THE CONDUCTION MECHANISM IN OXIDE-COATED CATHODES *

by R. LOOSJES and H. J. VINK

Summary

It has been found experimentally that, independently of the stage of activation, the log $\sigma$-$1/T$ curves can be divided into three parts ($\sigma$ being the conductivity of the oxide coating): in part I, up to 800 °K, the temperature dependency is rather low, and in part II (800-1000 °K) it is much higher, while at still higher temperatures (> 1000 °K, part III) it drops again. Also the temperature range in which the $I$-$V$ characteristics were measured can be divided into the same three parts: up to 800 °K they are linear, from 800 to 1000 °K they are curved towards the $V$-axis, and above 1000 °K they are again linear. In explaining these facts, according to our conception, one has to do essentially with two conduction mechanisms connected parallel to each other. One mechanism is the electron conduction through the particles of the oxide coating. The conductivity corresponding to this mechanism will be low, though the real conductivity in the BaO-SrO grains may be high, because the surfaces where the crystalline particles touch one another are very small. This mechanism is to be seen in part I of the temperature region; here the activation energy varies from 0.6 to 0.09 eV with increasing cathode activation.

The other mechanism is the conduction through the electron gas present between the emitting grains of the porous oxide coating. If the density of the electron gas is great enough ($T > 800$ °K), then the pores between the grains become conducting, so that, parallel to the mechanism of part I, another mechanism of conduction is then started, the properties of which will depend entirely upon the properties of conduction in an electron gas present in the pores. It can easily be shown that the $I$-$V$ characteristics of this second mechanism will be curved towards the $V$-axis. As a further confirmation of this theory it has been found experimentally that the activation energy of this second conduction mechanism (for $T < 1000$ °K) is substantially the same as the energy corresponding to the work function of the coatings at all degrees of activation ($2.2-0.8$ eV). Quantitative calculations have been made in order to see whether the density of the electron gas present in the pores is high enough. It was found that with the known emission of a well-activated cathode a conductivity could be calculated of the same order of magnitude as observed experimentally. A further quantitative examination of the properties of the conduction in this gas showed that the facts mentioned above, viz (1) that above 1000 °K the $I$-$V$ characteristics are linear again for the voltages we used, and (2) that above 1000 °K the log $\sigma$-$1/T$ graphs indicate a less pronounced temperature dependency, can easily be accounted for by these properties.

These two phenomena are interrelated and follow from the fact that at these temperatures the density of the electron gas in the pores becomes less and less homogeneous; the density inside of the pore increases less with temperature than the density at the emitting walls of the pore.

*) The experiments and most of the ideas described in this paper have been published as a thesis: H. J. Vink, Het geleidingsmechanisme in de oxydekathode, Leiden, July 1948.
Résumé

On a observé expérimentalement que, quel que soit le degré d'activation, les courbes \( \log \sigma - 1/T \) (\( \sigma \) étant la conductivité de la cathode à oxydes) peuvent être divisées en trois parties. Dans la partie I, jusqu'à 800 \(^\circ\)K, la dépendance de la température est faible; dans la partie II de 800 à 1000 \(^\circ\)K, elle est beaucoup plus élevée, puis décroît pour des températures encore supérieures (au-dessus de 1000 \(^\circ\)K, partie III). La forme des caractéristiques \( I-V \) conduit également à la même division en trois du domaine de température: jusqu'à 800 \(^\circ\)K, elles sont linéaires, de 800 à 1000 \(^\circ\)K elles s'incurvent vers l'axe des \( V \), et redeviennent linéaires au-dessus de 1000 \(^\circ\)K. Selon notre point de vue, on a à faire ici principalement à deux systèmes conducteurs branchés en parallèle. Un de ces systèmes est la conduction électronique due aux particules de la couche d'oxydes. La conductivité de ce système est probablement faible, même si la conductivité effective des grains de BaO-SrO est élevée, car les particules cristallines n'ont que des surfaces de contact très faibles. C'est ce système qu'on observe dans la partie I du domaine de température. L'énergie d'activation décroît de 0,6 à 0,09 eV lorsque le degré d'activation augmente.

L'autre système est la conduction du gaz d'électrons qui se trouve entre des grains émetteurs de la couche d'oxydes poreuse. Lorsque la densité de ce gaz d'électrons est suffisamment élevée (\( T > 800 \(^\circ\)K \)), les pores compris entre les grains deviennent conducteurs, de sorte qu'un autre système conducteur vient se placer en parallèle sur le système de la partie I. Les caractéristiques de ce système dépendent totalement de la conduction du gaz qui se trouve entre les pores. On peut montrer que les caractéristiques \( I-V \) de ce deuxième système sont incurvées vers l'axe des \( V \). Comme confirmation de cette théorie, on a pu montrer expérimentalement que l'énergie d'activation de ce deuxième système (pour \( T < 1000 \(^\circ\)K \)) était, pour tous les états d'activation (2-2-0-8 eV), égale au travail d'extraire de la cathode d'oxydes.

On a fait des calculs quantitatifs pour voir si la densité du gaz d'électrons était suffisamment élevée. Il apparaît qu'avec l'émission connue d'une cathode bien activée, on pouvait calculer une conductivité du même ordre de grandeur que celui enregistré expérimentalement. Un examen quantitatif plus approfondi des propriétés conductrices de ce gaz d'électrons montra qu'on pouvait expliquer les phénomènes cités plus haut, à savoir:

1) un retour à la linéarité, des caractéristiques \( I-V \) au-dessus de 1000 \(^\circ\)K pour les tensions utilisées par nous, et
2) la diminution de la dépendance de la température dans les caractéristiques \( \log \sigma - 1/T \), au-dessus de 1000 \(^\circ\)K. Ces phénomènes sont liés et sont une conséquence du fait qu'au-dessus de cette température la densité du gaz d'électrons dans les pores est de moins en moins homogène, car la densité à l'intérieur des pores augmente moins vite avec la température que la densité tout près des parois émettrices de ces pores.

1. Introduction

There is very little conformity between the results of the many investigations of the conductivity and the current-voltage characteristics of the coating of oxide-coated cathodes. Consequently no theory has yet been published which can explain satisfactorily the experimental facts between 500 and 1200 \(^\circ\)K. It has, therefore, been thought worthwhile to investigate this matter anew.
In section 2 the experimental set-up is described, and in sections 3 and 5 some of the results are given. In sections 4 and 6 these results are discussed and in 7 compared with those mentioned in literature. In section 8 an attempt has been made to interpret our results in terms of the modern theory of conduction through solids, but it appears impossible to give an adequate explanation of all the facts on this basis only. A new explanation is therefore proposed based on the fact that the pores in the oxide-coated cathode (which usually has a porosity of 50-60%) are filled by an electron gas formed by the electron clouds of the surrounding grains. In this electron gas conduction will take place when a field is applied. It will be shown that already by means of a rather simple argument it is thereby possible to account for some of the difficulties which could not be explained by the theory of conduction through solids.

In section 9 new experiments are described which were carried out in order to test this new idea. The results of these experiments are indeed in accordance with our theory. In section 10 the theory is treated quantitatively and it is found that the current densities observed can be calculated quite easily. On this quantitative basis it is shown in section 11 that it is indeed possible to explain all the observed facts. Finally in section 12 it is emphasized that this theory does not need any ad hoc hypothesis nor any parameter whose value has to be chosen arbitrarily to make the calculations fit in with the experimental results.

We wish to emphasize that Giorgi units are used throughout this article.

2. Experimental technique

In the experiments to be described in this paper use was made of cathodes with a flat surface of 8 mm² consisting of a nickel cylinder with a wall thickness of 0.15 mm and an external diameter of 3.2 mm, closed at one end and covered with a coating of BaSr(CO₃)₂, 50 μ thick.

This coating is built up of grains consisting of equimolecular mixed crystals of BaCO₃ and SrCO₃. The grain size is about 2-5 μ and the porosity of the layer is 50-60%. The filament is mounted inside the nickel cylinder (see fig. 1). The metal of the cylinder forming the core of the cathode consists of the usual cathode nickel, so that the oxide coating could be activated by heating only. When this “thermal” activation is performed at not too high a temperature the process of activation can be made to last for several hours, and thus we were able to interrupt the process in order to examine the cathode at a particular stage of activation.

The temperature of the cathode was measured by means of a thermocouple (chromel-alumel) welded to the outside of the Ni cylinder. The cathodes used were specially selected with a flat surface. Two of them were mounted in a tube in such a way (fig. 1) that the carbonate coatings
were pressed against each other by means of springs. This ensured that the layers were always pressed against each other by the same force, regardless of any change in the thickness of the separate layers caused by decomposition of the carbonates during the process of formation.

The tube was thoroughly baked and degassed. After converting the layer into oxide and sealing off, the pressure in the tube was < 10^{-5} \text{ mm Hg}. In order to maintain a good vacuum a Ba getter was evaporated before the sealing off.

In this manner we finally got a layer of BaO-SrO of about 0.1 mm thickness and 8 mm² cross-section between two Ni electrodes, which layer could be heated and thermally activated.

With the aid of these tubes it was possible to measure the conductivity of the oxide coating in various stages of activation as a function of temperature. In these investigations the temperature of the layers never exceeded 1100 °K, so that further activation during the experiments was excluded. The measurements were carried out with the "Philoscope" ¹), an A.C. Wheatstone bridge with a voltage of the order of 1 volt across the unknown resistance.

The $I-V$ characteristics of the same layers were also studied. A condenser was discharged through the layers and a known resistance connected in series. The time of relaxation was about $10^{-4}$ sec. The pulse frequency amounted to 50 c/s. It was possible to regulate at will the peak voltage across the layer during the pulse. The voltages across the layer to be investigated and across the known resistance were led respectively to the horizontal and vertical deflection plates of an oscilloscope; thus the $I-V$ characteristic was made visible on the screen and could be photographed. On the screen scales were drawn, the horizontal voltage scale being calibrated by means of a known A.C. peak voltage and the vertical current scale by substituting for the layer a known resistance of the same order of magnitude. Since with these known resistance there was in every case a straight line on the screen, it was safe to conclude that there was no distortion at the frequencies employed.
As a check the resistance computed from the $I-V$ characteristics at 1 volt was compared with the resistance found by means of the bridge. No difference between these two values was found at any of the temperatures and stages of activation investigated.

3. Experimental results of the conductivity measurements

In figs 2 and 3 the logarithms of the specific conductivity (in $\Omega^{-1}\text{m}^{-1}$), $\log \sigma$, as found with the bridge, are plotted against $1/T$ for two layers at various stages of activation. From these figures it is to be seen that the log $\sigma-1/T$ curves consist of two or three parts. There is the low-temperature part (part I), which in each case extends to about 700-800 °K, followed by part II where the temperature dependency of the conductivity is much stronger, whilst often for temperatures above 1000 °K (part III) the temperature dependence of the conductivity begins to become less pronounced (fig. 3).

Fig. 2. Log $\sigma-1/T$ curves for succeeding stages of activation (I $\rightarrow$ VIII), $\sigma$ being the specific conductivity in $\Omega^{-1}\text{m}^{-1}$. Tube 13 B-1.
It is to be noted that this kind of log $\sigma$-1/$T$ curves was obtained with several tens of tubes without a single exception. Only when the stage of activation was very low was it not possible to find part I in every case, the reason being that high resistances could not be measured with our experimental set-up. The fact that in these cases we could not find part I does, not, therefore, necessarily mean that this part was not present. When a layer that did not show part I in its early stage of activation was activated a little further, this low-temperature part invariably appeared.

Fig. 3. Log $\sigma$-1/$T$ curve for tube 236 A-3. Here part III of the curve is clearly visible. $\sigma$ is the specific conductivity in $\Omega^{-1}m^{-1}$.

4. Discussion of the results

Let us consider two conduction mechanisms (a and b) which depend exponentially on temperature, viz

$$\sigma = \sigma_0 e^{-e\varphi/kT},$$

(1)

such that for the two mechanisms the $\sigma_0$'s and the $\varphi$'s are different ($\sigma_0$ is the specific conductivity for $T = \infty$ and $e\varphi$ is the activation energy). If for each of these two mechanisms (a and b) log $\sigma$ is plotted against 1/$T$ we find the straight lines $a$ and $b$ of fig. 4. Now when $a$ and $b$ are connected in series, the resultant conductivity will at every temperature be determined mainly by the mechanism with the lowest conductivity. If one now plots the logarithm of the resultant conductivity against 1/$T$ one finds curve 1 of fig. 4.

If, however, these mechanisms are connected parallel to each other the resultant conductivity will at every temperature be determined
mainly by the mechanism with the highest conductivity. In that case if one plots the logarithm of the resultant conductivity against $1/T$ one finds curve 2 of fig. 4.

![Fig. 4. Log $\sigma$-$1/T$ curves of two conduction mechanisms $a$ and $b$ (straight lines), and the log $\sigma$-$1/T$ curves for the resultant conductivity when $a$ and $b$ are connected in series (1) or parallel to each other (2) (dashed lines).](image)

Thus, it may be concluded from these arguments that, according to our experiments (figs 2 and 3), in the oxide coating there are two conduction mechanisms, with a dependence on temperature given by (1), connected parallel to each other. One mechanism, the "low-temperature" mechanism, preponderates at low temperatures and the other, the "high-temperature" mechanism, preponderates at high temperatures. The resultant conductivity is in that case the sum of the conductivities of the separate mechanisms. However, if one tries to represent the temperature dependence of the conductivity $\sigma$ that is observed experimentally by

$$\sigma = \sigma_1 + \sigma_2 = \sigma_{01} \cdot e^{-\varphi_1/kT} + \sigma_{02} \cdot e^{-\varphi_2/kT}, \tag{2}$$

it appears that this is possible only for temperatures up to about 1000 °K. For higher temperatures the temperature dependence of the observed conductivity is less than that calculated from (2), if we use for $\sigma_{01}$, $\sigma_{02}$, $\varphi_1$ and $\varphi_2$ the values computed from the results at temperatures below 1000 °K.

This becomes more clearly evident if one replots the data above 800 °K, correcting for the low-temperature mechanism as has been done in fig. 5. Part III ($T > 1000$ °K), which is not always (figs 2 and 3), visible in the conductivity observed experimentally, becomes evident in the log $\sigma_2$-$1/T$ graphs of the pure "high-temperature" mechanism.

For the present we shall confine our considerations to temperatures not higher than 1000 °K, leaving it till section 11 to deal with the conduction at higher temperatures.
As for the activation energies we thus found that for the "low-temperature" mechanism with increasing activation the activation energy decreases from about 0.6 to ca 0.09 eV, whereas the "high-temperature" mechanism has much larger activation energies, decreasing from about 2.2 to 0.8 eV with increasing activation.

Fig. 5. Log $\alpha_2$-1/$T$ curves for the "high-temperature" mechanism in succeeding stages of activation (II $\to$ VII), calculated from the curves of fig. 2. Tube 13 B-1. ($\sigma_2$ in $\Omega^{-1}m^{-1}$)

5. Experimental results of the measurements of the $I$-$V$ characteristics

For the same stages of activation the $I$-$V$ characteristics of these layers were measured. Figs 6 and 7 give some examples. In these figures $V$ represents the voltage applied across the 100-$\mu$ coating. On examining these curves one sees that the $I$-$V$ characteristics can be linear or curved towards the $V$-axis. For every stage of activation three temperature regions are again to be distinguished. For temperatures below 800 °K the $I$-$V$ characteristics are always linear. For temperatures between 800 and 1000 °K the characteristics are curved, the curvature of the characteristics in this range passing through a maximum, so that at sufficiently high temperatures ($T > 1000$ °K) a temperature region is reached where the
curves become linear again. Among the numerous layers investigated there was not a single exception to this rule.

Fig. 6. $I-V$ characteristics of tube 167 A-4, $V$ being the voltage across a 100-µ coating.

Fig. 7. $I-V$ characteristics of tube 167 A-4. Same stage of activation as in fig. 6. $V$ is the voltage across a 100-µ coating.

6. Discussion of the results

From these results it seems reasonable to conclude that the "low-temperature" mechanism has a linear characteristic. From the observed $I-V$ characteristics for temperatures above 800 °K the $I-V$ characteristics of
the "high-temperature" mechanism can be calculated by subtracting the linear $I-V$ characteristics for temperatures below 800 °K, extrapolated to the desired temperature by means of the known activation energy of this "low-temperature" mechanism. Fig. 8 gives an example. It is seen that for the "high-temperature" mechanism the curvature is greatest at 800 °K, decreasing gradually till at 1000 °K the $I-V$ characteristics are linear.

![Graph](image-url)

Fig. 8. $I-V$ characteristics of the "high-temperature" mechanism, calculated from figs 6 and 7. Tube 167 A-4. $V$ is the voltage across a 100-μ coating.

To get a better insight into the temperature dependence of the curvature, we plotted log $I$ against log $V$, in fig. 9.

From these curves it becomes evident that for temperatures up to about 900-950 °K and for potential differences greater than 2 volts (across a coating of about 100 μ thickness) the current is proportional to the square root of the voltage.

7. Comparison of the results with those mentioned in literature

When examining carefully the results mentioned in literature and comparing them with our experiments, one is struck by the fact that although
they seem to be mutually contradictory. They are actually not so. Weak temperature dependence of conductivity has always been found at low temperatures (Reimann and Murgoci, Becker, Clausing) and at high temperatures, above 1000 °K (Meyer and Schmidt, Danforth and Goldwater, Eisenstein).

On the other hand authors who found strong dependency were invariably working at temperatures between 800 and 1000 °K (Reimann and Murgoci, Reimann and Treloar, Becker, Clausing, Meyer and Schmidt, Nishibori and Kawamura, Wright, Mahlman, Eisenstein). Almost all these authors give for this temperature region (800-1000 °K) activation energies that are lower than ours (for well-activated cathodes). This is because they were not aware of the existence of the "low-temperature" mechanism, as they did not extend their experiments to temperatures below 800 °K. As a matter of fact if one calculates an (apparent) activation energy directly from the temperature.

Fig. 9. Logarithmic representation of the I-V characteristics of the "high-temperature" mechanism of fig. 8. Tube 167-A-4. The numbers are the exponents (n) in I = aV^n.
dependency of the resultant conductivity for temperatures between 800 and 1000 °K (part II) one finds values that may be considerably lower than those calculated for the true activation energy of the pure “high-temperature” mechanism.

From the third and fourth columns of table I (page 466) one can see that the apparent activation energy sometimes can be as much as 0.5-0.8 eV lower than the true activation energy.

As regards the I-V curves, linear characteristics have always been found at low or at very high temperatures (Reimann and Murgoci 3), Reimann and Treloar 9), Becker and Sears 13), Clausing 5), Meyer and Schmidt 6)), whereas curved characteristics have been found exclusively for temperatures between 800 and 1000 °K (Reimann and Murgoci 3), Reimann and Treloar 9), Clausing 5), Meyer and Schmidt 6)).

However, in the same temperature region Becker and Sears 13), Nishibori and Kawamura 10) and also Mahlmann 12) found linear I-V characteristics.

It is important to note (see section 11) that these investigators used very low voltages, < 1 volt, across the layer (except perhaps Mahlmann, who did not mention the voltages he used).

The results obtained by Wright 11) cannot very well be applied because they seem to disagree with each other. The measurements of Danforth and Goldwater 7), Mutter 14) and Dillinger, 15), Finemann and Eisenstein 16) were obtained at very high voltages compared with the voltages we used, so that it is better not to deal with their characteristics in this article.

8. Interpretation of the results: A new explanation

It is difficult to interpret these results in terms of two kinds of electronic conduction mechanisms caused by two groups of impurity levels possessing different energies with regard to the lowest conduction level in the BaO-SrO crystals. The reason for this difficulty is two-fold.

In the first place, as Becker 4) already stated, with such a picture it is difficult to explain that the activation energy calculated for the “high-temperature” mechanism has the same value as is usually found for the energy corresponding to the work function of oxide-coated cathodes. As will be clear from fig. 10, one should expect on the basis of the modern theory of solids that the activation energy calculated for the conduction would be less than the energy corresponding to the work function.

Secondly, it is almost impossible to explain that the I-V characteristics are linear at low temperatures and curved at high temperatures.

Wright 11) tries to explain these curved characteristics by assuming that the electrons have to pass through a barrier layer situated at the interface between the core and the oxide coating. However, he did not extend the temperature region of his measurements to below 700 °K.
Applying Wright's explanation to our data this would imply that the electrons of one (the "high-temperature") mechanism would be subjected to a barrier-layer effect in passing the interface, whereas the electrons of the other (the "low-temperature") mechanism would not do so.

Another mechanism of electronic conduction is therefore proposed. In our opinion it is the conduction by means of the electrons present in the pores between the electron-emitting grains of the porous oxide coating that plays an important part in accounting for the properties of the conduction mechanism observed in the oxide coating.

In just the same manner as the outer grains of an oxide-coated cathode keep up an electron cloud in a layer immediately adjacent to the surface of the cathode, it is certain that the pores in the layer will be filled by an electron gas formed by the electron clouds of the surrounding grains. Whether this new conduction mechanism is sufficient to account for the conductive properties of the oxide cathode is purely a quantitative matter, which will be discussed below.

Our theory differs from that of Lowry [17], in which the layer becomes charged negatively because of the electrons coming from the core and diffusing through the coating. According to our theory the electrons in the pores come from the surrounding grains. These grains will therefore have a positive charge, and therefore the layer as a whole will be electrically neutral.
Accepting for a moment the idea of electronic conduction through the electron gas in the pores, it is obvious that the temperature dependency of the conductivity will be closely related to the temperature dependency of the density of the electron gas present in the pores. We shall calculate this density quantitatively later on, but it is at once clear that this temperature dependency of the density of the electron gas, at any rate in the layer immediately covering the surface of the emitting grains, will be the same as that of the emission *). This is exactly what has been found experimentally by us **) and also by Becker 4) for the "high-temperature" mechanism.

The curved $I-V$ characteristics of this "high-temperature" mechanism can also easily be explained by the picture of the conduction through the electron gas in the pores. This can be seen as follows. In an electron gas, in the absence of a field and in thermal equilibrium, the electrons have a mean velocity $\bar{v}$ in all directions, irrespective of whether the medium in which they move is a metal, a semi-conductor or vacuum.

Now when a field $F$ is applied the electrons (having a charge $e$ and a mass $m$) are subjected to an acceleration $a$ in the direction of the field applied during the time $t$ which the electrons take to cover their mean free path $l$.

$$a = \frac{eF}{m}.$$  

(3)

For the mean increase of the velocity, $\Delta v$, in the direction of the field during that time $t$ we find

$$\Delta v = \frac{eF}{2m} t.$$  

(4)

For the calculation of this time $t$ two cases are to be distinguished:

1. The mean velocity $\bar{v}$ in any direction in the absence of a field is high with respect to the mean increase of the velocity in the direction of the field. In this case the mean velocity $\bar{v}$ remains practically constant during the acceleration and we have

$$t = \frac{l}{\bar{v}}.$$  

(5)

and

$$\Delta v = \frac{eF}{2m} \frac{l}{\bar{v}}.$$  

(6)

*) In section II where this problem is dealt with quantitatively, it will be seen that this is true only for a not too high temperature ($T < 1000 ^\circ\text{K}$).

**) For example we found for the "high-temperature" mechanism of a well-activated cathode an activation energy of 0.94 eV and a work function of 0.87 eV.
At the end of the mean free path this increase in velocity will be destroyed through collision. Therefore $\Delta v$ represents the mean drift of the electrons in the direction of the field and the current density (in A/m²) will be

$$I = \varrho \frac{eF}{2m} \frac{l}{\Delta v}, \quad (7)$$

where $\varrho$ is the space charge density in coulomb/m³.

Obviously, in this case Ohm’s law is valid, as is experimentally found for metals and semi-conductors. It is clear that Ohm’s law is valid only if the time $t$ (as in this first case) is independent of the field applied.

(2) The mean velocity $\bar{v}$ in any direction in the absence of a field is small with respect to the mean increase of the velocity in the direction of the field. In an extreme case, we can write

$$t = \frac{l}{\Delta v}, \quad (8)$$

and

$$\Delta v = \frac{eF}{2m} \frac{l}{\Delta v}, \quad (9)$$

Hence

$$\Delta v = \sqrt{\frac{eF}{2m} l}. \quad (10)$$

In this case we have the following expression for the current density:

$$I = \varrho \sqrt{\frac{eF}{2m} l}. \quad (11)$$

Ohm’s law is now no longer valid because, as is seen from (8) and (10), $t$ is no longer independent of $F$. In this extreme case a parabolic $I-V$ characteristic would be expected.

Now for the conduction through the electron gas in the pores we have to do with this second case. The reason for this is that the mean free path of the electrons in the electron gas in the pores is much larger than that for the conduction electrons in metals and semi-conductors.

The mean free path in metals and semi-conductors is of the order of about 1 mµ, but for the electrons in the electron gas present in the pores the mean free path is given by the size of the pores: The porosity being about 50%, it may be said that the mean free path is half the mean grain size, i.e. 1-3 µ. This is larger by a factor of about $10^3$. 

CONDUCTION MECHANISM IN OXIDE-COATED CATHODES 463
In the time during which the electrons cover the large mean free path in the pores the increase of the velocity in the direction of the field will be of the same order or even higher than the mean velocity \( \bar{v} \) in the absence of the field. It is easy to see that this is indeed possible. The mean kinetic energy of the electrons in the electron gas is of the order of \( kT \); at 800 °K \( kT \) is about 0.07 eV. Now if the thickness of the coating is 100 \( \mu \) and the potential difference across the coating is 2 V, then the potential difference over a distance of 2 \( \mu \) (the mean free path) is 0.04 volt. Thus even at low voltages we can expect an \( I-V \) characteristic curved down towards the \( V \)-axis for this mechanism of conduction. In this manner the hypothesis of the conduction through the electron gas in the pores would account for two experimental findings viz: 1) that the activation energy for the conduction of one mechanism (the "high-temperature" mechanism) has the same value as is usually found for the energy corresponding to the work function and 2) that for this mechanism the \( I-V \) characteristic is curved. It being reasonable to assume that the "low-temperature" mechanism represents the electron conduction through the grains, the following picture of the conduction through the oxide coating is proposed.

For temperatures below 800 °K we have to do with the electron conduction through the particles of the oxide coating. The conductivity of this "low-temperature" mechanism is small. There are two possible reasons for this low conductivity: either, case (1), the true conductivity of the grains is low or, case (2), the true conductivity is high but the apparent conductivity is low because (a) the area of contact between the crystalline particles may be small (and barriers at the contact may also be present) and (b) the area of contact is not small but barriers may be present between the grains.

For temperatures above 800 °K the density of the electron gas between the grains has become large enough to produce a conductivity through the pores which is higher than the conductivity associated with the "low-temperature" mechanism. Now in case (1) the conduction path for the "high-temperature" mechanism will be through the pores, most of which are linked to each other because of the high porosity. In case (2a) the bulk conductivity of the grains will come into play because the electrical contact will no longer be limited by the small surfaces of mechanical contact, the pores between the grains having become conducting. If the bulk conductivity of the grains is higher than that of the surrounding electron gas, the conduction path associated with the "high-temperature" mechanism will be partly through the grains and partly through the gas; however, because of the series connection, the total conductivity is determined by the properties of the electron gas. In case (2b) the increase in electrical contact area will not be important and the conduction path will be again mainly through the pores. Note that in all cases the conductivity associated
with the "high-temperature" mechanism is determined by the properties of the electron gas.

9. Experiments to test the new explanation

So far it has only been stated that for well-activated cathodes the activation energy for the conduction of the "high-temperature" mechanism has the same value as is usually found for the energy corresponding to the work function of well-activated cathodes. Our picture requires that the activation energy for this mechanism has the same value as the energy corresponding to the work function at every stage of activation. We have tried to prove experimentally that this was correct. For this purpose the following construction was employed. Instead of the previous construction in which the two cathodes were pressed against each other by means of springs, one cathode was mounted on springs, whereas the second cathode was fastened to two degassed nickel cylinders, each weighing 50 grams, the cylinders sliding on parallel rods in such a manner that the cathodes could either be brought into close contact, or could be separated by a distance of 5 mm when the valve was inverted. With the cathodes in contact the conductivity was measured as a function of temperature. With the valve in an inverted position an anode was introduced into the space between the cathodes and the work function of each cathode was measured according to the method of Richardson.

To preclude any doubt about the flatness of the surfaces, cathodes were used of the same form as before but with a much thicker core (2 mm instead of 1.5 mm) and 28 mm² cross-section so that it was impossible for the core, and therefore for the oxide coating to sag during the activation and the measurements. Before the spraying of the Ba and Sr carbonates the surface of the core was thoroughly polished. Because of this very thorough preparation, it sometimes happened that after some hours of activation (1100 °K) the two cathodes were found to be firmly attached to each other, so that when they were separated again, in order to measure the emission, parts of the oxide layer of one cathode were torn from the core and found on the surface of the other cathode. In some cases, after the emission had been measured, we succeeded in pressing the cathodes against each other in such a manner that the part of the coating that had been torn from the core again fitted into its old place exactly. From such observation it is apparent that good contact was obtained over the entire surface of both cathodes.

As already explained, by activating the cathodes exclusively thermally at rather low temperatures, we were able to measure the cathodes at various succeeding stages of activation.

Thus it was possible, with valves of the construction just described, to
measure the temperature dependency of the conductivity and the emission at six succeeding stages of activation. In every case the \( \log \sigma - 1 / T \) graphs revealed the two parts already discussed, from which the activation energies of the two mechanisms connected parallel to each other were calculated. For a comparison with the values given in literature, also the apparent activation energy for the mechanism preponderating at temperatures above 800 °K was calculated directly from the slope of part II of the \( \log \sigma - 1 / T \) curve without taking into account the parallel mechanism preponderating at low temperatures. At every stage of activation for which the \( \log \sigma - 1 / T \) curves were measured, the emission also was measured as a function of temperature (for temperatures below 750 °K). By means of the Richardson formula,

\[
I_s = A T^2 e^{-\psi/kT},
\]

where \( I_s \) is the saturated-current density, \( A \) a constant and \( \psi \) the work function, we calculated from these data the work function \( \psi \), at this stage of activation. In this way work functions were derived for the two separate coatings, but as these work functions did not differ appreciably \( \left( \Delta \psi < 0.1-0.2 \text{ V} \right) \), only the mean value is given. In Table I the data for the activation energies of the "low-temperature" mechanism, the true and apparent activation energies for the "high-temperature" mechanism, and the work functions have been tabulated for some layers in various stages of activation.

An examination of the data given in this table shows that, as is to be expected from our theory, in every stage of activation the activation energy of the "high-temperature" conduction mechanism is within the limits of experimental error indeed the same as the energy corresponding to the work function calculated from the emission data.

**TABLE I**

<table>
<thead>
<tr>
<th>Tube number</th>
<th>Activation energy of &quot;low-temperature&quot; mechanism in eV</th>
<th>Apparent activation energy of &quot;high-temperature&quot; mechanism in eV</th>
<th>True activation energy of &quot;high-temperature&quot; mechanism in eV</th>
<th>Work function calculated from Richardson's formula in V</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 B-1</td>
<td>0.22</td>
<td>0.84</td>
<td>0.98</td>
<td>1.07</td>
</tr>
<tr>
<td>coating</td>
<td>0.14</td>
<td>0.60</td>
<td>1.14</td>
<td>—</td>
</tr>
<tr>
<td>getting more and more activated</td>
<td>0.12</td>
<td>0.54</td>
<td>0.96</td>
<td>1.24</td>
</tr>
<tr>
<td>83 B-1</td>
<td>0.39</td>
<td>0.93</td>
<td>1.63</td>
<td>1.38</td>
</tr>
<tr>
<td>83 B-3</td>
<td>0.34</td>
<td>1.08</td>
<td>1.20</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>1.08</td>
<td>1.20</td>
<td>1.13</td>
</tr>
</tbody>
</table>
10. Calculation of the Density of the Electron Gas in the Pores

If the "high-temperature" mechanism is in fact the conduction through the electron gas in the pores, then this would mean that at "working" temperatures (1000 °K) about 90% of the current would be transported through this electron gas. The question then arises whether the density of the electron gas is sufficient to make the passage of such high current densities possible. We have tried to make some calculations. In order to avoid mathematical difficulties these calculations were carried out for a simplified model.

Let us consider the case of two infinite flat surfaces \((K_1\) and \(K_2\)) of emitting material at a distance \(d\) (2 \(\mu\) or 5 \(\mu\)) from each other (fig. 11). At a point \(x\), with the potential \(V(x)\) with respect to the surfaces, the electrons emerging from the surface with velocities between \(v_0\) and \(v_0 + dv_0\) will give rise to the space charge

\[
\rho(x,v_0) = -\frac{e n(v_0) dv_0}{v},
\]

where \(v\) is the velocity of these electrons at \(x\), \((v < v_0)\), and \(n(v_0)\) is the number of electrons emitted per \(m^2\) and per sec with velocities between \(v_0\) and \(v_0 + dv_0\).

Three groups of electrons will pass this point \(x\), viz

1. A group of electrons which, coming from \(K_1\), have too low an initial velocity to pass through the potential minimum \((V_m)\) between the two emitting surfaces; these electrons will return having the same speed at the same point and therefore make a double contribution to the space charge.

2. A group of electrons coming from \(K_1\) and having a high enough initial velocity to pass through the potential minimum.

3. A group of electrons that, coming from \(K_2\), have already passed the potential minimum.

Fig. 11. Potential distribution between two infinite flat electron-emitting surfaces \(K_1\) and \(K_2\) of the same material. The three groups of electrons are also indicated.
Since the emitting properties of the two surfaces are assumed to be the same, the second and third groups will give an equal contribution to the space charge. Therefore the total space charge $\rho$ at a point $x$ is

$$\rho(x) = -2e \int_0^\infty \frac{n(v_0) dv_0}{v} \sqrt{\frac{2eV(x)}{m}},$$

(14)

The equation of Poisson is

$$\frac{d^2V}{dx^2} = -\frac{\rho}{\varepsilon_0},$$

(15)

where $\varepsilon_0$ is the permittivity of free space. It is clear that for $x = d/2$ ($V = V_m$) we have $dV/dx = 0$.

Hence

$$\left(\frac{dV}{dx}\right)^2 = \frac{4e}{\varepsilon_0} \int_{V_m}^{V(x)} dV \int_0^\infty \frac{n(v_0) dv_0}{v} \sqrt{\frac{2eV}{m}},$$

(16)

where

$$v = \sqrt{\frac{2e}{m} (V_0 + V)} \quad \text{if} \quad \frac{1}{2} m v_0^2 = eV_0.$$  

(17)

Supposing that the distribution of the velocities of the emitted electrons is Maxwellian \(^3\) one has

$$n(v_0) dv_0 = Ne^{-mv_0^2/(2kT)} \frac{mv_0}{kT} dv_0,$$

(18)

where

$$N = \frac{I_s}{e}$$

(19)

and $I_s$ represents the density of the saturated emission current for the temperature in question.

This gives for $dV/dx$:

$$\frac{dV}{dx} = -B \sqrt{e^{eV/kT} - e^{eV_m/kT}},$$

(20)

where

$$B^2 = \frac{4Ne}{\varepsilon_0} \left(\frac{kT}{e}\right) \sqrt{\frac{m}{2kT}}.$$  

(21)

After integration we have

$$Bx = \frac{2kT}{e} e^{-eV_m/(2kT)} \arctan \frac{\sqrt{e^{eV_m/kT} - 1} - \sqrt{e^{(V-V_m)/kT} - 1}}{1 + \sqrt{e^{eV_m/kT} - 1} \cdot \sqrt{e^{(V-V_m)/kT} - 1}}.$$  

(22)
The value of \( V_m \) can be found by putting \( x = d/2 \) and \( V = V_m \). When \( V_m \) is known the mean density \( r \) (in coulomb/m\(^2\)) of the space charge between the two parallel surfaces can be calculated by writing

\[
\frac{d}{dx} \int_0^{d/2} \varrho \, dx = - \frac{2\varepsilon_0}{d} \int_0^{d/2} \frac{d^2 V}{dx^2} \, dx = \frac{2\varepsilon_0}{d} \left( \frac{dV}{dx} \right)_0.
\]

From (20)

\[
\left( \frac{dV}{dx} \right)_0 = - B \sqrt{1 - e^{V_m/kT}},
\]

so that

\[
r = - \frac{2\varepsilon_0}{d} B \sqrt{1 - e^{V_m/kT}}.
\]

The values for \( V_m \) and \( r \) are given in table II for various temperatures and for two distances \( d \) between the two emitting surfaces. The emission of the surfaces is taken to be the same as the emission of a well-activated oxide-coated cathode viz \( I_s = 8.10^4 \text{ A/m}^2 \) at 1000 °K and \( \vartheta \psi = 1.10 \text{ eV} \).

<p>| TABLE II |
|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>( T ) °K</th>
<th>( V_m ) (volt)</th>
<th>( r ) (coulomb/m(^2))</th>
<th>( V_m ) (volt)</th>
<th>( r ) (coulomb/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>769</td>
<td>-0.0014</td>
<td>2.42.10(^{-2})</td>
<td>-0.0077</td>
<td>2.26.10(^{-2})</td>
</tr>
<tr>
<td>800</td>
<td>-0.0027</td>
<td>4.74.10(^{-2})</td>
<td>-0.014</td>
<td>4.21.10(^{-2})</td>
</tr>
<tr>
<td>833</td>
<td>-0.0051</td>
<td>9.30.10(^{-2})</td>
<td>-0.025</td>
<td>7.71.10(^{-2})</td>
</tr>
<tr>
<td>868</td>
<td>-0.0097</td>
<td>1.78.10(^{-1})</td>
<td>-0.042</td>
<td>1.34.10(^{-1})</td>
</tr>
<tr>
<td>909</td>
<td>-0.018</td>
<td>3.41.10(^{-1})</td>
<td>-0.068</td>
<td>2.29.10(^{-1})</td>
</tr>
<tr>
<td>952</td>
<td>-0.032</td>
<td>6.07.10(^{-1})</td>
<td>-0.100</td>
<td>3.61.10(^{-1})</td>
</tr>
<tr>
<td>1000</td>
<td>-0.055</td>
<td>1.08</td>
<td>-0.141</td>
<td>5.64.10(^{-1})</td>
</tr>
<tr>
<td>1053</td>
<td>-0.090</td>
<td>1.93</td>
<td>-0.202</td>
<td>9.19.10(^{-1})</td>
</tr>
<tr>
<td>1111</td>
<td>-0.126</td>
<td>2.92</td>
<td>-0.259</td>
<td>1.32</td>
</tr>
</tbody>
</table>

In (22) the distance is already given as a function of the potential so that, in order to get the potential and the space charge as a function of the distance, it is now necessary to know the space-charge density as a function of the potential. From (20) we derive by differentiation

\[
\frac{d^2 V}{dx^2} = \frac{kT}{2e} e^{V/kT} = - \frac{\varrho}{\varepsilon_0}.
\]

Figs 12 and 13 show for \( d = 2 \mu \) and \( d = 5 \mu \) respectively the space-charge density and the potential as functions of the distance \( (T = 952 \degree \text{K}) \).
From these curves it is seen that it is not always allowed to consider the density of the electron gas as being homogeneous, but for the present we shall ignore the complication caused by inhomogeneity of the density of the electron gas. As a further simplification it is assumed that it is allowed to use the zero-field density, just calculated, for the computation of the current when a field is applied.

Fig. 12. The electron density and the potential between two infinite flat emitting surfaces

\[ I_s = 3.82.10^4 \text{ A/m}^2, \quad T = 952 \text{ °K}, \quad \text{distance } d = 2 \mu. \]

From the experimental results (fig. 9) it is known that at 960 °K the \( I-V \) characteristics still have an almost completely \( \sqrt{V} \) character. Therefore one obtains by using formula (11) for the current density:

\[ I = r \sqrt{\frac{eVb}{2ma}}, \quad (27) \]

where \( r \) is given by (25) or table II, and \( a \) and \( b \) represent respectively the thickness of the coating and the mean free path. Now it is assumed that with a grain size of 2 \( \mu \) and a porosity of 50\%, the density of the electron gas in the pores between the grains is equal to the density calculated for two emitting surfaces at a distance of 2 \( \mu \). In reality the former density will be greater than the latter because the pores will be bordered by say four walls, compared with the two walls in the simplified model.

Now in our case \( a = 100 \mu \) and \( b = 1 \mu \) for a grain size of 2 \( \mu \). We then find for the current density \( I = 1.8.10^4 \sqrt{V} \text{ A/m}^2 \). Taking a grain size of 5 \( \mu \) the current density is \( 1.7.10^4 \sqrt{V} \text{ A/m}^2 \). Comparing these figures
Table II shows that with increasing temperatures the depth of the potential minimum increases rather considerably. This means that the distribution of the space charge between the two surfaces becomes less and less homogeneous, and in fact at high temperatures the space-charge density in the middle lags more and more behind the density at the emitting surfaces. This result is in complete agreement with a general result arrived at by Von Laue 19), who proved that for a cavity surrounded by emitting walls the space-charge density close to the walls varies with temperature in the same manner as the saturated emission current, but that in the middle of the cavity at sufficiently high temperatures the density varies linearly with temperature.

From these considerations it is already clear that if a log $\sigma - 1/T$ curve is plotted for the conduction in the electron gas we shall find curved lines. Now the mean space-charge density $r$ for various temperatures has already been calculated. By plotting a log $r - 1/T$ graph it is shown

*) Note that since the calculated values are somewhat higher than the observed ones, even if a ten-fold lower value of $I_e$ corresponding to the D.C. emission had been chosen, the final result would still be of the right order of magnitude.

Fig. 13. The electron density and the potential between infinite flat emitting surfaces. $I_e = 3.82 \times 10^4$ A/m$^2$, $T = 952$ °K, distance $d = 5\mu$.

11. The inhomogeneity of the electron gas

Table II shows that with increasing temperatures the depth of the potential minimum increases rather considerably. This means that the distribution of the space charge between the two surfaces becomes less and less homogeneous, and in fact at high temperatures the space-charge density in the middle lags more and more behind the density at the emitting surfaces. This result is in complete agreement with a general result arrived at by Von Laue 19), who proved that for a cavity surrounded by emitting walls the space-charge density close to the walls varies with temperature in the same manner as the saturated emission current, but that in the middle of the cavity at sufficiently high temperatures the density varies linearly with temperature.

From these considerations it is already clear that if a log $\sigma - 1/T$ curve is plotted for the conduction in the electron gas we shall find curved lines. Now the mean space-charge density $r$ for various temperatures has already been calculated. By plotting a log $r - 1/T$ graph it is shown

*) Note that since the calculated values are somewhat higher than the observed ones, even if a ten-fold lower value of $I_e$ corresponding to the D.C. emission had been chosen, the final result would still be of the right order of magnitude.
(fig. 14) that a curve is indeed obtained, and not a straight line. However, for temperatures below 950 °K the graphs are substantially linear and from the slope an activation energy of 1·1 eV is calculated *). For temperatures above about 950 °K the temperature dependence is less.

![Graph showing the mean electron density as a function of temperature.](image)

**Fig. 14.** The mean electron density \( r \) between the two infinite flat emitting surfaces as a function of temperature; \( r \) is given in coulomb/m\(^3\).

*) In computing table II we used for the variation of the emission current with temperature the Richardson formula

\[
I_s = A T^2 e^{-\varphi / kT},
\]

with \( \varphi = 1·10 \) V.

For the mean space-charge density \( r \) one has to a first approximation

\[
r = I_s \left( 2\pi m/kT \right)^{1/2}
\]

as follows from elementary kinetic theory.

From (21), (23) and (25) it follows that to a higher approximation

\[
r = I_s \left( 2\pi m/kT \right)^{1/2} \left( 1 - \frac{1}{2} \frac{eV_m}{kT} \right) \text{const.} e^{-e\varphi/kT} T^{1/4} \left( 1 - \frac{1}{2} \frac{eV_m}{kT} \right).
\]

The fact that from the log \( r-1/T \) curve \((T < 1000 \text{ °K})\) one calculates an activation energy which again has a value of about 1·1 eV (fig. 14) is a consequence of two counteracting causes, viz an increase of the slope due to the factor \( T^{1/4} \) and a decrease due to the increasing influence of space charge \((V_m)\) with increasing temperature.
This is exactly in accordance with what was found experimentally for the “high-temperature” conduction mechanism. Therefore it is tempting to assume that part III in the experimental log $\sigma$-$1/T$ curves is also due to the electron-gas conduction-mechanism, since for these “high temperatures”, because of the increasing inhomogeneity of the electron gas, the mean density of the electron gas increases less with temperature than the emission. Possibly this increasing inhomogeneity would also be the explanation for the fact that for temperatures above 1000 $^\circ$K the $I$-$V$ characteristics (at least for the voltages used by us) are straight again. As already seen, an $I$-$V$ characteristic is ohmic only if the time between two collisions is independent of the field applied. Now the applied field is not the only field to which the electrons in the electron gas are subjected. There is also the field caused by the presence of the space charge. With no applied field present it is this space-charge field which will determine the time during which the electrons will be in the pores.

When a field is applied there are, therefore, two fields determining the time $t$. It depends on their relative magnitude which field will have the greater influence. If the space charge field has the greater influence then the time $t$ no longer depends on the applied field and a linear $I$-$V$ characteristic is to be expected.

From the calculated values of $V_m$ at various temperatures it is seen that at low temperatures this potential minimum is so low as to have no influence upon the time $t$. With increasing temperature, however, this potential minimum increases rather strongly. At 1100 $^\circ$K we calculated for our simplified case values of 0·2-0·25 V (in reality these values will be still higher). In that case an applied field of the order of at least 0·25 V across 2·5 $\mu$, that is 10 volts across the total thickness, is necessary to determine the time $t$. For potential differences less than this value linear $I$-$V$ characteristics are therefore to be expected.

There is still another reason why the $I$-$V$ characteristics will always be linear for low voltages of the order of 0·2 volt or less across the oxide coating. At these low voltages, as will be clear from the argumentation in section 8 page 464, the mean increase of the velocity in the direction of the field will be small compared with the mean velocity of the electrons in the electron gas at these temperatures (1000 $^\circ$K). In this case the time $t$ is independent of the applied field, as already stated, and we have to expect a linear $I$-$V$ characteristic.

From these considerations it therefore follows that as a general rule at all temperatures the $I$-$V$ characteristics of the conduction in the electron gas will be linear for low voltages and become more and more curved for higher voltages until ultimately with sufficiently high voltages the current will be proportional to the square root of the voltage.
It depends upon the emission, the temperature and the size of the pores up to what voltages the \( I-V \) characteristics will be linear. This may be a possible explanation for the fact observed by some authors that for temperatures between 800 and 1000 °K a linear characteristic is found, because in these cases the \( I-V \) characteristics have been investigated only for very low voltages.

12. Conclusion

From the foregoing it will be clear that it is possible to explain all the experimental results by means of the theory of the conduction through the electron gas present in the pores of an oxide coating. From the properties of this conduction mechanism all the features can be explained by straightforward reasoning, without requiring any further ad hoc hypotheses. This explanation is not a qualitative one only, but can be founded on a quantitative basis. It has been found possible to calculate \( \sigma \) as a function of \( T \) (for low voltages) and \( I \) as a function of \( V \), and these calculations proved to be in satisfactory agreement with the experimental facts observed, without using parameters of special value chosen to make the calculated results agree with the experimental ones. On the contrary, the only parameters used were the grain size, the porosity and the electron-emitting properties of the normal oxide coating, to which parameters the values taken from the literature were assigned.

Acknowledgement

We wish to thank Dr A. van der Ziel, Dr W. de Groot and Dr E. S. Rittner for valuable discussions and Mssrs A. J. van Genuchten and H. A. C. van der Linden for their skilful assistance. We are indebted to Dr H. C. Hamaker for suggesting the subject of this investigation.

Note added in proof

Hannay (J. appl. Phys. 10, 680, 1949) has quite recently advanced some experimental arguments designed to prove that our picture of conduction through the electron gas is incorrect. Of these experiments we believe that the one most likely to represent a crucial test of the matter is that in which helium is introduced at high pressure and the effect on the conductivity noted. However, Hannay has estimated the mean free path of a thermal electron in helium under the conditions of his experiments to be \( 1.10^{-4} \) cm and since the pore diameter is also of this order, no appreciable change in conductivity on introducing the helium is to be expected in his experiments. A second argument advanced by Hannay against our picture is that the current-voltage curves were found to be ohmic up to a voltage gradient of about 50 V/cm. As shown in section 11, the current-voltage
CONDUCTION MECHANISM IN OXIDE-COATED CATHODES

characteristics are linear up to this relatively small field strength but deviate markedly from linearity in part II at higher fields. This constitutes a serious objection to the conduction mechanism postulated by Hannay. We further believe that Hannay’s other experiments in this connection do not permit a definite choice between the two pictures considered.

Eindhoven, July 1949

REFERENCE

3) A. L. Reimann and R. Murgoci, Phil. Mag. 9, 440-464, 1930.
8) A. S. Eisenstein, Advances in Electronics, 1, 1-64, 1948.
14) W. E. Mutter, quoted by Eisenstein 8).
15) J. R. Dillinger, quoted by Eisenstein 8).