1 + \frac{n_0}{\nu}\right)\right); \quad y = \frac{eV}{kT} \qquad (11)$$

Since $n^+ = n_{\mathrm{c}}^-(1 + (n_0/\nu))$ one has in the interior without an external field

$$n_{\mathrm{c}}^-{}_{\mathrm{int}} = \left(\frac{\delta}{1 + \dfrac{n_0}{\nu}}\right)^{1/2}; \quad n^+{}_{\mathrm{int}} = \delta\left(1 + \frac{n_0}{\nu}\right)^{1/2} \qquad (12)$$

If one applies a potential which is $V(x)$ for each point x of the crystal

$$n_{\mathrm{c}}^- = n_{\mathrm{c}}^-{}_{\mathrm{int}} \exp\left(\frac{+eV(x)}{kT}\right) = \left(\frac{\delta}{1 + \dfrac{n_0}{\nu}}\right)^{1/2} e^{+y}$$

When the equilibrium between n_{c}^- and n^+ is maintained while the field is varying with time, $n^+ = (\delta(1 + n_0/\nu))^{1/2}e^{-y}$ and similarly for $n_{\mathrm{t}}^- = (\delta/(1 + n_0/\nu))^{1/2}e^{+y}$, even when the n^+ are not free. This means that the localized charges also follow the field when equilibrium between the free and localized charges is established fast enough.

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = +\frac{1}{2}\frac{1}{\lambda_0^2}(\rho^y - e^{-y})$$

$$\lambda_0 = \sqrt{\frac{\epsilon_{\mathrm{r}}kT}{8\pi e^2(n_{\mathrm{c}} + n_{\mathrm{t}})}} = \sqrt{\frac{\epsilon_{\mathrm{c}}kT}{8\pi e^2\left(\delta\left(1 + \dfrac{n_0}{\nu}\right)^{1/2}\right)}} \qquad (13)$$

λ_0 is the Debye length of the system. This is not identical with λ_{eff}; only for $y < 1$ are both the same. λ_0 then gives the penetration depth of the field as can be easily seen when the exponentials are developed as powers of y.

Equation 13 is different from Debye's original equation[1] only because it contains also the density of bound charges. For the same δ, this means for the same number of charge pairs produced per second either thermally or radiatively, λ_0 decreases considerably when trapped electrons are present. This is due to the assumption that the equilibrium between n_{c}^- and n_{t}^- and also n^+ follows the variations of the field. Therefore, with $n_0 = 10^{15}$ trap levels available at a depth of about 0.5 e.v., the traps determine the penetration depth completely. At room temperature one would have in such case $n_{\mathrm{c}}^-/n_{\mathrm{t}} \sim 10^5$ and thus λ_0 is only one-tenth as large as without traps for a given δ. It may be noted that the dependence on n_0 is of the one-fourth power. The time constant τ for the trap following case $= (1/S)e^{-E_{\mathrm{t}}/kT} \sim 10^{-3}$ sec.

Now the cases where n_{t}^- or n^+ do not follow the variation of the field will be considered. This means that they are independent of the applied potential and are constant throughout the sample and $n_{\mathrm{t}} = n_{\mathrm{c}}^-{}_{\mathrm{int}} n_0/\nu$ or $n^+ = n_{\mathrm{c}}^-{}_{\mathrm{int}}(1 + (n_0/\nu))$. Equation 13 then changes to 14 for the case that the traps follow and the positive charges do not follow

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = \frac{1}{(\lambda_0')^2}(e^{-y} - 1)$$

$$\lambda_0' = (2)^{1/2}\sqrt{\frac{\epsilon_{\mathrm{c}}kT}{8\pi e^2\left[\delta\left(1 + \dfrac{n_0}{\nu}\right)\right]^{1/2}}} \qquad (14)$$

and for the case that the traps do not follow but the positive charges do one has

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = -\frac{1}{(\lambda_0'')^2} \times$$

$$\left[(e^{-y} - 1) + \frac{e^y - 1}{\left(1 + \dfrac{n_0}{\nu}\right)^{1/2}} + \frac{n_0}{\nu\left(1 + \dfrac{n_0}{\nu}\right)^{1/2}}\right]$$

$$\lambda_0'' = \sqrt{\frac{\epsilon_{\mathrm{c}}kT}{4\pi e^2\left(1 + \dfrac{1}{1 + \dfrac{n_0}{\nu}}\right)\left[\delta\left(1 + \dfrac{n_0}{\nu}\right)\right]^{1/2}}} \qquad (15)$$

One sees that eq. 14 and 15 are different from eq. 13 and also give different results. Only for $y < 1$ are the results for these three cases almost the same. But this is only so when at least one type of bound charges follow.

Similar equations to those above are known in the literature, however, without traps being present. Equation 13 has been treated by MacDonald.[5]

The essential point in our calculation is that the existence of traps changes the lengths λ_0 and also λ_{eff} considerably. How λ_{eff} depends on n and on V_0 depends very strongly upon the assumptions made, whether n_{t} and/or n^+ follow the conduction electrons because of the establishment of the equilibrium during

(5) J. R. MacDonald, J. Chem. Phys., 29, 1346 (1958); 30, 806 (1959).

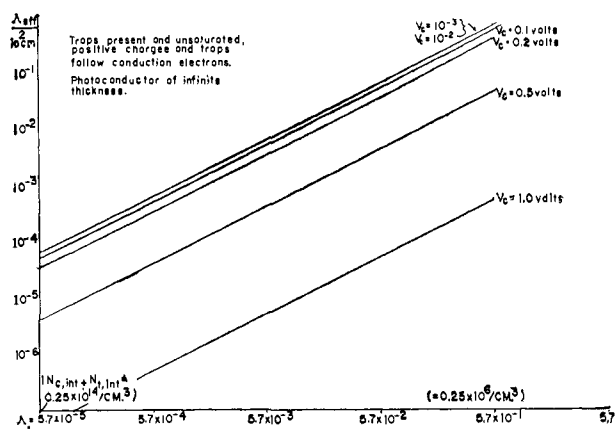Fig. 1.—Effective penetration depth *vs.* electron density for various voltages. Traps and activators follow; infinite photoconductor.

Fig. 2.—Effective penetration depth *vs.* crystal voltage for two values of electron density. Traps and activators follow; infinite photoconductor.

the variation of the field or not. The integration of eq. 13 to 15 yields the results presented in Fig. 1 to 4 for various cases of finite and infinite crystal thicknesses.

The integration is performed for a given V_c. Then E_{sc}, the surface field strength in the crystal, is determined, and from $E_{sc}\lambda_{eff} = V_c$, λ_{eff} is computed.[6] The following points should be noted. Figures 1 and 2 give λ_{eff} for an infinite crystal and for the case that n_t and n^+ follow. The equations fail of course when $\lambda \sim d_c$. Further, it may be noted that λ_{eff} is twice the λ-value given in the curve of Fig. 1 and 2 since the displacement of charges is symmetric; on each side of the crystal one has the same penetration depth. Figures 3 and 4 present the case that only the trapped electrons follow and n^+ do not follow. In these figures for finite crystal thicknesses λ_{eff} itself is plotted since the penetration depths are different on both sides. The dotted line indicates the result for an infinite crystal. In the case that n_t does not follow but n^+ follows, one finds similar results as those of Fig. 3 and 4.

Since λ_{eff} depends on V_c one has to determine V_c for a given external voltage V_0 from the equation

$$E_i d_i + E_i \epsilon \lambda_{eff} = V_0$$

Since $E_i \epsilon \lambda_{eff} = V_c$, one obtains

$$\frac{\epsilon \lambda_{eff}}{d_i} = \frac{V_c}{V_0 - V_c} \qquad (16)$$

Plotting curve 16 for λ_{eff} in Fig. 2 or 4 as functions of V_c will give the actual V_c at the point where the two λ_{eff} curves intersect. For the case of following traps and positive charges, λ_{eff} decreases with increasing crystal voltage. For small V_0 and V_c

$$\frac{\epsilon \lambda_0}{d_i} = \frac{V_c}{V_0}$$

and gives the actual V_c directly. For larger V_0 the ratio V_c/V_0 begins to decrease for a given charge density since λ_{eff} decreases with increasing V_c.

For the nonfollowing case the situation is reversed; λ_{eff} increases with V_c and the screening of the crystal becomes smaller with increasing V_0, V_c/V_0 increases and eventually no screening may be possible; but for

(6) For further details and for further references, see B. M. Jaffe, Ph.D. Thesis, New York University (unpublished), 1962.
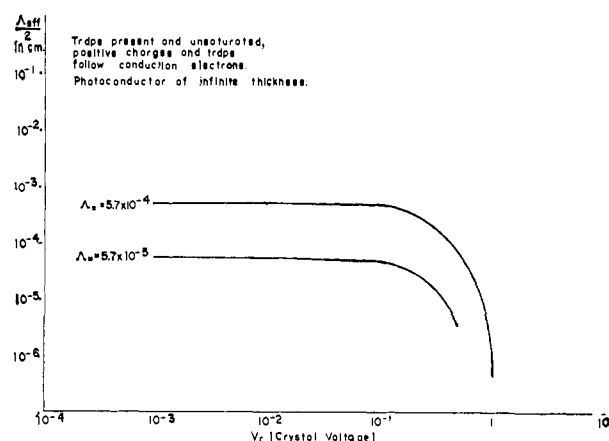
small V_0 and thus for small enough V_c, the screening is the same in the following and nonfollowing case, but with different λ_{eff} for the nonfollowing case the penetration depth becomes large on one side of the crystal, because no charge is supplied at this side of the crystal to screen it from the external field. Thus λ_{eff} becomes larger with increasing external voltage.

When, however, neither the trapped electrons nor the positive charges follow, $\lambda_{eff}/2$ becomes much larger and equals

$$\sqrt{\frac{\epsilon_c k T \left(1 + \dfrac{n_0}{\nu}\right)^{1/2}}{4\pi e^2 \delta^{1/2}}}$$

for small V_c with the factor $(1 + (n_0/\nu))^{1/2}$ in the numerator and not in the denominator, and is still larger for larger y.

The reason for this is that only the relatively small number of electrons in the conductivity band are available for screening. It may be emphasized again that the following of the positive charges does not mean that they are actually free and have a finite mobility. They follow and contribute to the screening because of their equilibrium with the conduction electrons.

These considerations show that trapping has a very remarkable influence on the screening thickness of such conductors. Summarizing, one has the following screening lengths for the various cases for $y < 1$.

$$\text{(a)} \qquad \frac{\lambda_{eff}}{2} = \sqrt{\frac{\epsilon_c k T}{8\pi \delta^{1/2}}}$$

No trapping, positive charges follow, λ_{eff} decreases with V_0; if they do not follow, 8 has to be replaced by 4 and λ_{eff} increases with V_0.

$$\text{(b)} \qquad \frac{\lambda_{eff}}{2} = \sqrt{\frac{\epsilon_c k T \left(1 + \dfrac{n_0}{\nu}\right)^{1/2}}{4\pi e^2 \delta^{1/2}}}$$

Trapping, no following of traps and positive charges; λ_{eff} increases with V_0.

$$\text{(c)} \qquad \frac{\lambda_{eff}}{2} = \sqrt{\frac{\epsilon_c k T}{8\pi \left[\delta \left(1 + \dfrac{n_0}{\nu}\right)\right]^{1/2}}}$$
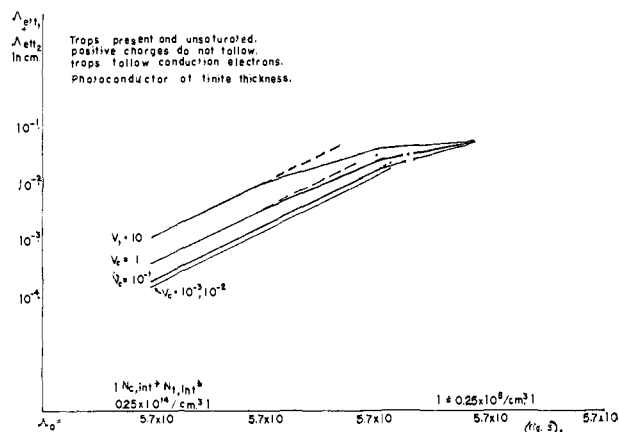
Fig. 3.—Effective penetration depth *vs.* electron density at various voltages. Traps follow, activators do not follow; finite photoconductor.
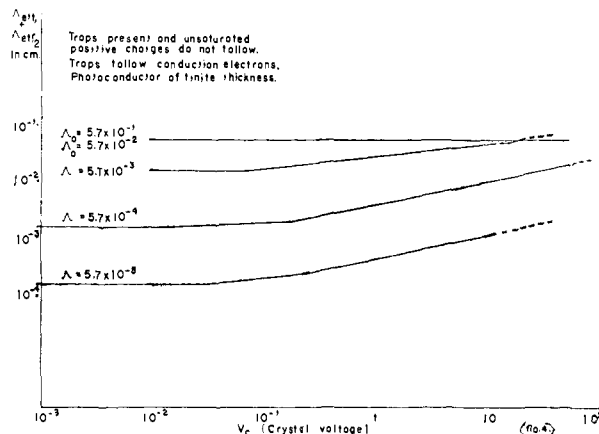

Fig. 4.—Effective penetration depth *vs.* voltage for five values of electron density. Traps follow, activators do not follow; finite photoconductor.

Trapping, n_t^- and n^+ both follow, when λ_{eff} decreases with V_c, only traps or positive charges follow, 8 has to be replaced by 4 for $n_0/\nu \gg 1$; λ_{eff} increases with V_0.

Let us now discuss eq. 1 and 7. For large n_0^- there is no difference between (1) and (7) since λ_{eff} is very small and approaches atomic dimensions. In Fig. 2 the curve for λ_{eff} would lie very low and thus according to (16), V_c is small even for large V_0. For an E_i of 10^6 v./cm., V_0 would still be only 10^{-2} v. Thus for good conductors diffusion effects play no role. For small $n_c^- + n_t^-$ (1) and (7) differ appreciably. According to (1), C_m always approaches C_i no matter how small the n_c^- and thus δ may be, if only ω is made small enough. It always approaches the same saturation value for small ω. According to (7) this is not so. There $C_{m,\text{sat}}$ decreases with decreasing δ because λ_{eff} limits $C_{m,\text{sat}}$ independent of how small ω is made. This follows from (13) and its integrated curves. Saturation is obtained eventually for $(\tau\omega) \gg 1$, but $C_{m,\text{sat}}$ is

$$C_{m,\text{sat}} = \epsilon_i/4\pi(d_i + \epsilon\lambda_{\text{eff}})$$

where the penetration depth is given by $(n_c^- + n_t^-)$ in the interior, when no field is applied. If δ is determined by external radiation, one would expect that $C_{m,\text{sat}}$ decreases with decreasing radiation intensities, when $(n_c^- + n_t^-)$ only decreases enough.

Such experiments have been carried out with ZnCdS phosphors in powdered and single crystal forms for various light excitation intensities (I). Variation of I over four to five orders of magnitude gives almost the same value of $C_{m,\text{sat}}$ in many cases. This shows that in these instances enough low-lying trap levels and positive charges play an important role in the screening of these materials, since the conductivity electrons alone would not give a sufficiently small penetration depth. One knows from luminescent measurements that in these substances many more trapped electrons than conduction electrons are present and that the positive charges have a very small mobility. Thus if not enough trapped electrons and positive charges would follow a decrease of $C_{m,\text{sat}}$ would be observed with increasing V_0. This occurs only in rare cases. In a paper by Mark and Kallmann[2] an indication of changes in $C_{m,\text{sat}}$ has been reported. There are other consequences which can be drawn from these

calculations. This will be done at another place where the measurements will be discussed in detail.

We want now to discuss the meaning of the time τ introduced in (6). For high conductivity, when n_c is not reduced appreciably by the field, the relaxation time is determined by $\tau = \epsilon_0/(en_c \times 300\mu)$ which gives the time necessary to bring the charges to the surface. In the case that electrons are delivered from traps, one has the following equation for τ

$$\tau n_t Se^{-E_i/kT} = \frac{V_0\epsilon_i}{300 \times 4\pi d_i} = n_s\lambda_{\text{eff}}e$$

$$\tau = \frac{n_s\lambda_{\text{eff}}e}{d_c n_t Se^{-E_i/kT}} \qquad (17)$$

Thus the time determining the rise of C_m corresponding to various ω is a measure not only for the conductivity but also for the number of trapped electrons released into the conductivity band during the sweeping of the field. One can also say that n_c is decreased by the sweeping of the field and its actual density is determined by the supply from traps or the valence band. Equation 17 assumes that the transit time for bringing an electron from the interior of the sample to the surface is smaller than the τ in (17). These transit times are indeed rather small even for small field strengths. For a field strength of 1 v./cm., $\mu = 200$, and $d_c = 10^{-2}$ cm., the transit time would be of the order of 15×10^{-5} sec. Relaxation times for conductivity of this magnitude occur only when the samples are highly excited and n_c^- is already large enough to provide for a small λ_{eff}.

The supply of electrons from the valence band may be another time determining factor. The number of charges produced per cm.^{3} per sec. by thermal action or radiation is $\beta n_c^2(1 + (n_0/\nu))$ or αI, respectively, and these expressions have to be introduced in (17) instead of $n_t Se^{-E_i/kT}$

$$\beta n_c^2 \left(1 + \frac{n_0}{\nu}\right)$$

is actually the number of charges recombining per second, but for the equilibrium they equal the number of charges created. For $n_c \sim 10^{10}/\text{cm.}^3$, the thermal formation would supply 10^{12} charges/sec./cm.^{3} without trapping and with trapping more, since β is of the

order of 10^{-8}. This is enough charge for screening. For light excitation 10^8 quanta absorbed in a thin crystal would already supply enough charge for screening within 1 sec. for a voltage of 1 v. across the system. These figures indicate that the creation of charges from the valence band will follow the variation of field in many important cases; this means that n^+ follows and it may be that the evaporation of electrons from traps does not follow as readily.

Another consequence of this interpretation of the relaxation time is the following: if several different trap levels are present, they may provide for different decay times because

$$n_t S e^{-E_t/kT}$$

may be different for different levels. As a consequence of this, the charge accumulation toward the surface may not be supplied with one time constant but with two or more. One described by σ/ϵ and one described by (17) which may change with time and thus with ω because $n_t S e^{-E_t/kT}$ may change. This means that the dependence of C_m on ω for a given excitation [given $\delta(1 + (n_0/\nu))$] may be different from that of eq. 7 and may be broader than with a constant τ. This was indeed observed[2] and was interpreted to mean that different conductivities exist. In a powdered sample one could indeed assume that different grains have different conductivities. Such a broadening of the C_m vs. ω curve was, however, also observed in single crystals where the assumption of different conductivities does not seem to be very meaningful.

The present interpretation presents an explanation for this broadening of the C_m–ω curves; it may be due to the varying evaporation of electrons from traps which occurs also in single crystals, but one would expect that this broadening decreases with voltage.

Summary

The theory of the a.c. impedance or of the apparent dielectric constant of a system containing poor conductors has been revised, taking also into account the diffusion of the charges inside the poor conductor. The equation for the capacity of the whole system is augmented by terms which contain the effective penetration depths of the field into the conductor, which are closely connected to the Debye lengths. Because of this length, the saturation capacity of the system may be different for various excitation, whereas the usual theory gave the same saturation capacity for all excitations if the frequencies are only low enough. Further, it was shown that not only the free carriers contribute to the penetration depth but also trapped electrons and positive charges when the equilibrium between conduction electrons and traps and positive charges is established during the period of the external field. Thus the existence of such trap levels reduces the penetration depth not because they are polarizable, but because they evaporate into the conduction band and thus contribute to the displacement of free electrons. In many cases, even at low excitation levels, there are enough trapped electrons which are in equilibrium with the conduction electrons, to make the penetration depth rather small so that it does not influence the saturation capacity very much. Without traps, screening becomes smaller at conductivity levels of 10^{12} electrons/cm.[3], and with a ratio of 10^4 for trapped to free electrons a decrease of screening becomes noticeable only for 10^8 conduction electrons/cm.[3].

The behavior is different when trapped electrons or positive charges do not establish equilibrium during the period of the field. For small voltages, $V_c < kT/e$ across the crystal, the result is similar to the case when equilibrium is established; for larger V_c, however, the penetration depth increases so that screening becomes much less effective. For the case of equilibrium following the field, larger voltages, however, decrease λ_{eff}.

This contribution of trapped electrons via the conduction band to the screening of the crystal influences also the C_m–ω curve, since ϵ/σ may no longer be the time which determines the charge accumulation; instead, the time necessary to establish the equilibrium between trapped electrons and positive charges and the conduction band becomes the important factor. This results in a broadening of the C_m–ω curves.