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

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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 directly 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.

(A) 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.

(B) According to Drude[2] and Zener[3] 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.

(C) 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 to predominate 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 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 Loeb[4] 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 nonabsorbing 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 percent transmitting. Their index of refraction is therefore effectively unity, so that Case III of the above reference[4] applies here:

$$R=\frac{|(Z_{0a}-Z_{a0})i\sin K_a a|^2}{|2\cos K_a a-i(Z_{0a}+Z_{a0})\sin K_a a|^2},\tag{1}$$

$$T=\frac{4}{|2\cos K_a a-i(Z_{0a}+Z_{a0})\sin K_a a|^2},\tag{2}$$

where R = fraction of incident radiation reflected, T = fraction of incident radiation transmitted, $Z_{0a}=n+ik$, n = index of refraction of conducting film, k = absorption coefficient of conducting film, $Z_{a0}=1/Z_{0a}$, $i=\sqrt{-1}$, $K_a=(2\pi/\lambda)(n+ik)$, λ = wavelength of incident radiation, and a = thickness of conducting film. The optical constants are related to the conductivity and permittivity of the media by the relations

$$nk=\tfrac{1}{4}\mu c\sigma a(\lambda/\pi a),\tag{3}$$

$$n^2-k^2=(\mu\varepsilon/\mu_0\varepsilon_0),\tag{4}$$

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[1] L. Harris and J. K. Beasley, J. Opt. Soc. Am. 42, 134 (1952).

[2] P. Drudé, *The Theory of Optics* (Longmans, Greene and Company, New York, 1902).

[3] C. Zener, Nature 132, 968 (1933).

[4] Harris, Beasley, and Loeb, J. Opt. Soc. Am. 41, 604 (1951).

where σ = conductivity of the conducting film, ε = permittivity of the conducting film, ε_0 = permittivity of vacuum, μ = permeability of the conducting film, μ_0 = permeability of vacuum, and c = velocity of radiation in vacuum. The quantity $\mu c\sigma a$ 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):

$$n^2=\tfrac{1}{2}\mu\varepsilon c[\{c^2+(\mu c\sigma a)^2(\mu\varepsilon c\cdot 2\pi a/\lambda)^{-2}\}^{\frac{1}{2}}+c] \quad (5)$$

$$k^2=\tfrac{1}{2}\mu\varepsilon c[\{c^2+(\mu c\sigma a)^2(\mu\varepsilon c\cdot 2\pi a/\lambda)^{-2}\}^{\frac{1}{2}}-c] \quad (6)$$

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 $|(n+ik)2\pi a/\lambda|^2$ is small,[5] for n and k rarely exceed 3.5. The following approximations may be used when $|(n+ik)2\pi a/\lambda|^2\ll 1$:

$$\sin K_a a \cong K_a a,$$
$$\cos K_a a \cong 1-\tfrac{1}{2}(K_a a)^2.$$

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

$$R=\frac{|i2\pi a/\lambda\{(\mu\varepsilon/\mu_0\varepsilon_0)-1\}+\frac{1}{2}i\mu c\sigma a(\lambda/\pi a)|^2}{|2[1-(2\pi^2a^2/\lambda^2)\{(\mu\varepsilon/\mu_0\varepsilon_0)+\frac{1}{2}i\mu c\sigma a(\lambda/\pi a)\}]-i(2\pi a/\lambda)\{(\mu\varepsilon/\mu_0\varepsilon_0)+1+\frac{1}{2}i\mu c\sigma a(\lambda/\pi a)\}|^2}, \quad (7)$$

$$T=\frac{4}{|2[1-(2\pi^2a^2/\lambda^2)\{(\mu\varepsilon/\mu_0\varepsilon_0)+\frac{1}{2}i\mu c\sigma a(\lambda/\pi a)\}]-i(2\pi a/\lambda)\{(\mu\varepsilon/\mu_0\varepsilon_0)+1+\frac{1}{2}i\mu c\sigma a(\lambda/\pi a)\}|^2}. \quad (8)$$

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

$$A/T=(\pi a/\lambda)^2(\mu c\sigma a)^2+\{1+(2\pi^2a^2/\lambda^2)\}\mu c\sigma a. \quad (9)$$

Equation (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/λ approaches zero, $\mu c\sigma a$ approaches A/T asymptotically, and ceases to depend explicitly on a/λ. Thus, for thin films, the explicit dependence of $\mu c\sigma a$ 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 $A/T\equiv(1-T-R)/T$ depends for metal blacks largely on the transmission, and less so on reflection. This is 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.

[5] When the wavelength is small compared to the film thickness, the optical density ($\log_{10}1/T$) is directly proportional to $\mu c\sigma a^1$. For long wavelengths interference effects must be taken into account as is done in this paper.

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 is 300 to 500 times as small as that of bulk gold.[1] Table I also contains values of $\pi a/\lambda$ 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 $x=500$. Equation (9) is not applicable to all cases enumerated in Table I, particularly for $x=500$ because the requirement $|(n+ik)2\pi a/\lambda|^2\ll 1$ is certainly not satisfied when $\pi a/\lambda\sim 1$.

TABLE I[a]. Observed reflection and transmission of gold black deposits at different wavelengths; calculated $\pi a/\lambda$ values for the deposits, assuming different densities.

Sample	λ microns	R percent	T percent	$\pi a/\lambda$ $x=150$	$\pi a/\lambda$ $x=500$
53	105	13.0	25.5	0.295	0.984[b]
	345	16.2	25	0.0900	0.300
	455	19.5	21.6	0.0682	0.227
57	105	10.7	41.2	0.162	0.539[b]
	345	7.8	40.8	0.0492	0.164
	455	8.8	37.1	0.0373	0.124
58	105	10.1	39.4	0.196	0.653[b]
	345	9.7	36.8	0.0597	0.199
	455	8.8	34.1	0.0452	0.151
52	105	2.2	73.4	0.0693	0.231
	345	2.6	69	0.0211	0.0703
	455	5	67	0.0160	0.0533

[a] Reliability of data is ~1 percent.
[b] Equation (9) not applicable.
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 $\mathfrak{y}c\sigma a$, namely one for each of four samples at three wavelengths, assuming two values of the density ratio of bulk gold to 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 $\mathfrak{y}c\sigma a$ the optical constants n and k were calculated, using Eqs. (5) and (6). For these calculations a knowledge of $\mathfrak{e}$ and $\mathfrak{y}$ is required. The latter quantity can, for non-magnetic films, be set equal to that of vacuum, i.e. $\mathfrak{y}=\mathfrak{y}_0$. 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 $\mathfrak{e}\sim\mathfrak{e}_0$. 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 $\mathfrak{y}=\mathfrak{y}_0$ and $\mathfrak{e}=\mathfrak{e}_0$ 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 $\mathfrak{y}c\sigma a$ 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) $\mathfrak{y}c\sigma a=A/T$ 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 black deposits.

Sample	λ	$\mathfrak{y}c\sigma a$		A/T calculated		A/T observed
	microns	$x=150$	$x=500$	$x=150$	$x=500$	
53	105	1.8	1.4	2.4	2.4	2.4
	345	2.3	2.0	2.3	2.3	2.35
	455	2.7	2.4	2.7	2.7	2.7
57	105	1.2	1.0	1.1	1.2	1.2
	345	1.3	1.3	1.3	1.3	1.3
	455	1.5	1.5	1.5	1.4	1.5
58	105	1.2	1.0	1.2	1.3	1.3
	345	1.4	1.4	1.5	1.5	1.5
	455	1.7	1.6	1.7	1.7	1.7
52	105	0.33	0.33	0.33	0.33	0.33
	345	0.41	0.41	0.41	0.41	0.41
	455	0.42	0.42	0.42	0.42	0.42

x is the ratio of the density of bulk gold to that of the gold black deposit.
$\mathfrak{y}c\sigma a$ is the reduced conductivity per square of deposit.
A is the fraction absorbed.
T is the fraction transmitted.

TABLE III. The dc conductivity for gold blacks

Sample	$\mathfrak{y}c\sigma_{dc}a$[a] By extrapolation in Fig. 1[b] $x=150$	$x=500$	From resistance measurements
53	2.6	2.3	1.8
57	1.4	1.4	0.96
58	1.6	1.5	1.2
52	0.44	0.44	0.38

[a] $\mathfrak{y}c\sigma_{dc}a$ is the reduced dc conductivity per square of film.
[b] x is the ratio of the density of bulk gold to that of the gold black deposit.

THEORY, PART II: RELAXATION TIME OF ELECTRONS IN METAL BLACKS

The experimental results indicate that the conductivity at 455μ is consistently higher than at 105μ. Harris and Beasly[1] have indicated a decreasing conductivity as the wavelength increases form 7μ to 15μ, this conductivity being about 1.75 times their dc conductivity and about twice the value reported in Table II for 105μ. Thus the conductivity goes through a minimum between 7μ and 455μ. 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 $105\mu<\lambda<455\mu$, though the exact position of the minimum is not known. The following analysis shows, at least semiquantitatively, that the condenser effect may be neglected in the wavelength region $\lambda\geq 105\mu$.

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 nonconducting 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 λ_c. At this critical wavelength the admittance of the shunt condenser at least equals that of the shunted resistance, i.e. $C\omega_c = G$, where $\omega_c = 2\pi c/\lambda_c$, where c is the velocity of radiation in vacuo, C the capacitance of the condenser and G the conductance of the shunted resistance. Therefore $\lambda_c = 2\pi cC/G$. The conductance and capacitance can be expressed in terms of the conductivity of a metal strand, σ_s; the permittivity of a gap, ε; 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:

$$G = \sigma_s A/l \quad \text{and} \quad C = (\varepsilon A)/(4\pi d).$$

Therefore,

$$\lambda_c = \tfrac{1}{2} cl\varepsilon/(\sigma_s d).$$

When the permittivity of the gaps equals that of vacuum, $c\varepsilon = (376.7)^{-1}$ mho. For bulk gold the conductivity is of the order of 10^5 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 $\sigma_s \sim 10^5 h$ mho/cm, $0 < h < 1$. Therefore $\lambda_c \sim 1.33 \times 10^{-4}\ l/dh$ microns. The assumption that the condensers do not contribute appreciably to the conductivity of the black is justified if

$$\lambda_c < 100\mu, \quad \text{i.e., if} \quad dh/l > 1.33 \times 10^{-6}.$$

As conservative estimates, let h be not more than 10^{-2}, and let the total length of gaps in a strand add up to not more than 1 percent 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 1.33×10^{-6} by a large factor. Therefore it may be concluded that $\lambda_c < 100\mu$, 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 100μ. Drude[2] 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:

$$\sigma = \frac{2\pi n_0 e^2 \tau \lambda^2}{4\pi^2 c^2 \tau^2 + \lambda^2}, \tag{10}$$

where σ = conductivity, n_0 = concentration of electrons, e = electronic charge, τ = time necessary for average velocity to drop to a fraction $1/e$ times its original value (relaxation time), c = velocity of radiation in vacuo, and λ = wavelength of radiation. Letting λ go to infinity in Eq. (10) produces

$$\sigma_{dc} = \lim_{\lambda\to\infty} \sigma = 2\pi e^2 n_0 \tau. \tag{11}$$

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

$$(\mathfrak{u} c\sigma_{dc} a / \mathfrak{u} c\sigma a) = 1 + \tau^2 (2\pi c/\lambda)^2. \tag{12}$$

From Eq. (11) it 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

The dc Conductivity

Equation (12) can be used to determine the relaxation time if the reduced conductivity per square, $\mathfrak{u} c\sigma_{dc} a$, is known. This value was found by plotting, in Fig. 1, $(\mathfrak{u} c\sigma a)^{-1}$ *vs* $(2\pi/\lambda)^2$, using as experimental values those reported in Table II. Extrapolating this curve, which theoretically should be a straight line, gives as the ordinate intercept $(\mathfrak{u} c\sigma_{dc} a)^{-1}$, for the ordinate axis represents $\lambda = \infty$. 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 $\mathfrak{u} c\sigma_{dc} a$ 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 the result of 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 7μ 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 100μ. Thus the dc conductivity and the conductivity for very long wavelengths increase on sintering. At 7μ the admittance of the gaps is so much larger that they do not inhibit current flow; on this basis the higher conductivity at 7μ as compared with that at 100μ was explained above. The removal of gaps therefore does not increase the conductivity at 7μ nearly as much as that at 100μ. It has been observed that a sample that sintered sufficiently so that a brownish cast was observed, had at least a threefold 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 7μ are not nearly as sensitive to sintering as those made in the wavelenegth region beyond 100μ and with direct current.

The Relaxation Time

From the slopes and intercepts of the curves drawn in Fig. 1 the relaxation time is computed. The results are

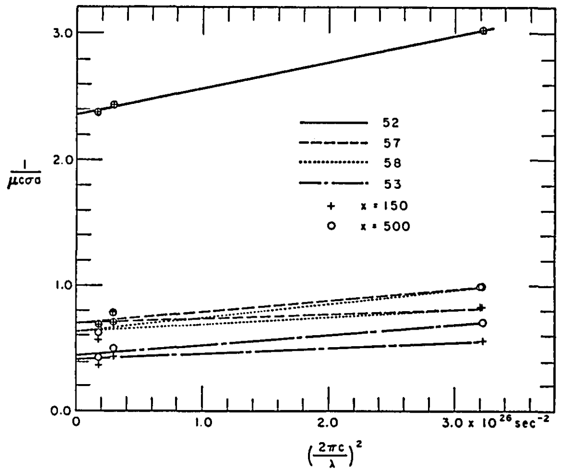

FIG. 1. (Reduced conductivity per square, $\mu c\sigma a)^{-1}$ *vs.* (wavelength/$2\pi c)^{-2}$ of four gold black samples. x is the ratio of the density of bulk gold to gold black.

listed in Table IV, and agree remarkably well with each other and with the value $\tau \sim 10^{-13}$ sec reported[6] for bulk metal. The agreement between the values calculated assuming different values of the density ratio is reassuring. Thus a relaxation time of electrons in gold blacks of the same order of magnitude as that of electrons in bulk gold can account for the wavelength dependence of the conductivity observed for four gold black samples.

The choice of wavelengths $\lambda = 345\mu$ and $\lambda = 455\mu$ 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 $105\mu < \lambda < 345\mu$ in order to check the linear dependence of the reciprocal reduced conductivity per square on the square of the reciprocal wavelength.

CONCLUSIONS AND SUMMARY

The range of wavelengths larger than 105μ appears very useful for the investigation of the behavior 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 electrons to radiation of wavelength greater than 100μ.

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 (A) it determines directly the optical behavior of the film and at long wavelengths approaches the absorption per unit transmission asymptotically, (B) it is dimensionless, and (C) 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.

TABLE IV. Relaxation time of electrons in gold black deposits.

Sample	Relaxation time (sec) $x=150$[a]	$x=500$
53	3.8×10^{-14}	4.5×10^{-14}
57	2.5×10^{-14}	3.7×10^{-14}
58	3.2×10^{-14}	4.1×10^{-14}
52	3.2×10^{-14}	3.2×10^{-14}

[a] x is the ratio of the density of bulk gold to that of the gold black deposit.

As the blacks have an extremely low density and yet conduct direct current, they probably consist of yarn-like strands relatively far apart. The dc conductance of metal blacks is about 10^{-5} 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.

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[6] Frederick Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), first edition, p. 639.