

IMPEDANCE OF DIELECTRIC LAYERS

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Summary

It is shown that, according to a theory on amorphous dielectrics as given earlier by Gevers and Du Pré, a correlation must exist between the real and the imaginary component of the impedances of a dielectric layer. This correlation has, in fact, been observed with the dielectric layers formed by the anodic oxidation of Al and Ta, which are known to be amorphous. New data on these layers are presented. They reveal no indication that these layers have any strongly asymmetric structure, as has been suggested in literature in connection with experiments on niobium oxide. Moreover, the experimental results with aluminium-oxide layers, containing some boehmite, can only be explained by the present theory.

Résumé

On a montré, suivant une théorie sur des matières diélectriques amorphes de Gevers et Du Pré, qu'une corrélation doit exister entre la composante réelle et la composante imaginaire de l'impédance d'une couche diélectrique. En effet, cette corrélation est observée également avec des couches diélectriques amorphes, préparées par oxydation anodique de l'aluminium et du tantale. Des expériences nouvelles sur ce sujet ont été présentées ici. On a conclu que l'existence de cette corrélation en soi ne donne pas d'indications pour une structure fortement asymétrique dans ces couches, comme il est proposé dans la littérature dans le cas des couches d'oxyde sur le niobium. En outre, les résultats avec des couches d'oxyde sur l'aluminium, dans le cas où ceux-ci contiennent de Boehmite, ne peuvent être expliqués que par la théorie présentée ici.

Zusammenfassung

Es wird gezeigt, daß aus einer Theorie über amorphe Dielektrika von Gevers und Du Pré auch ein Zusammenhang folgt zwischen der reellen und der imaginären Komponente der Impedanz einer dielektrischen Schicht. Diesen Zusammenhang hat man jetzt auch an dünnen Schichten beobachtet, welche durch anodische Oxydation des Aluminiums und des Tantals angefertigt wurden. Bekanntlich sind diese Schichten amorph. Es werden die Ergebnisse neuer Messungen an solchen Schichten in dieser Arbeit mitgeteilt. Man kommt zu dem Schluß, daß das Bestehen des erwähnten Zusammenhanges an sich noch nicht auf eine sehr stark asymmetrische Struktur hinweist, wie in der Literatur auf grund der analogen Messungen an Niob-Oxidschichten angegeben ist. Außerdem können die Experimenten mit jenen Al-Oxidschichten, welche etwas Böhmit enthalten, nur mit der hier gegebenen Theorie erklärt werden.

1. Introduction

When metals like Al, Ta and Nb are oxidized anodically, the formed oxide exhibits dielectric properties. Generally, this oxide is supposed to be of asymmetric constitution, e.g. by having more metal ions near the metal side and less near the electrolytic side as compared with stoichiometric

conditions. This asymmetric constitution is often considered as the basis for explanation of rectification, photo-effect and other properties.

The impedance of such a layer is in general given in literature by the R_s and C_s components, as these result directly from the measurements with an A.C. bridge, in which a resistance R_s in series with a capacitance C_s forms the measuring branch.

Now there appears a peculiar relation between the dependencies of R_s and C_s on the frequency f in many (but not all) experiments. It is found that to some approximation (at room temperature and f between 50 and 10^4 c/s)

$$R_s = R_0 + a/f, \quad 1/C_s = 1/C_c + b \ln f, \quad b/a = 4, \quad (1)$$

R_0 , C_0 , a and b being constants. This was first pointed out by Young¹⁾ with measurements on niobium oxide. In his paper also a theoretical calculation was given based on a strongly varying conductivity in the layer, which was suggested to be caused by a strongly asymmetric structure of this layer. The result of this calculation was in perfect agreement with the experiments.

It is the aim of the present paper to show that, starting from a general theory on dielectrics as developed by Gevers and Du Pré²⁾, a relation like eq. (1) can be derived. This implies that all dielectrics satisfying some general conditions will show this property to some approximation, without any special assumption concerning the electrical conductivity.

In section 4 some measurements with Al and Ta oxide are given, showing partly the same effect as mentioned by Young with his experiments on niobium oxide. In the case of a different behaviour still the more general assumptions of this paper appear to be fulfilled.

2. Theoretical considerations

We will give here only the approach of the problem as followed by Gevers and Du Pré in their theory²⁾. Details can be found in the original papers.

The dielectric is considered as a substance in which the positions of ions and (or) the orientation of dipoles can be influenced by applying an external field. Apart from the bulk contribution, also these movable particles will contribute to the dielectric polarization. For these particles a relaxation time is defined by

$$\tau = \tau_0 \exp (q/kT), \quad (2)$$

in which q is the depth of the potential valley.

Now supposing q not to be a constant throughout the dielectric, i.e. supposing the dielectric to be of some "glass-like" structure, a function $G(q)$ is introduced, such that $G(q)dq$ is proportional to the number of

particles present in potential valleys with q between q and $q + dq$. This $G(q)$ is supposed to be a flat function of q . With these general assumptions one can derive for the real and imaginary components of the dielectric constant (ϵ' and ϵ'' respectively)

$$\epsilon' = \epsilon_{\infty} + 4\pi N \int_0^{q_0} G(q) \alpha(q) dq, \quad (3)$$

$$\epsilon'' = 2\pi N G(q_0) \alpha(q_0) kT, \quad (4)$$

in which $\alpha(q)$ is proportional to the polarizability of the corresponding particles, ϵ_{∞} is the dielectric constant at very high frequency, and q_0 is defined by $\omega\tau_0 \exp(q_0/kT) = 1$ in which $\omega = 2\pi f$. From eqs (3) and (4) one can derive

$$\frac{1}{\epsilon'} \frac{\partial \epsilon'}{\partial \omega} = - \frac{2\epsilon''}{\pi \omega \epsilon'} \quad (5)$$

which is equivalent to

$$\frac{1}{\epsilon'} \frac{\partial \epsilon'}{\partial \ln \omega} = - \frac{2}{\pi} \tan \delta. \quad (6)$$

These formulae can be found in the cited papers ²⁾.

Now we apply formula (6) to the measurements on the impedances of thin oxide layers. In these cases, as mentioned in the introduction, one measures R_s and C_s (being the equivalent series resistance and capacity of the impedance) both as a function of frequency. The power factor of the dielectric is given by

$$\tan \delta = \omega R_s C_s. \quad (7)$$

With this expression, eq. (6) yields

$$\frac{1}{C_s} \frac{\partial C_s}{\partial \ln \omega} = - \frac{2}{\pi} \omega R_s C_s \quad *), \quad (8)$$

which is equivalent to

$$\frac{\partial(1/C_s)}{\partial \ln f} = 4 \frac{R_s}{1/f}, \quad 2\pi f = \omega. \quad (9)$$

*) Actually, ϵ' is connected with the equivalent parallel capacity C_p with $C_p = C_s/(1 + \tan^2 \delta)$. This yields (instead of eq. (9))

$$\frac{\partial(1/C_s)}{\partial \ln f} + \frac{\partial \ln(1 + \tan^2 \delta)}{C_s \partial \ln f} = 4 \frac{R_s}{1/f}. \quad (9')$$

However, it follows from the general theory ²⁾ that $\tan \delta$ (being small as compared with 1) will vary only slightly with f . From this one can deduce that the second term in eq. (9') can be neglected in general.

This is a relation like the one mentioned by Young (eq. (1)), although eq. (9) is somewhat more general. We will come back to this question below. Young's explanation of eq. (1) was based on the assumption of an exponential dependence of the resistivity ρ of the layer on the place x in that layer, the boundary conditions being independent of thickness. In order to calculate $R_s(f)$ and $C_s(f)$, the layer was thought to consist of an (infinite) number of parallel RC -units in series. This was an extension of the hypothesis already mentioned earlier³⁾. From these assumptions also relation (9) in the form of eq. (1) can be found. This seems rather remarkable especially in view of the fact that only with a purely exponential dependence of ρ on x (and not with any other simple dependence) can relation (1) be derived. The mathematical background of this fact will be connected with the exponential shape of eq. (2).

The way in which eq. (9) is derived here, however, is more satisfactory from a physical point of view. Starting from a well-defined microscopic physical picture already applied with success to dielectrics, a general relation is derived without specifying any parameter quantitatively. Moreover it suggests that eq. (9) will be valid for various kinds of dielectrics, without the restriction to a thin oxide layer with quantitative assumptions about a strongly varying conductivity.

Finally it must be remarked that eq. (9) is somewhat more general than the one given by Young. For eq. (1) implies that both members of eq. (9) are exactly constant, whereas according to Gevers' and Du Pré's theory this need not be the case. As will be seen in the next section, in fact eq. (1) is not always fulfilled, whereas in such cases eq. (9) remains still valid.

3. Experimental details

3.1. We have carried out measurements of the impedances of oxide layers on tantalum and aluminium. These are of course not the first experiments on this subject, but it was thought preferable to rely on new measurements, carried out with this purpose in mind, for several reasons.

First, the experiments with Al-oxide layers published earlier³⁾ are not completely representative of the amorphous oxide film, because these layers certainly contained some boehmite. Secondly, the experiments with Ta are of interest, not only to complete the "set" Al-Ta-Nb, but also because one can use an electrolyte of low resistivity in this case.

3.2. The tantalum used had a purity of 99.9% (0.1% Nb). A plate of 6 cm² was cleaned by chemical etching, after which it was boiled in distilled water⁴⁾. It was oxidized in a dilute H₂SO₄ solution to a certain voltage. At this voltage the oxidation was continued until a low leakage current was reached. In order to measure the impedance, the Ta plate was placed

between two platinized platinum plates of a larger size. In this case the electrolyte was an aqueous solution of KCl.

The aluminium used had a purity of 99.99%. A plate of 8 cm² was cleaned by a chromic-acid treatment, after which it was oxidized and measured like the Ta plate. The electrolyte used was an aqueous solution of borax and boric acid.

The A.C. bridge is described in one of the mentioned papers³). In order to increase the accuracy of the present measurements, the two constant resistors of 50 Ω and 500 Ω were replaced by 0.1- and 0.01- μ F capacitors, whilst also the actual performance of the bridge has been changed largely*).

4. Results

4.1. The results obtained with tantalum are given in fig. 1 and fig. 2. It

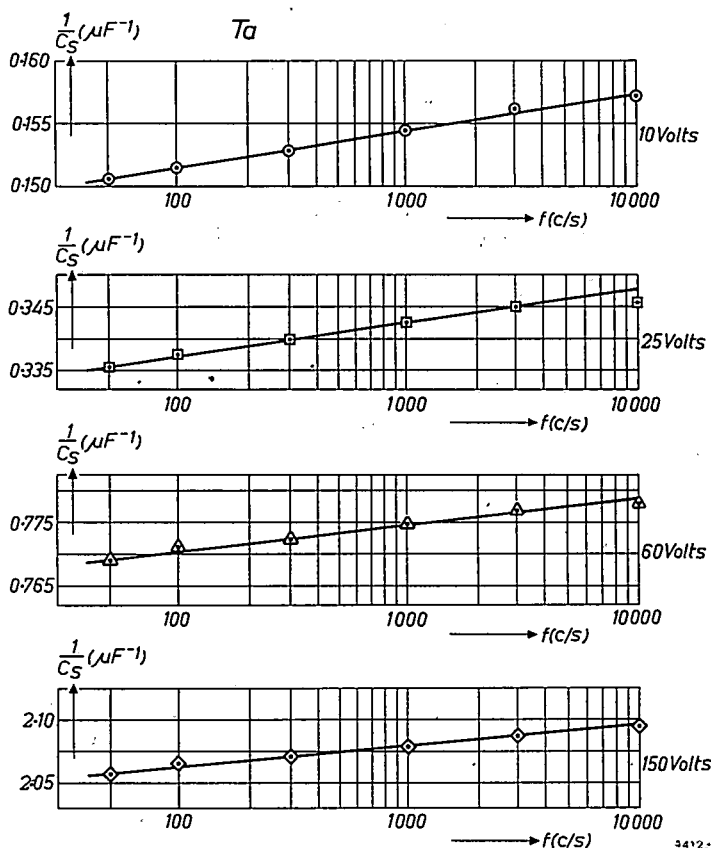


Fig. 1. $1/C_s$ as a function of frequency for Ta-oxide layers of different thickness (1 V corresponds to about 20 Å).

* The authors are indebted in this respect to Dr M. Gevers and Mr A. van de Grijp.

is seen that $1/C_s$ is perfectly proportional to $\ln f$, whereas the resistance R_s is found to be a linear function of $1/f$. The slope of $1/C_s$ vs $\ln f$ is increasing with the thickness of the layer, which is also the case with the slope of R_s vs $1/f$.

In fig. 7, the slope of $1/C_s$ vs $\ln f$ (fig. 1) is plotted as a function of $R'_s f$ (fig. 2), R'_s being R_s corrected for the vertical intercept at $1/f = 0$. In this case $R'_s f$ is equal to the slope of R_s vs $1/f$. It is seen that eq. (9), indicated by the drawn line, is satisfied. Apparently, the same result is obtained as was found with niobium¹).

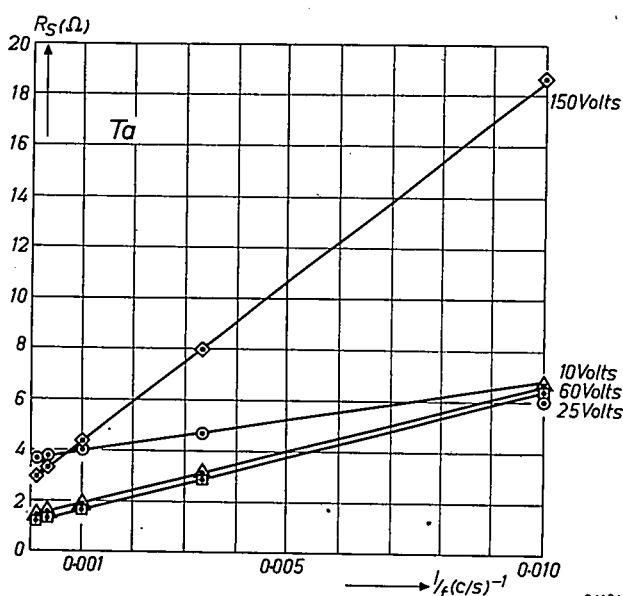


Fig. 2. R_s as a function of the reciprocal of the frequency for the Ta-oxide layers of fig. 1.

We wish to make still a remark about the intercept at $1/f = 0$ in fig. 2. These intercepts are due to (and determined by) the extra series resistance caused by the other parts of the electrolytic system. A priori they should have the same value in all cases. On the other hand, it turns out that, especially in the case of low resistance values, there exists some discrepancy between different sets of experiments. Apparently, fig. 7 implies that this does not influence the correlation between R_s and C_s . Also the increase of the slope of R_s vs $1/f$ as a function of thickness is not regular like, for example, is seen in fig. 4 in case of aluminium. Nevertheless the correlation is found to remain valid. Therefore we reproduced especially these data in this paper, although smoother results (like fig. 3 and fig. 4) have also been obtained in other sets of experiments on tantalum.

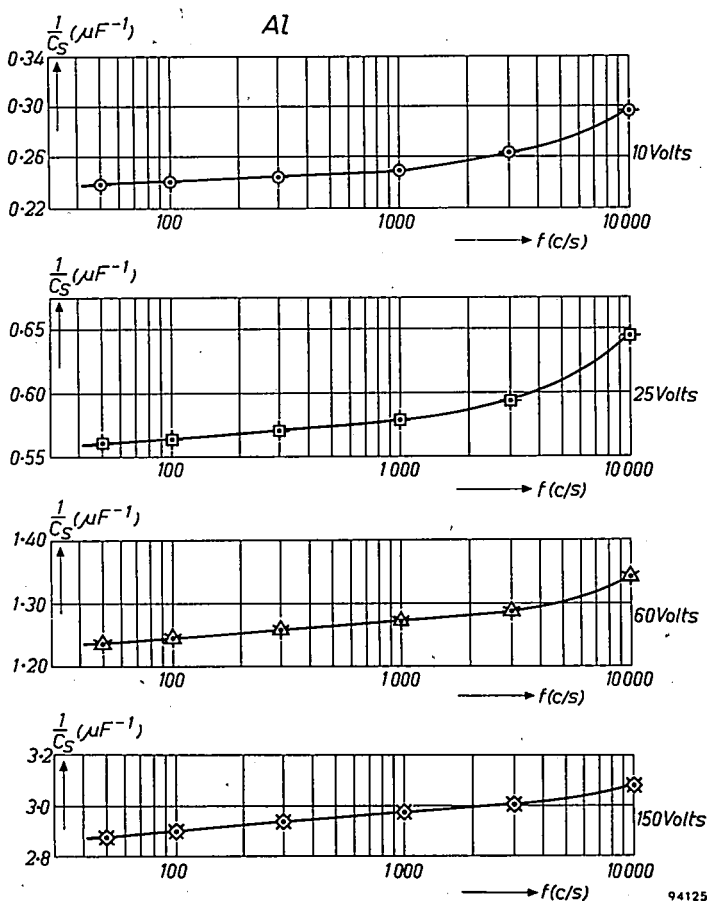


Fig. 3. $1/C_s$ as a function of frequency for Al-oxide layers of different thickness (1 V corresponds to about 13 Å).

4.2. The results with aluminium oxide are given in fig. 3 and fig. 4. In case $f < 1000$ to 10 000 c/s, the linear relationships are observed again; the correlation is given also in fig. 7 and is found to be in agreement with eq. (9). Apparently eq. (9) is fulfilled with all the oxide layers under consideration.

At higher frequencies a curvature of the $1/C_s$ curves is observed, whilst the R_s curve leaves linearity at the same time. This is qualitatively not in contradiction with eq. (9), but — as a result of many experiments — we are inclined to attribute this effect to some interface layer which is influenced by the electrolyte. Probably we will come back to this question in a subsequent paper.

4.3. As was already mentioned in section 3.1, the Al-oxide layers containing some boehmite show a definitely different behaviour with respect to the

dependence of C_s and R_s on frequency. Therefore we carried out also some experiments with these layers.

To this purpose, the Al plate was put — after it had been cleaned — in boiling water for several minutes after which the oxidation took place in the usual way. It is known that in this way the layer contains some boehmite, which forms a relatively large portion in the case of the thinnest layers.

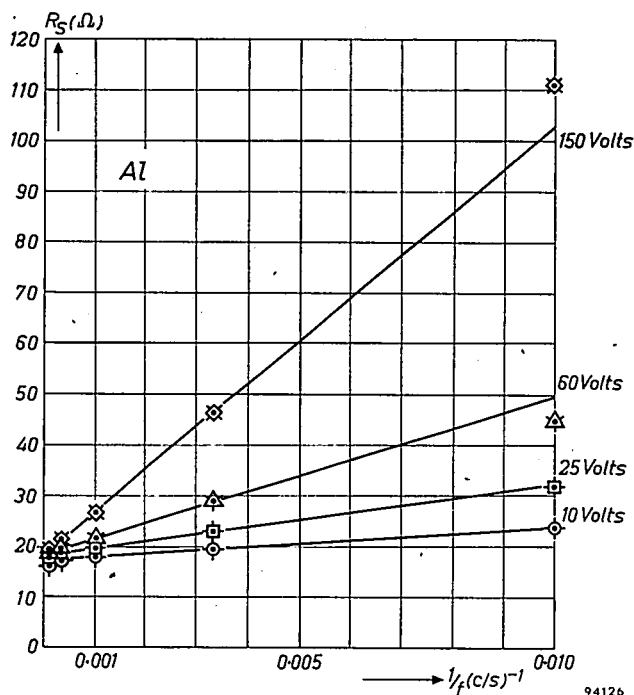


Fig. 4. R_s as a function of the reciprocal of the frequency for the Al-oxide layers of fig. 3.

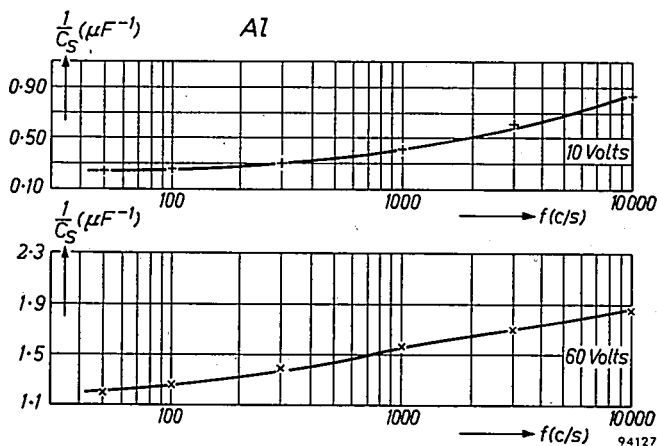


Fig. 5. $1/C_s$ as a function of frequency for two Al-oxide layers containing some boehmite.

The results are given in figs 5 and 6. A quite different behaviour is observed: neither $1/C_s$ vs $\ln f$ nor R_s vs $1/f$ show the linear relationship as was observed in sections 4.1 and 4.2. This would be in contradiction with eq. (1), but it is not necessarily so with respect to eq. (9). Actually, by plotting the derivative of $1/C_s$ vs $\ln f$ as a function of $R_s'f$ — being the slope of the dotted lines of fig. 6 pointing towards the intercept on the R_s axis —

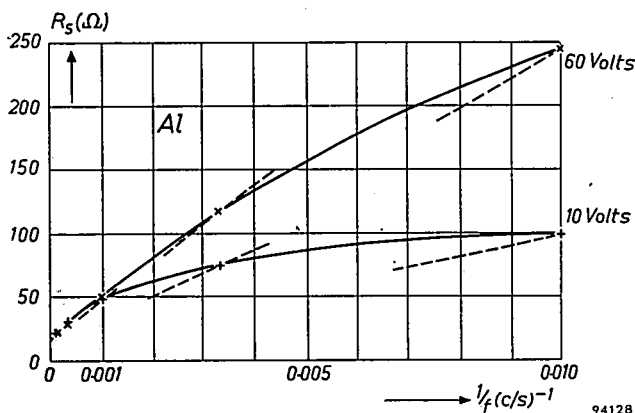


Fig. 6. R_s as a function of the reciprocal of the frequency for the two Al-oxide layers of fig. 5.

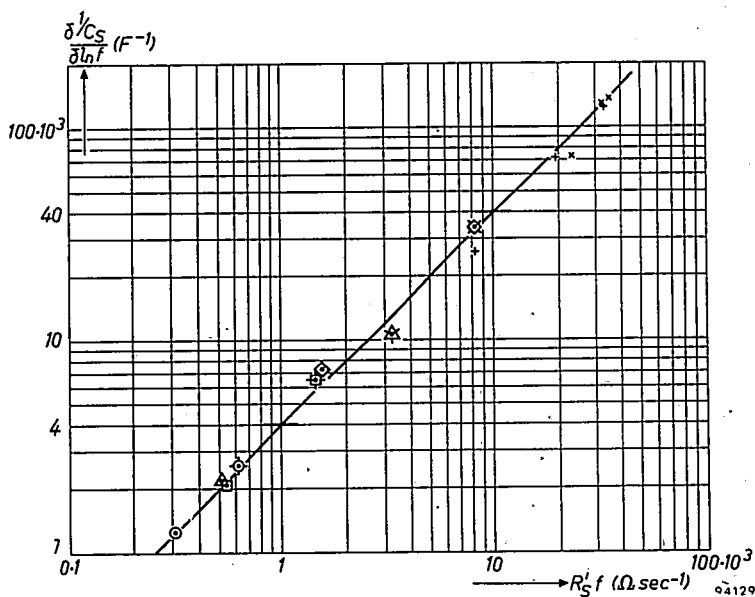


Fig. 7. The values of $\delta(1/C_s)/\delta \ln f$ — derived from figs 1, 3 and 5 — as a function of the corresponding values of $R_s'f$ — derived from figs 2, 4 and 6 —. The theoretical prediction of eq. (9) is given by the drawn line.

the condition (9) is still satisfied. This is shown in fig. 7, where the given data are derived from figs 5 and 6 at $f = 100, 300$ and 1000 c/s respectively.

5. Conclusions

It has been the aim of the present paper to point out that on the basis of a general theory on amorphous dielectrics, a correlation between the behaviour of R_s and $\dot{C}_s$ — being the equivalent series resistance and capacitance respectively — as a function of frequency can be predicted.

It is observed that this behaviour is realized in fact with the oxide layers of Al, Ta and also with Nb. This implies that, in this respect, these oxide layers behave like ordinary amorphous dielectrics. Therefore, one cannot deduce from these experiments the existence of a conductivity function of exponential shape, caused by some strongly asymmetric structure of the layer.

A second argument in favour of the present theory is given by the Al-oxide layers containing some boehmite. In this case the observed behaviour is in contradiction with the behaviour of a layer with exponentially varying conductivity, whereas it remains in accordance with the present approach of the problem.

We did not check other amorphous dielectrics in connection with this correlation effect, because a number of other consequences of the mentioned theory has already been verified experimentally with the same kind of experiments⁵⁾. Also, we found in literature some graphs like those of figs 1-4 concerning data on a dielectric called "carnubawax"⁶⁾ in agreement with the present theory.

The authors are indebted to Dr W. Ch. van Geel for his supervision and the interest shown in this work.

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