Conductance and Relaxation Time of Electrons
in Gold Blacks from Transmission and Reflection Measurements
in the Far Infrared.

Louis Harris and Arthur L. Loeb
Department of Chemistry
Massachusetts Institute of Technology,
Cambridge, Massachusetts

*This work supported in part by ONR under contract
N5 ori-07539 MRO 15309
The electrical conductivity of gold blacks is evaluated from reflection and transmission measurements in the far infrared. For sufficiently thin samples and sufficiently large wavelengths a closed expression is derived, relating the electrical conductivity of the gold black direction to the absorption and transmission coefficients. It is found that the electrical conductivity varies with wavelength, and for wavelengths larger than 105 microns this variation is attributed to a relaxation effect. The relaxation time of electrons in gold blacks is found to agree closely with that in bulk gold.

INTRODUCTION

Metal blacks have been found\(^1\) to have a very low density, and yet


they conduct a direct current. This has led to the conclusion that their structure is yarn-like, with conducting strands spaced relatively far apart. Maxwell's theory of electromagnetic radiation has been applied to correlate the optical (infrared) and electrical properties of the blacks. When radiation is incident on a black, a rapidly alternating field acts on the electrons in the black, and the conductivity expresses the response of the electrons to the imposed electrical field. Several factors may make the conductivity dependent on the wavelength; these are:

- Gaps in the metal strands consisting of either insulating impurities or air, do not pass a direct current, but may act as condensers.
Since the impedance of a branch of an electrical network containing a condenser depends on the frequency, the apparent conductivity of interrupted strands in gold black changes with the frequency of the incident infrared radiation. Thus the "optical conductivity" computed from transmission and reflection data is actually an admittivity. With increasing frequency of the incident radiation more strands become capable of conducting current. Therefore this "condenser effect" causes the optical conductivity to decrease with increasing wavelength of the incident radiation.

According to Drude and Zener\(^2\) electrons have a finite relaxation time, which causes them to lag behind the imposed emf. This lag increases with increasing frequency of the imposed field. This "relaxation effect" causes the effective conductivity to increase with increasing wavelength of the incident radiation.

At resonance frequencies the optical absorptivity, and hence the conductivity computed from optical measurements, passes through a maximum.

For gold blacks the effects of the three factors A, B, and C appear \(\text{predominently}\) to \(\text{predominently}\) in different wavelength regions. Resonance frequencies lie mostly in the visible and near infrared regions. For wavelengths greater than 100 microns only those strands appear to conduct which can conduct direct current. Conductivity across gaps only occurs appreciably for wavelengths shorter than 100 microns, as will be shown below. Since the

---


\(^3\)C. Zener, Nature 132, 968 (1933)
4.

\[ k = \text{absorption coefficient of conducting film.} \]

\[ \epsilon_{\infty} = \frac{1}{\pi \omega} \]

\[ i = \sqrt{-1} \]

\[ \Gamma = (2\pi/\lambda) (n + ik) \]

\[ \lambda = \text{wavelength of incident radiation} \]

\[ a = \text{thickness of conducting film.} \]

The optical constants are related to the conductivity and permittivity of the media by the relations:

\[ nk = \frac{1}{\mu \epsilon_{\infty}} (\lambda/\sigma) \] (Eq. 3)

\[ \sigma^2 - k^2 = (\mu \epsilon_{\infty}/\mu_0 \epsilon_0) \] (Eq. 4)

where

\[ \sigma = \text{conductivity of the conducting film} \]

\[ \epsilon = \text{permittivity of the conducting film} \]

\[ \epsilon_0 = \text{permittivity of vacuum} \]

\[ \mu = \text{permeability of the conducting film} \]

\[ \mu_0 = \text{permeability of vacuum} \]

\[ c = \text{velocity of radiation in vacuum.} \]

The quantity \( \mu/\epsilon_{\infty} \) is dimensionless, and is called "reduced conductivity per square" of conducting film. As will be seen below, it is directly related to the optical properties of films.

The inverse relations of Eqs. (3) and (4) are given by Eqs. (5) and (6):

\[ \epsilon^2 = \frac{1}{2} \mu c \left[ \left( c^2 + (\mu/\epsilon_{\infty})^2 (\mu c/2m/\lambda)^2 \right) \frac{h}{\epsilon} \right] + c \] (Eq. 5)

\[ \mu^2 = \frac{1}{2} \mu c \left[ \left( c^2 + (\mu/\epsilon_{\infty})^2 (\mu c/2m/\lambda)^2 \right) \frac{h}{\epsilon} \right] - c \] (Eq. 6)
measurements reported in this paper were all made with radiation of wavelength greater than 100 microns, the relaxation effect is the dominant one to be considered here.

**THEORY, Part I  CONDUCTIVITY AS A FUNCTION OF ABSORPTION AND TRANSMISSION**

Harris, Beasley and Leeb⁴ have derived expressions for the reflection and transmission of radiation by thin conducting films as functions of the optical constants, \( n \) and \( k \), of the film, the thickness of the film, the index of refraction of a non-absorbing backing for the film, and the wavelength of the incident radiation. The backings used for the gold blacks under consideration here were examined separately in the far infrared, and were observed to be 100 per cent transmitting. Their index of refraction is therefore effectively unity, so that Case III of the above applies here:

Reference⁴

\[
R = \frac{|(z_{oa} - z_{ao})| \sin |ka|}{|2 \cos k_a = i(z_{oa} + z_{ao}) \sin |ka||} \tag{Eq. 1}
\]

\[
T = \frac{4}{|2 \cos k_a = i(z_{oa} + z_{ao}) \sin |ka||} \tag{Eq. 2}
\]

where

\( R \) = fraction of radiation reflected

\( T \) = fraction of radiation transmitted

\( z_{oa} = n + ik \)

\( n \) = index of refraction of conducting film.
Eq. (9) is very useful for applications in the infrared, for it relates the electrical conductivity of the film directly to the absorption per unit transmission of the film. The only condition to its application is that the ratio of film thickness to wavelength be sufficiently small. While reflection and transmission are themselves extremely complicated functions of both conductivity and permittivity of the film as demonstrated by Eqs. (7) and (8), the right hand side of Eq. (9) is independent of the permittivity of the film, and is a simple quadratic function of the reduced conductivity per square of film. As the ratio \( a/\lambda \) approaches zero, \( a/\lambda \) approaches \( A/T \) asymptotically, and ceases to depend explicitly on \( a/\lambda \). Thus, for thin films, the explicit dependence of \( \mu \sigma \alpha \) on film thickness is only very slight. This is very important when the conductivity per square film of metal blacks is to be determined from experimental data on \( A/T \), for the density and consequently the thickness of the blacks are not easily found accurately. The expression \( A/T = \frac{(1-T-E)/T}{\lambda} \) depends for metal blacks largely on the transmission, and less so on reflection. This because blacks have rather indistinct surfaces and hence small reflectivity. This reflectivity may be somewhat diffuse rather than completely specular, a fact not recognized when the measurements reported here were made. The value for the reflection used may therefore be somewhat low, but this error does not affect the value of \( A/T \) very much.

RESULTS, Part I

Table I lists the results of reflection and transmission measurements made at The Johns Hopkins University on four gold black samples at three different wavelengths in the far infrared. The density of these samples
In the present paper the reduced conductivity is considered more fundamental than the optical constants. However, the optical constants can be calculated, where desired, by the use of Eqs. (5) and (6). When the wavelength is large compared to the thickness of the gold black, the expression \[ |(n + ik) 2na/\lambda|^2 \] is small, for \( n \) and \( k \) rarely exceed 3.5. The following approximations may be used when \[ |(n + ik) 2na/\lambda|^2 \ll 1: \]

\[
\sin K_a = K_a \\
\cos K_a = 1 - \frac{1}{2} (K_a)^2
\]

Substitution of these expressions and Eqs. (3) and (4) into Eqs. (1) and (2) produces:

\[
R = \frac{1 \frac{2na}{\lambda} \left\{ (p\varepsilon/p_\sigma e_0) - 1 \right\} + \frac{1}{2} i \mu \sigma a (\lambda/na) \}^2}{2 \left[ 1 - (2na^2/\lambda^2) \right\{ (p\varepsilon/p_\sigma e_0) + \frac{1}{2} i \mu \sigma a (\lambda/na) \} - \frac{1}{2} \mu \sigma a (\lambda/na) \}]^2 \tag{7}
\]

\[
T = \frac{4 \left[ 1 - (2na^2/\lambda^2) \right\{ (p\varepsilon/p_\sigma e_0) + \frac{1}{2} i \mu \sigma a (\lambda/na) \} - \frac{1}{2} \mu \sigma a (\lambda/na) \}^2}{2 \left[ 1 - (2na^2/\lambda^2) \right\{ (p\varepsilon/p_\sigma e_0) + \frac{1}{2} i \mu \sigma a (\lambda/na) \} - \frac{1}{2} \mu \sigma a (\lambda/na) \}]^2 \tag{8}
\]

Defining the absorption coefficient \( A \) as:

\[
A = 1 - R - T
\]

and substituting for \( R \) and \( T \) the expressions given in Eqs. (7) and (8) produces:

\[
\frac{A}{T} = \left( \frac{na}{\lambda} \right)^2 (\mu \sigma a)^2 + \left\{ 1 + (2na^2/\lambda^2) \right\} \mu \sigma a \tag{9}
\]
is 300 to 500 times as small as that of bulk gold. Table I also contains values of \( m / \lambda \) for all samples and wavelengths, computed from the weight per unit area of sample, using for the ratio of the density of bulk gold to that of the gold black the values \( x = 150 \) and \( x = 500 \). Eq. (9) is not applicable to all cases enumerated in Table I, particularly for \( x = 500 \) because the requirement \( |(a + ik) 2m / \lambda|^2 < 1 \) is certainly not satisfied when \( m / \lambda \sim 1 \). The cases where Eq. (9) is not applicable are indicated by an asterisk.
TABLE I  
Observed reflection and transmission of gold black deposits at different wavelengths; calculated \( \text{nm}/\lambda \) values for the deposits, assuming different densities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \lambda ) (microns)</th>
<th>( R ) (percent)</th>
<th>( T ) (percent)</th>
<th>( \text{nm}/\lambda ) ( x = 150 )</th>
<th>( \text{nm}/\lambda ) ( x = 500 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>105</td>
<td>13.0</td>
<td>25.5</td>
<td>0.295</td>
<td>0.984*</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>16.2</td>
<td>25</td>
<td>0.0900</td>
<td>0.300</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>19.5</td>
<td>21.6</td>
<td>0.0682</td>
<td>0.227</td>
</tr>
<tr>
<td>57</td>
<td>105</td>
<td>10.7</td>
<td>41.2</td>
<td>0.162</td>
<td>0.539*</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>7.8</td>
<td>40.8</td>
<td>0.0492</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>8.8</td>
<td>37.1</td>
<td>0.0373</td>
<td>0.124</td>
</tr>
<tr>
<td>58</td>
<td>105</td>
<td>10.1</td>
<td>39.4</td>
<td>0.196</td>
<td>0.653*</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>9.7</td>
<td>36.8</td>
<td>0.0597</td>
<td>0.199</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>8.8</td>
<td>34.1</td>
<td>0.0452</td>
<td>0.151</td>
</tr>
<tr>
<td>52</td>
<td>105</td>
<td>2.2</td>
<td>73.4</td>
<td>0.0693</td>
<td>0.231</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>2.6</td>
<td>69</td>
<td>0.0211</td>
<td>0.0703</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>5</td>
<td>67</td>
<td>0.0160</td>
<td>0.0533</td>
</tr>
</tbody>
</table>

*Eq. (9) not applicable

**Reliability of data is \( \sim 1\% \)

\( x \) is the ratio of the density of bulk gold to that of the gold black deposit.
The cases where Eq. (9) applies were solved first, and by extrapolation from the results thus obtained first estimates were made for the other cases. This procedure thus yielded twenty-four values for \( m_s a \), namely one for each of four samples at three wavelengths, assuming two values of the density ratio of bulk gold to \( m_b \) gold black. Of these twenty-four values most were assumed to be good approximations because they were obtained from Eq. (9) under conditions where this equation is presumably applicable. The remainder were considered only first estimates in a series of successive approximations. The entire set of values was subjected to the following test which served both as a check on the approximate method, and as part of a successive approximation method where the need for more accurate computations was indicated.

From the estimate of \( m_s a \) the optical constants \( n \) and \( k \) were calculated, using Eqs. (5) and (6). For these calculations a knowledge of \( \varepsilon \) and \( m \) is required. The latter quantity can, for non-magnetic films, be set equal to that of vacuum, i.e. \( m = m_o \). The permittivity of a mixture is a linear combination of the permittivities of the components, each component being weighted by its relative concentration. Gold blacks consist of only a fraction of a volume percent of gold; their permittivity can therefore be approximated by that of air \( \varepsilon = \varepsilon_o \). It should be emphasized that this approximation is only used in testing the applicability of Eq. (9), but never to obtain results when Eq. (9) does apply.

Setting \( m = m_o \) and \( \varepsilon = \varepsilon_o \) in Eqs. (5) and (6) enables one to obtain \( n \) and \( k \). When \( n \) and \( k \) are known, \( R \) and \( T \) can be calculated from Eqs. (1) and (2); this computation was carried out on Whirlwind I, the electronic digital computer at the Massachusetts Institute of Technology. From the values of \( R \) and \( T \) thus obtained \( A/T \) was calculated and compared with the
observed value. The values of $\mu_0 \omega$ leading to computed values of $A/T$ in agreement with the observed ones are listed in Table II together with the observed and calculated values of $A/T$. Two interesting observations can be made in Table II, namely that for the thinnest sample (sample 52) $\mu_0 \omega = A/T$ within the accuracy reported and that the results for the two extreme values of the density ratio assumed are not very different. Only two digits are experimentally significant.
### TABLE II. Reduced conductivity per square, and absorption per unit transmission for different densities of gold blacks deposits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ microns</th>
<th>$\mu$ cm$^{-1}$</th>
<th>$\lambda$ calculated</th>
<th>$A/T$ observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x = 150$</td>
<td>$x = 500$</td>
<td>$x = 150$</td>
<td>$x = 500$</td>
</tr>
<tr>
<td>53</td>
<td>105</td>
<td>1.8 1.4</td>
<td>2.4 2.4</td>
<td>2.4 2.4</td>
</tr>
<tr>
<td>345</td>
<td>2.3</td>
<td>2.0</td>
<td>2.3 2.3</td>
<td>2.3 2.3</td>
</tr>
<tr>
<td>455</td>
<td>2.7</td>
<td>2.4</td>
<td>2.7 2.7</td>
<td>2.7 2.7</td>
</tr>
<tr>
<td>57</td>
<td>105</td>
<td>1.2  1.0</td>
<td>1.1 1.2</td>
<td>1.2 1.2</td>
</tr>
<tr>
<td>345</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3 1.3</td>
<td>1.3 1.3</td>
</tr>
<tr>
<td>455</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5 1.5</td>
<td>1.5 1.5</td>
</tr>
<tr>
<td>58</td>
<td>105</td>
<td>1.2  1.0</td>
<td>1.2 1.3</td>
<td>1.3 1.3</td>
</tr>
<tr>
<td>345</td>
<td>1.4</td>
<td>1.4</td>
<td>1.5 1.5</td>
<td>1.5 1.5</td>
</tr>
<tr>
<td>455</td>
<td>1.7</td>
<td>1.6</td>
<td>1.7 1.7</td>
<td>1.7 1.7</td>
</tr>
<tr>
<td>52</td>
<td>105</td>
<td>0.33 0.33</td>
<td>0.33 0.33</td>
<td>0.33 0.33</td>
</tr>
<tr>
<td>345</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41 0.41</td>
<td>0.41 0.41</td>
</tr>
<tr>
<td>455</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42 0.42</td>
<td>0.42 0.42</td>
</tr>
</tbody>
</table>

$x$ is the ratio of the density of bulk gold to that of the gold black deposit.

$\mu$ cm$^{-1}$ is the reduced conductivity per square of deposit.

$A$ is the absorption.

$T$ is the transmission.
The experimental results indicate that the conductivity at 455 μm is consistently higher than at 105 μm. Harris and Beasley have indicated a decreasing conductivity as the wavelength increases from 7 μm to 15 μm, this conductivity being about 1.75 times their dc conductivity and about twice the value reported in Table II for 105 μm. Thus, the conductivity goes through a minimum between 7 μm and 455 μm. The increase of conductivity with increasing wavelength on the long wavelength side of the minimum indicates that the relaxation effect predominates here. The decrease of the conductivity with increasing wavelength on the short wavelength side of the minimum indicates that here the condenser effect predominates.

The relaxation effect therefore appears to predominate in at least the major portion of the wavelength region 105 μm < λ < 455 μm, though the exact position of the minimum is not known. The following analysis shows, at least semi-quantitatively, that the condenser effect may be neglected in the wavelength region λ > 105 μm.

The admittance of a system of strands can be estimated by an equivalent electrical circuit containing condensers and resistors. The fact that blacks conduct direct currents indicates that there are uninterrupted conducting paths in the black. These paths may be quite devious and much longer than the shortest distance between the electrodes used to measure direct current conductivity; they are represented in the network by a series of resistances. There may be shorter paths between the electrodes which pass through gaps or through non-conducting impurities in the strands. Such gaps are represented by shunt condensers in the equivalent circuit. The admittance of these condensers is zero for direct current, but increases with increasing frequencies. Therefore, an increasing number of paths
participate in passing current as the frequency increases, so that the conductivity will increase appreciably when the wavelength becomes less than a critical value \( \lambda_c \). At this critical wavelength the admittance of the shunt condenser at least equals that of the shunted resistance, i.e.
\[ G_C = G, \]
where \( G_C = 2\pi c/\lambda_c \), where \( c \) is the velocity of radiation in vacuo, \( G \) the conductance of the condenser and \( G \) the conductance of the shunted resistance. Therefore \( \lambda_c = 2\pi c/G \). The conductance and capacitance can be expressed in terms of the conductivity of a metal strand, \( \sigma_s \), the permittivity of a gap, \( \varepsilon_g \), the cross-sectional area of a strand, which is also the plate area of the condenser, \( A \), the length of a strand, \( l \), and the total length, \( d \), of all the gaps in the strand:
\[ G = \frac{\sigma_s A}{l} \quad \text{and} \quad C = \frac{(\varepsilon_g A)/(4\pi d)}{\frac{1}{2} c \varepsilon_g / (\sigma_s d)} \]
when the permittivity of the gaps equals that of vacuum, \( c \varepsilon_g = (376.7)^{-1} \) mho. For bulk gold the conductivity is of the order of \( 10^6 \) mho/cm; this value is an upper limit for the conductivity of a strand. Denoting the ratio of the conductivity of a gold strand to that of bulk gold by \( h \), one obtains \( \sigma_s \sim 10^6 \) mho/cm, \( 0 < h < 1 \). Therefore \( \lambda_c \sim 1.33 \times 10^{-4} \) microns \( l/(d \cdot \sigma_s) \). The assumption that the condensers do not contribute to the conductivity of the black is justified if
\[ \lambda_c \ll 10^5 \lambda, \text{ i.e. if } dh/l \gg 1.33 \times 10^{-4} \]
As conservative estimates, let \( h \) be not more than \( 10^{-3} \), and let the total length of gaps in a strand add up to not more than 1 per cent of the length of the strand. These values would lead to a lower limit of \( dh/l \), namely \( dh/l \sim 10^{-4} \), which still exceeds \( 1.33 \times 10^{-4} \) by a large factor. Therefore
it may be concluded that $\lambda_a \ll 100 \mu$, so that the condenser effect need not be considered in the wavelength region $\lambda > 100 \mu$.

The relaxation effect is therefore very suitably studied by means of radiation of wavelength greater than 100 $\mu$. Drude$^3$ and Zener$^3$ have considered forces acting on the electrons that are proportional and opposite in direction to their velocity, hence frictional in nature. They derived the following expression for the conductivity:

$$\sigma = \frac{2n_0 e^2 \lambda^2}{9ne^2 \frac{\lambda}{\tau} + \lambda^2}$$  

(eq. 10)

where $\sigma$ = conductivity

$n_0$ = concentration of electrons

e = electronic charge

$\tau$ = time necessary for average velocity to drop to a fraction 1/e times its original value; this is called the relaxation time.

c = velocity of radiation in vacuo

$\lambda$ = wavelength of radiation

Letting $\lambda$ go to infinity in equation (10) produces

$$\sigma_{dc} = \lim_{\lambda \to \infty} \sigma = \frac{2n_0 e^2}{9ne^2} \frac{c}{\tau}$$  

(eq. 11)

Dividing eq. (11) by eq. (10) gives

$$\left(\frac{\mu_0 \sigma_{dc}}{\mu_0 \sigma}\right) = 1 + \frac{\tau^2}{c^2} \left(\frac{2m_e}{\lambda^2}\right)^2$$  

(eq. 12)

From eq. (11) is is seen that dc measurements only give information about the product of the electron concentration and the relaxation time.

Eq. (12) shows that measurement of the conductivity at various wavelengths can produce data from which to derive the relaxation time independently.

It is hoped that a series of Hall effect measurements now being performed will yield independent information about the electron concentration.
RESULTS, Part II

A. The dc conductivity

Eq. (42) can be used to determine the relaxation time if the reduced conductivity per square, $\rho_{d0} a$, is known. This value was found by plotting, in Fig. 1, $\left(\rho_{d0} a\right)^{-1}$ vs. $(2\pi c/\lambda)\nu$, using as experimental values those reported in Table II. Extrapolating this curve, which theoretically should be a straight line, gives as the ordinate intercept $\left(\rho_{d0} a\right)^{-1}$, for the ordinate axis represents $\lambda = 00$. Harris and Beasley\(^1\) have reported values of dc conductivity obtained by direct electrical measurements, which are applicable to the samples described here. Table III lists the values of $\rho_{d0} a$ determined both by extrapolation of the data of Table II and by direct measurements performed on these samples prior to the long wavelength measurements. The extrapolated values do not agree very closely with those obtained by direct measurement. The discrepancy is believed to be due to slight sintering of the samples as a result of the measurements with long wavelengths. While the samples did not appear to the eye to be sintered, and while the transmission at 7 $\mu$ was found to be practically unchanged after the longer wavelength measurements had been made, slight sintering does not affect the optical properties equally at all wavelengths. The physical reason is that sintering removes some of those gaps that prevent current flow through interrupted strands at wavelengths greater than 100 $\mu$. Thus the dc conductivity and the conductivity for very long wavelengths increase on sintering. At 7 $\mu$ the admittance of the gaps is so much larger that they do not inhibit current flow; on this basis the higher conductivity at 7 $\mu$ as compared with that at 100 $\mu$ was explained above.
Fig. 1. (Reduced conductivity per square, $pc0a^{-2}$ vs. $(wavelength/2mc)^{-2}$ of four gold black samples. $x$ is the ratio of the density of bulk gold to gold black.

$\mu$ : bold face greek #38

$\sigma$ : 10 point. #28
TABLE III: The dc conductivity for gold blacks

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \frac{\mu_a \sigma_{dc}}{\mu_a} ) by extrapolation in Fig. 1</th>
<th>( \frac{\mu_a \sigma_{dc}}{\mu_a} ) from resistance measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x = 150 )</td>
<td>( x = 500 )</td>
</tr>
<tr>
<td>53</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>57</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>55</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>52</td>
<td>0.44</td>
<td>0.44</td>
</tr>
</tbody>
</table>

\( x \) is the ratio of the density of bulk gold to that of the gold black deposit.

\( \frac{\mu_a \sigma_{dc}}{\mu_a} \) is the reduced dc conductivity per square of film.
The removal of gaps therefore does not increase the conductivity at 7 μ nearly as much as that at 100 μ. It has been observed that a sample that sintered sufficiently so that a brownish cast was observed, had at least a three fold increase in dc conductivity. Since the discrepancy between the values obtained by the two measurements reported in Table III is much less than threefold, the amount of sintering that would account for the dc discrepancy is not nearly enough to alter the appearance of the sample in visible radiation. For the same reason the measured values at 7 μ are not nearly as sensitive to sintering as those made in the wavelength region beyond 100 μ and with direct current.

B. The relaxation time.

From the slopes and intercepts of the curves drawn in Fig. 1 the relaxation time is computed. The results are listed in Table IV, and agree remarkably well with each other and with the value \( t \approx 10^{-13} \) sec. reported for bulk metal. The agreement between the values calculated assuming different values of the density ratio is reassuring. A relaxation time of electrons in gold blacks of the same order of magnitude as that of electrons in bulk gold accounts for the wavelength dependence of the conductivity observed for four gold black samples.

The choice of wavelengths \( \lambda = 345 μ \) and \( \lambda = 455 μ \) was made before the theoretical analysis was performed. In Fig. 1 these two values are seen to be so close together for the study of relaxation times as hardly to represent independent measurements. It is hoped that the results presented here may stimulate further measurements in the region \( 105 μ < \lambda < 345 μ \) in order to check the linear dependence of the reciprocal reduced conductivity per square on the square of the reciprocal wavelength.
TABLE IV. Relaxation time of electrons in gold black deposits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relaxation time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x = 150 )</td>
</tr>
<tr>
<td>53</td>
<td>( 3.8 \times 10^{-14} )</td>
</tr>
<tr>
<td>57</td>
<td>( 2.5 \times 10^{-14} )</td>
</tr>
<tr>
<td>58</td>
<td>( 3.2 \times 10^{-14} )</td>
</tr>
<tr>
<td>52</td>
<td>( 3.2 \times 10^{-14} )</td>
</tr>
</tbody>
</table>

\( x \) is the ratio of the density of bulk gold to that of the gold black deposit.
CONCLUSIONS AND SUMMARY

The range of wavelengths larger than 105 μm appears very useful for the investigation of the behaviour of electrons in metal blacks and their absorptive power. While dc conductivity measurements only give the product of electron concentration and relaxation time, the determination of the conductivity by optical means at various wavelengths provides an independent means of determining the relaxation time.

The relaxation time of electrons in blacks was found to be of the same order of magnitude as that in bulk gold. This would indicate that the amplitude of oscillation of the electrons is so small that the fine state of division of gold in a black does not hinder the response of the electron to radiation of wavelength greater than 100 μm.

A closed expression was derived for finding the conductivity of thin films at large wavelengths in terms of the observed transmission and absorption of any film, whether a black deposit or a bright film. It has been shown that the reduced conductivity per square of film is a very fundamental property of metal films and a very useful one because:

1. It determines directly the optical behaviour of the film and at long wavelengths approaches the absorption per unit transmission asymptotically.

2. It is dimensionless.

3. It can be determined without a very accurate knowledge of the density of the film.

The optical constants are not nearly as useful because they are strongly dependent on the density of the black. While it was originally thought
that they had to be determined first from optical measurements in order to find the conductivity, it now turns out that by means of Eq. (9) the conductivity is found much more easily than are the optical constants.

The following conclusions can be drawn from the present investigation about the structure of metal blacks:

As the blacks have an extremely low density and yet conduct direct current, they probably consist of yarn-like strands of crystallites relatively far apart. The conductance of metal blacks is about $10^{-3}$ times that of bright deposits of comparable weight per unit area. This low ratio is due both to the longer conducting path in blacks and to the lower concentration of electrons in the blacks. This comparatively low concentration has two causes, namely the low concentration of metal in blacks, and the low concentration of electrons in the metal strands. The concentration of metal in the blacks is determined by the density ratio $x = 500$. That the concentration of electrons in the strands is comparatively low is suggested by the comparatively low conductivity of thin, bright gold films.

Hall effect measurements are being planned to find the electron concentration in the black deposits; combining the results of these measurements with the estimated density ratio $x = 500$ enables one to find the concentration of electrons in the strands. Combining the results of Hall-effect measurements with
the values for dc conductivity and relaxation time, reported in this paper,
should give the average length of the uninterrupted metal strands in blacks.

ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of Mr. William E. Krag who
prepared the samples and of Professor John Streng and Dr. W. M. Sinton of
The Johns Hopkins University who made the far infrared measurements.

We are also grateful to Professor Charles W. Adams, Miss Donna Need
and Mr. Irand Saxenian of the MIT Digital Computer Laboratory for their
assistance in using the Whirlwind I computer.