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Investigation of the Optical Properties of Au by Means of Thin Semitransparent Films

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Both the real and imaginary parts of the dielectric constant of Au were accurately determined in the 0.5–6-eV range from measurements of the reflectance and transmittance of thin semitransparent films. The results obtained on well-crystallized films were in general agreement with previous data on bulk samples. They allowed a thorough analysis of the absorption spectrum of Au in terms of intra- and interband transitions. Deviations from the Drude theory were observed, and the values of the optical mass and relaxation time of the conduction electrons are discussed. The absorption edge was investigated very accurately. Further information on the absorption processes was also obtained by studying films with different crystallographic structures. In particular, the supplementary absorption often observed in Au below the absorption edge was shown to be due to impurities.

I. INTRODUCTION

During the last ten years, the analysis of the optical properties of noble metals in connection with their electronic structure proved to be very useful in order to test the applicability of band theory to metals. A considerable amount of theoretical and experimental work has been performed, mainly on copper. At the present time, the general features of the optical properties of noble metals are well known and interpreted with respect to the theoretical band-structure calculations. However, there still remain discrepancies, either between the experimental results obtained by different methods on different samples or between the experimental results and the statements of the one-electron theory.

The purpose of the present work is more particularly to deal with these discrepancies by an accurate determination and analysis of the optical properties. The samples used in the previous experiments were either bulk electropolished samples[1–8] or thick evaporated layers.[9–12] In all cases, the optical constants were deduced from reflection measurements only, and the results were found to be very sensitive to the quality of the surface of the samples: roughness, surface contamination, etc.[7,13] In the present work, a somewhat different kind of sample was studied: semitransparent films, the properties of which were identical to the bulk properties and which proved to be very suitable samples for optical measurements because of the smoothness and flatness of their surface. Both reflectance and transmittance measurements can be performed on such films, which allows a straightforward and accurate determination of both the real and imaginary parts of the complex refractive index $\tilde{n}$. Moreover, the crystallographic structure of the films can be modified (while generally conserving the quality of the surface) by modifying the conditions of preparation; in this way, the influence of structural defects on the optical properties can be investigated. Au was chosen because it is stable against oxidation and because very thin Au films with bulk properties were found to be easier to prepare.

In Sec. II, the experimental methods are briefly described. The structure of the films is analyzed in more detail. The principle of the analysis of the experimental results is given. In Sec. III, the absorption due to the conduction electrons is considered; values of their optical mass and relaxation time are deduced and discussed in relation with the film structure and the results of electrical-resistivity measurements. In Sec. IV, the absorption spectrum due to interband transitions is accurately investigated. In Sec. V, the origin of the supplementary absorption which appears for some films is discussed.

II. EXPERIMENTS

A. Sample Preparation

The samples used in the present experiments were thin semitransparent films of Au, the thickness of which usually ranged from 100 to 250 Å. They were deposited by vacuum evaporation of 99.99% Au from a tungsten boat in an oil-free ultrahigh vacuum system. (The pressure which was 10^{-11} Torr reached 10^{-10} Torr at the end of the evaporation process.) The rate of deposition was a few Å/sec. The substrates were amorphous fused-silica plates which had been very carefully polished to a supersmooth finish, cleaned, and then outgassed under vacuum; some of them were also submitted to an ionic cleaning. The deposition was generally performed at room temperature, sometimes at about 100 °C. After their deposition, the films were annealed under the same vacuum, usually up to 100 or 150 °C, the annealing process being monitored by simultaneous electrical-dc-resistance measure-

FIG. 1. Transmission electron micrograph of a well-crystallized Au film ($d = 158$ Å).

ments made by a four-point method. A detailed survey of these experiments conducted in order to obtain very thin, but continuous, metallic films with the same properties as the bulk material will be published elsewhere together with a thorough analysis of the physical characteristics of these films.

The structure of the films was investigated by various x-ray and electron-microscopy methods. A brief description of the so-called "good" films will be given. These films, deposited on amorphous substrates, were polycrystalline but continuous. They were formed of joined regularly shaped crystallites, the average lateral size of which ranged from 3000 to 5000 Å, and the thickness of which was equal to the thickness of the film. These grains were all oriented with their [111] crystallographic axes perpendicular to the substrate, leading to a fiber structure with a texture of 2° or 3°. Their orientation parallel to the substrate was naturally random. The amount of structural defects (mainly twin crystals) inside the grains was very small, due to the recrystallization taking place during the annealing process. So the main defects were grain boundaries. Figure 1 shows a transmission electron micrograph of a Au film of thickness 158 Å, which illustrates the preceding comments.

The thickness of the films was determined by two independent methods using x-rays. One of these methods is based on the analysis of the fringes due to interferences between the x-ray beams reflected at very low angles of incidence on the two surfaces of the film[14]; this method requires only flat, parallel, and smooth surfaces, is not sensitive to the crystallographic structure of the film, and gives a "mechanical" thickness. The second method uses the interference fringes which appear around the (111) x-ray-diffraction peak when the crystallographic structure of the film (mainly the size and the orientation of the grains) is good enough.[15,16] This method gives a "crystalline" thickness. Both methods, when applicable, are very accurate (within 1%), and for well-crystallized films, their results agree within 1%.

A thorough comparison between the theoretical and experimental x-ray reflection-interference fringe system gives detailed information about the surfaces of the films.[17] The positions of the maxima and minima are those expected from the theory, which proves that there are no thickness fluctuations and justifies the claimed accuracy of the thickness determination. The observed decrease in the mean intensity is due to correlated irregularities on the two film surfaces; the decrease in the contrast is due to small uncorrelated irregularities. These experiments show that the free surface of a film in this thickness range reproduces exactly the surface of the substrate; thus, the flatness and smoothness of the film surfaces are those of the fused silica surface, which are very good. The only supplementary defects which exist on the free surface are less than 5 Å high; electron-microscope studies show that they consist either in small depressions along grain boundaries or in slightly distorted crystalline planes showing up at the surface.[18] Therefore, these films prove to be particularly suitable to optical measurements, and the results must be as free as possible from any surface phenomenon.

It was easy by modifying the conditions of preparation of the films (for example, the deposition rate, the deposition temperature, the annealing process) to obtain films with different crystallographic structures: crystallites of various sizes (down to a few hundreds Å), misorientation of the grains, various amounts and types of structural defects, etc. Figure 2 presents, for example, a transmission electron micrograph of a nonannealed film of thickness 232 Å. It was shown that when the films contained no holes (holes could be observed either in very thin films which had never been continuous or in films which were continuous at first but suffered granulation through an excess of annealing), their surface was still flat and smooth enough so that the observed changes in the optical properties could be attributed to a real modification of the bulk absorption spectrum rather than to an influence of surface irregularities on the measurements.

The electrical dc resistivity of the films was found to be very sensitive to the conditions of preparation, i.e., to the film structure. Typically, the resistivity of the 158-Å-thick film of Fig. 1 is 2.97 $\mu\Omega$cm (the ideal bulk resistivity of Au is 2.30 $\mu\Omega$cm[19]); thicker films (about 400 to 500 Å thick) prepared in the same way had resistivities as low as 2.45 $\mu\Omega$cm. The difference between the film and the bulk values of the resistivity is mainly due to grain boundaries and surfaces; this point will be considered later.

B. Optical Measurements and Determination of the Optical Constants

The optical properties of a metal are characterized by a complex refractive index $\tilde{n}=n+ik$ (or a complex dielectric constant $\epsilon=\tilde{n}^2=\epsilon_1+i\epsilon_2$) which depends on the wavelength λ. At a wavelength λ, the reflectance R and transmittance T in normal incidence of a thin semitransparent metal film of thickness d can be expressed as functions of n, k, and d/λ.[20] If the film thickness is known, both n and k can be computed at each wavelength from the measured values R_{ex} and T_{ex} of the film reflectance and transmittance at the same wavelength by solving

$$R(n,k)-R_{\text{ex}}=0\ , \qquad T(n,k)-T_{\text{ex}}=0\ , \tag{1}$$

A numerical iterative method performed on a computer was used.[21] The results were corrected for the influence of multiple reflections inside the transparent substrate.

It was shown that when this method is correctly used its accuracy is very good. Moreover, it is not as sensitive to oxide layers and surface contamination as methods based on reflection measurements only. It must, however, be emphasized that in some cases (for some combinations of n, k, and d/λ) very small experimental errors on R_{ex} or T_{ex} may cause very large errors in the determination of n and k; even no solution of the system (1) can be found.[22–24] These difficulties were overcome in the present case of Au films by changing the value of d/λ, i.e., by studying films of thickness comprised between 100 and 250 Å.

The measurements of reflectance and transmittance were performed on a Cary 14 double-beam spectrophotometer in a large spectral range, 0.5–6.2 eV (i.e., 2.5–0.2 μ). Accurate absolute values of the reflectance were obtained by means of a V-W-type attachment.[25] The value of the film thickness, which was needed for the computation of the optical constants, was measured with high accuracy as indicated above. (The thickness uniformity was controlled by various local measurements by the diffraction fringe method.)

The relative uncertainties on n and k are estimated to be of a few percent, and of 1 to 2%, respectively.

FIG. 2. Transmission electron micrograph of a nonannealed Au film ($d=232$ Å).

C. Principle of the Analysis of the Results

The discussion of the optical properties of Au will be conducted on the complex dielectric constant ϵ which represents the response of the electrons in the metal to the incident electromagnetic field. Depending on the frequency, there may be excitation of intraband transitions of the conduction electrons, or interband transitions due to internal photoelectric effect, or both of them. If these excitations are considered as independent, ϵ can be written[3]

$$\epsilon(\omega)=\epsilon^{(c)}(\omega)+\epsilon^{(i)}(\omega)\ ,$$

where $\epsilon^{(c)}$ and $\epsilon^{(i)}$ represent the contributions due to intra- and interband transitions, respectively.

Interband transitions can only take place at energies higher than some energy onset $\hbar\omega_0$ characteristic of the metal. As the imaginary part of the dielectric constant ϵ_2 is directly related to the optical absorption (which is proportional to $\epsilon_2\omega$), $\epsilon_2^{(i)}$ is equal to zero for $\hbar\omega<\hbar\omega_0$ (when no indirect transition or absorption tail takes place below the onset). The real part of ϵ, ϵ_1, is a polarization term. It is related to ϵ_2 by a Kramers-Kronig dispersion relation

$$\epsilon_1(\omega)=\epsilon_\infty+\frac{2}{\pi}\int_0^\infty \frac{\omega'\epsilon_2(\omega')}{(\omega')^2-\omega^2}\,d\omega' \ .$$

$\epsilon_1^{(i)}$, representing the polarization due to interband transitions, can be computed in this way from $\epsilon_2^{(i)}$. It is practically a constant for energies well below the onset $\hbar\omega_0$.

Thus, at low energies (here practically from 0.5 to 1.5 eV), the optical properties are due to intraband transitions of the quasifree conduction electrons only. The experimental values of ϵ_1 and ϵ_2 can tentatively be analyzed in terms of the classical Drude theory

$$\epsilon_1=\mathcal{P}-\frac{\lambda^2}{\lambda_0^2}\frac{1}{1+(\lambda/\lambda_\tau)^2} \ , \qquad \epsilon_2=\frac{\lambda^3}{\lambda_0^2\lambda_\tau}\frac{1}{1+(\lambda/\lambda_\tau)^2} \ .$$

λ_0 and λ_τ are the plasma and relaxation wavelength, respectively, which are related to the effective "optical" mass m_0 and the "optical" relaxation time τ of the conduction electrons by

$$\lambda_0^{-2}=Ne^2/\pi m_0 c^2 \ , \qquad \lambda_\tau=2\pi c\tau \ .$$

(N is the number of conduction electrons, equal here to the number N_a of atoms per unit volume.) $\mathcal{P}$ is equal to

$$\mathcal{P}=1+4\pi N_a\alpha_a+\epsilon_1^{(i)}(\omega) \ ,$$

where α_a is the atomic polarizability.

As in the present experiments, $\lambda_\tau \gg \lambda$, the quantity $(\lambda/\lambda_\tau)^2$ (10^{-2}–10^{-3}) can be neglected with respect to 1, so the Drude relations can be written

$$\epsilon_1\simeq\mathcal{P}-\lambda^2/\lambda_0^2 \ , \qquad \epsilon_2\simeq\lambda^3/\lambda_0^2\lambda_\tau \ .$$

ϵ_1 depends on the optical mass only; it yields a value of m_0. ϵ_2 depends on both the optical mass and the relaxation time.

As a matter of fact, in the present experiments, the so-called anomalous skin effect has to be taken into account in the interpretation of the optical properties due to the conduction electrons. The penetration depth $\delta_0=\lambda_0/2\pi$ of light in Au is about 200 Å, which is of the same order of magnitude as the mean free path l of the conduction electrons. ($l=380$ Å for pure bulk Au at room temperature.) The electric field can no longer be considered as a constant. The assumption that the current density at a point depends only on the electric field at the same point, which is basic in the Drude theory, is no longer valid. The electronic distribution is not uniform and depends on the boundary conditions for the electrons at the sample surface. This surface is characterized by a phenomelogical scattering parameter p which is equal to 1 when all electrons are specularly reflected at the surface and to 0 when they are completely diffusely scattered. When a thin film is considered, both surfaces have to be taken into account and not only the free surface, since the film thickness is also of the same order of magnitude as the penetration depth and the mean free path. The anomalous skin effect in thin films has been treated[26] along the lines of Dingle's computations for bulk samples.[27] The reflectance and transmittance of a film in the near infrared have been expressed (approximate relations) as functions of the parameters λ_0, λ_τ, and p. The results can be summarized as follows: (i) The optical mass does not depend on p, and is approximately the same as the one deduced from the Drude theory. (ii) The relaxation time τ is equal to the one deduced from the Drude theory corrected by a term which depends on p, λ_0, and d:

$$\frac{1}{\tau}=\frac{1}{\tau_{\mathrm{Drude}}}-\frac{6\pi}{8}\,v\,\frac{1}{\lambda_0}\,\frac{1+\cosh^2(2\pi d/\lambda_0)}{\sinh(2\pi d/\lambda_0)\cosh(2\pi d/\lambda_0)+2\pi d/\lambda_0} \times (1-p) \ , \tag{2}$$

v being the Fermi velocity of the conduction electrons.

Later on, the discussion will follow the Drude theory which is more familiar, but the corrections due to the anomalous skin effect will be made when necessary.

Once the microscopic parameters of the conduction electrons have been determined from the analysis of the optical properties at low energies, it is easy to compute at each wavelength the contribution to ϵ due to the intraband transitions by the Drude formula. This contribution is then subtracted from the total dielectric constant; the quantity thus obtained is $\epsilon^{(i)}$, the contribution due to the interband transitions, which can then be analyzed in relation with the electronic energy-band structure.

Figure 3 shows the variation with energy of the optical absorption ϵ_2/λ for three films of approximately the same thickness ($\simeq 150$ Å) which are representative of different types of crystallographic structure. Curve 1 corresponds to a well-crystallized film (cf. Fig. 1). For such films, the results are very reproducible from film to film, regardless of its thickness, in the interband-transition region, but may differ in the infrared because the conduction electrons are much more sensitive to slight changes in the film structure. Curve 2 corresponds to a nonannealed film deposited at low rate in poor vacuum, which is still continuous but consists of very small and misoriented crystallites. The absorption in the interband-transition region is found to decrease for this film. Moreover, supplementary absorption appears between 1 and 2 eV, i.e., below the absorption edge, which cannot be explained by the usual one-electron theory. When the absorption

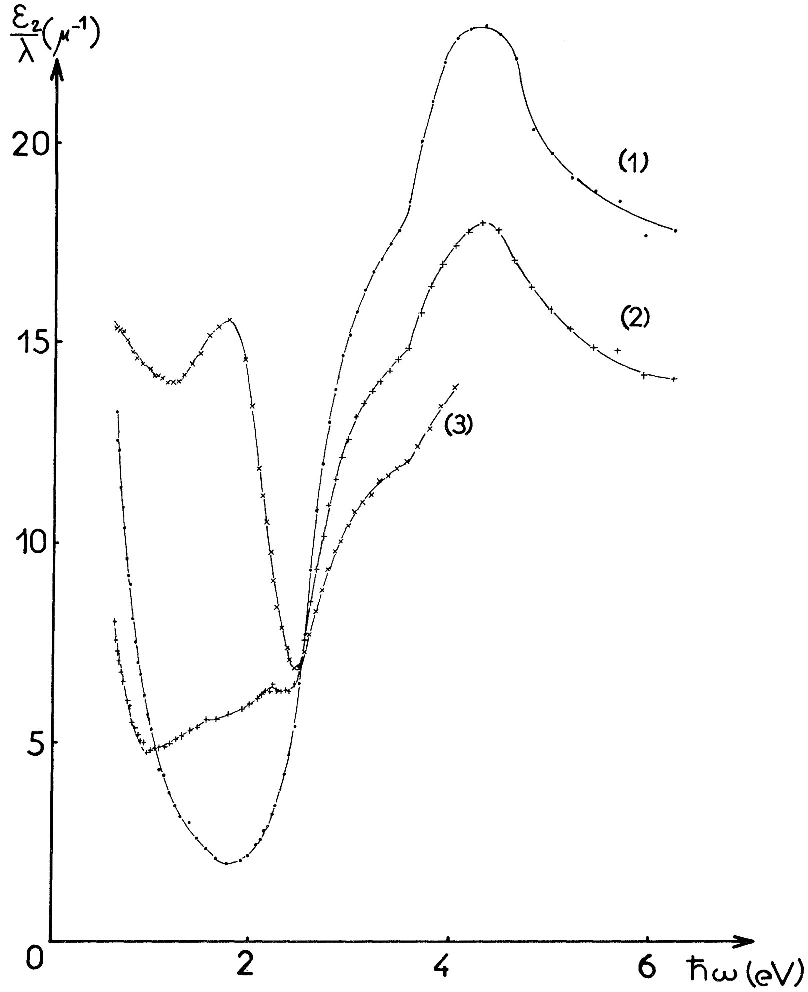

FIG. 3. Optical absorption ϵ_2/λ versus energy $\hbar\omega$ for three films of approximately the same thickness but of different structures: (1) well-crystallized film, (2) nonannealed film with very small and misoriented crystallites, (3) "island" film.

due to the inter- and intraband transitions is subtracted, an additive absorption band clearly shows up. Its origin will be discussed below. Finally, curve 3 corresponds to a highly discontinuous granular or so-called "island" film. Films of this type have not been retained in the present work because they differ too much from an ideal thin film, and the interpretation of their specific optical properties must take into account their discontinuities. Only a few comments will be made about them.

III. CONDUCTION ELECTRONS

This section discusses the optical results in the spectral range 0.5–1.2 eV (2.5–1 μ). A great number of films were investigated; only a few typical cases will be presented.

A. Optical Mass

According to the Drude formula, $-\epsilon_1$ must vary linearly with λ^2. The slope yields the value of the optical mass m_0, the ordinate at the origin the polarization term $\mathcal{P}$. Figure 4 shows the experimental results for a number of films.

The optical mass is found to be equal to

$$m_0 = 0.94 \pm 0.01 \quad .$$

The quality of the film does not influence very much the value of m_0; m_0 is only slightly increasing (a few percent) when the grain size decreases and the amount of structural defects increases. As a consequence, as the transmittance of a film in the infrared depends only (besides on its thickness) on the optical mass, films of the same thickness but of different structures have the same transmittance, while their reflectance, however, may be very different. When the film contains a small amount of large holes among well-crystallized areas (when the annealing process has been conducted too far), the optical mass appears to increase more rapidly, roughly proportionally to the hole area. This could be interpreted as a decrease of the effective mean number of conduction electrons rather than as a real increase of their optical mass.

The present experimental value of the optical mass has to be compared with the other values deduced from different experiments.

(a) Thick (opaque) annealed layers, the reflection measurements being performed: At the film-substrate interface, we obtain

$$m_0 = 0.98 \text{ (Ref. 9)} , \quad m_0 = 0.96 \text{ (Ref. 12)} ;$$

at the free surface,

$$m_0 = 1.03 \text{ (Ref. 12)} , \quad m_0 = 1.06 \text{ (Ref. 28)} .$$

(b) Electropolished bulk samples:

$$m_0 = 1.04 \text{ (Ref. 4)} , \quad m_0 = 1.06 \text{ (Ref. 6)} .$$

(c) Thick nonannealed layers probably with low-filling coefficient:

$$m_0 = 1.68 \text{ (Ref. 29)} , \quad m_0 = 1.45 \text{ (Ref. 30)} .$$

All these values are higher than 0.94. The last two values can be rejected because of the poor quality of the samples; Motulevich and Shubin,[28] who used the same technique as Padalka and Shklyarevskii[29] but annealed their films, obtained a drastic decrease of m_0. Most of the other values are close to 1.05. However, Hodgson[12] found a surprising discrepancy between the values of m_0 measured at the two surfaces of the same opaque film; the value corresponding to the film-substrate interface was very close to the present value of 0.94. Hodgson attributed the discrepancy to the existence of holes in the skin layer of thick films or polished bulk samples. We have indeed observed that the free sur-

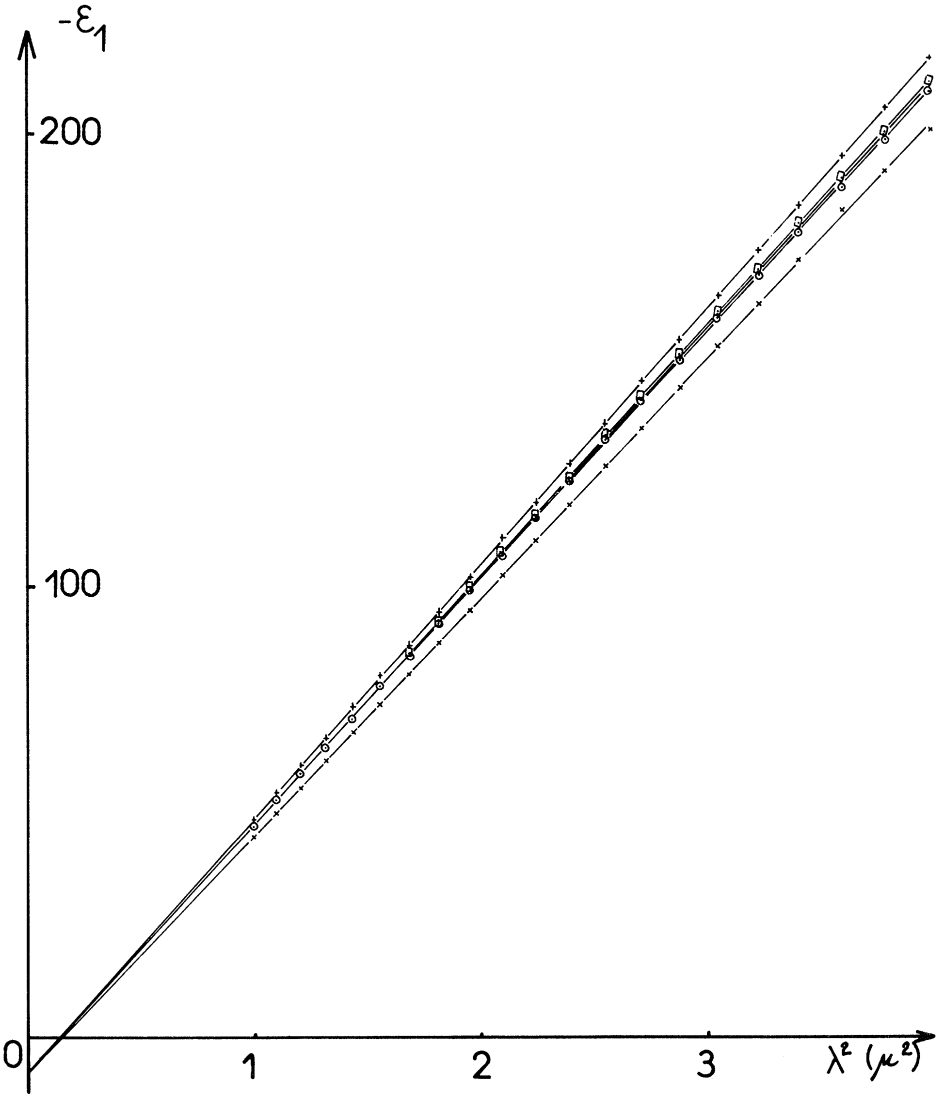

FIG. 4. $-\epsilon_1$ versus λ^2 in the infrared for different films.

face of thick films ($d > 1000$ Å) is much rougher than the free surface of very thin films which reproduces, as indicated above, the surface of the substrate. Since only reflection measurements can be made on opaque samples, the influence of the surface quality is very important. On the contrary, the value of m_0 in our experiments is determined mainly by the transmittance value which is more likely to be correct.

The optical mass m_0 can be expressed as[31]

$$N/m_0 = (1/12\pi^3\hbar)\int_{S_F}\vec{v}\cdot d\vec{s}\ ,$$

$\vec{v}$ being the Fermi velocity of the conduction electrons, and the integration being carried out over the Fermi surface. m_0 is therefore related to a mean value of the electron velocity on the Fermi surface which in Au is not very different from a sphere. The experimental value of m_0 could be influenced by the fiber structure of the films (the compact crystalline planes being parallel to the substrate surface) which would favor the contribution of one part of the Fermi surface. m_0 could also be modified by the strains which exist in the films and change slightly the crystallographic parameter; this would modify the Fermi surface. However, the parameter changes are not sufficient to account for the observed low value of m_0.[32]

It must be noticed that the thermal mass in Au is 1.09,[33] thus, in any case, higher than the optical mass. This discrepancy might be explained[31] by the anisotropy of the Fermi surface. But interactions between electrons or between electrons and phonons have also to be taken into account. The phonon dressing certainly increases the thermal mass,[34] but is not effective at optical frequencies. On the other hand, the influence of electron-electron interaction on the optical mass, when modified by the presence of the periodic lattice potential, is not yet well understood.[35,36]

The polarization term $\mathcal{P}$ which appears in the Drude formula is approximately equal to 7 for all the films. However, for films where a supplementary absorption exists, $\mathcal{P}$ is slightly greater. This term includes the polarization $\epsilon_1^{(i)}(\omega)$ due to interband transitions:

$$\epsilon_1^{(i)}(\omega) = \frac{2}{\pi}\int_{\omega_0}^{\infty}\frac{\omega'\epsilon_2^{(i)}(\omega')}{(\omega')^2-\omega^2}\,d\omega'\ .$$

It has been shown in the case of alkali metals[37] that $\epsilon_1^{(i)}(\omega)$ is indeed a constant at energies smaller than the energy onset $\hbar\omega_0$. This can be seen very simply because when $\hbar\omega \ll \hbar\omega_0$, we obtain

$$\epsilon_1^{(i)}(\omega) \simeq \frac{2}{\pi}\left(\int_{\omega_0}^{\infty}\frac{\epsilon_2^{(i)}(\omega')}{\omega'}\,d\omega' + \omega^2\int_{\omega_0}^{\infty}\frac{\epsilon_2^{(i)}(\omega')}{(\omega')^3}\,d\omega'\right)\ .$$

The first term is a constant. The second one varies as ω^2, but is always very small and can be neglected. Anyhow, it cannot have an influence on the determination of the optical mass.

B. Relaxation Time

According to the Drude formula, ϵ_2/λ must vary linearly with λ^2. The slope, equal to $(\lambda_0^2\lambda_\tau)^{-1}$, yields a value of the optical relaxation time when the optical mass is known. Figure 5 shows the experimental results obtained for a few typical films of different structures. The variation of ϵ_2/λ versus λ^2 is linear, indeed. But the experimental straight lines do not pass through the origin as predicted by the Drude theory, even for the best films. The observed behavior of ϵ_2/λ is

$$\epsilon_2/\lambda = A\lambda^2 + B\ .$$

In all cases, the B term is well above the experimental uncertainties. It is approximately equal to $0.2\ \mu^{-1}$ for the best films (the line 1 corresponds to the 158-Å-thick film of Fig. 1), thus almost negligible. It increases for films with a greater amount of structural defects and usually reaches 1 or 2 μ^{-1} for nonannealed films. ($B = 1.5\ \mu^{-1}$ for the 172-Å-thick film to which the line 3 corresponds.)

Such a constant term in ϵ_2/λ cannot be found in the theory of the anomalous skin effect in thin films. Neither can it be explained by the existence of an absorption band located at smaller energies, which is very unlikely to occur and would rather give a contribution to ϵ_2/λ proportional to λ.

As a matter of fact, the Drude theory has been established under the assumption that the interaction of light and conduction electrons was a pure transport phenomenon. However, in the presence of an electromagnetic field of frequency ω, the interaction process involves both the absorption of a quantum of electromagnetic energy $\hbar\omega$ by the electrons and the scattering of the electrons by the lattice vibrations (and impurities). The Drude theory is certainly valid when $\hbar\omega$ is small enough ($\hbar\omega \ll kT$). But at higher frequencies, the situation may be different. It has been first pointed out by Holstein[38] that at sufficiently low temperature ($T \ll \Theta_D$) the optical absorption must then differ from the classical Drude absorption. Indeed, the former has still a finite value since, as $\hbar\omega \gg k\Theta_D$, the emission of the whole phonon spectrum remains possible, while the latter tends to zero because it corresponds to a pure scattering process in which both phonon absorption and emission are limited ($kT \ll k\Theta_D$). Their ratio must be of the order of Θ_D/T. But, at high temperature ($T > \Theta_D$), when phonon absorption and emission happen more or less equally, there must be no difference between the two processes.[39] It has been shown in both cases of scattering by phonons[40] and by static impurities[41] that a quantum-

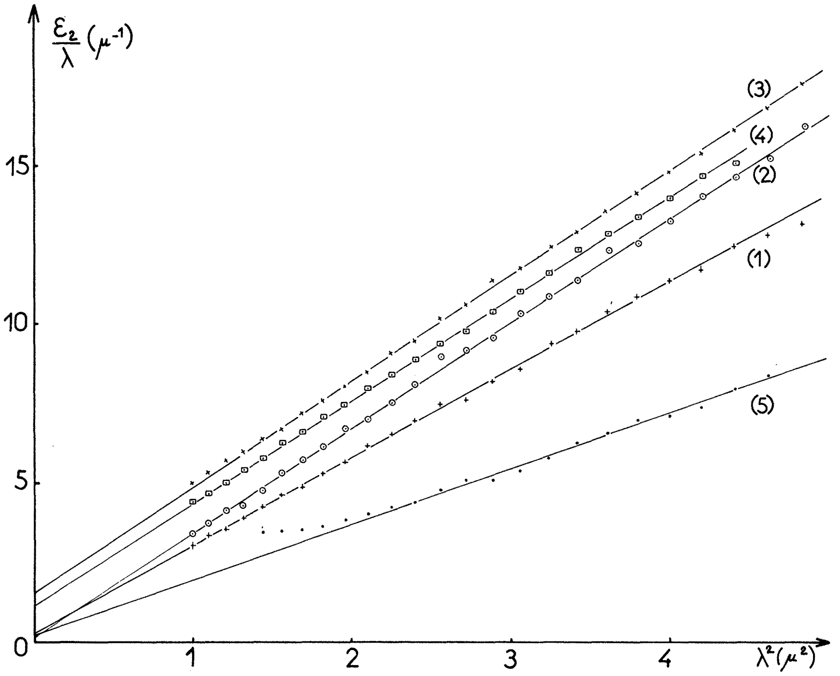

FIG. 5. ϵ_2/λ versus λ^2 in the infrared for films of different structures. Well crystallized films: (1) $d = 158$ Å and (2) $d = 146$ Å, nonannealed films: (3) $d = 172$ Å and (4) $d = 210$ Å, film deposited at high temperature and annealed, presenting anomalous absorption between 1 and 2 eV: (5) $d = 196$ Å.

mechanical treatment of the optical absorption at high frequencies ($\hbar\omega \gg kT$) gives approximately the same result as the classical Drude theory for metals, provided that the electromagnetic energy is smaller than the energy of the conduction electrons, $\hbar\omega < E_F$.

In the present experiments at room temperature, the energy varies from 0.5 to 1.5 eV. It is, of course, much greater than $kT = 0.025$ eV but still smaller than the Fermi energy of Au, $E_F = 5.5$ eV. Therefore, a way of interpreting the experimental results is to consider the Drude theory as valid and to define an effective relaxation time $\tau_{\rm eff}$ by the relation

$$(\epsilon_2/\lambda)_{\rm exp} = (\lambda^2/\lambda_0^2)(1/2\pi c\tau_{\rm eff}) \quad . \qquad (3)$$

$\tau_{\rm eff}$ is no longer a constant but depends on the frequency as

$$1/\tau_{\rm eff} = 1/\tau_0 + b\omega^2 \quad .$$

τ_0 is the value of the optical relaxation time at zero frequency, and b a constant characterizing the dependence of $\tau_{\rm eff}$ on frequency.

Figure 6 represents the variation of $(\tau_{\rm eff})^{-1}$ as a function of $(\hbar\omega)^2$ for the films corresponding to the lines 1 and 3 in Fig. 5. Both τ_0 and b are found to vary with the film structure. A similar dependence on frequency of the optical relaxation time was also deduced from measurements on thick evaporated layers of Au[12] and on alkali metals.[37,42] In the same way, Bennet and Bennet[10] could only reconcile the experimental reflectivity of opaque evaporated Au films at wavelengths smaller than 3 μ with the theoretical Drude reflectivity by assuming that the relaxation time then became frequency dependent.

Such a phenomenon has been interpreted as due to electron-electron interaction. It was shown by a many-body perturbation theory[43] that the effect of electron correlation on the optical properties of metals should be negligible for a free-electron gas, but should become important when band-structure effects are present. A quantitative estimation of the electron-electron interaction was given by Gurzhi[44] in the framework of the Fermi-liquid theory of Landau.[45–47] He found that the total relaxation time $\tau_{\rm eff}$ of the conduction electrons must include a term $\tau_{\rm ee}$ which accounts for the electron-electron scattering and is given by

$$\frac{1}{\tau_{\rm ee}} = \frac{1}{\tau^0_{\rm ee}}\left[1 + \left(\frac{\hbar\omega}{2\pi kT}\right)^2\right] \quad .$$

The value at zero frequency $\tau^0_{\rm ee}$ is related to the plasma frequency ω_0 ($\omega_0 = 2\pi c/\lambda_0$) and varies as T^2 [48]:

$$(\tau^0_{\rm ee})^{-1} = \omega_0(kT/\hbar\omega_0)^2 \quad .$$

Such a theoretical variation of $(\tau_{\rm ee})^{-1}$ with $\hbar\omega$ is consistent with the experimental results. It is found that

$$\tau^0_{\rm ee} = 5.4 \times 10^{-12} \text{ sec for film 1 (158 Å)} \quad ,$$

$$\tau^0_{\rm ee} = 1.1 \times 10^{-12} \text{ sec for film 3 (172 Å)} \quad .$$

The first value, which is typical of well-crystallized films, is very close to the one determined by Hodg-

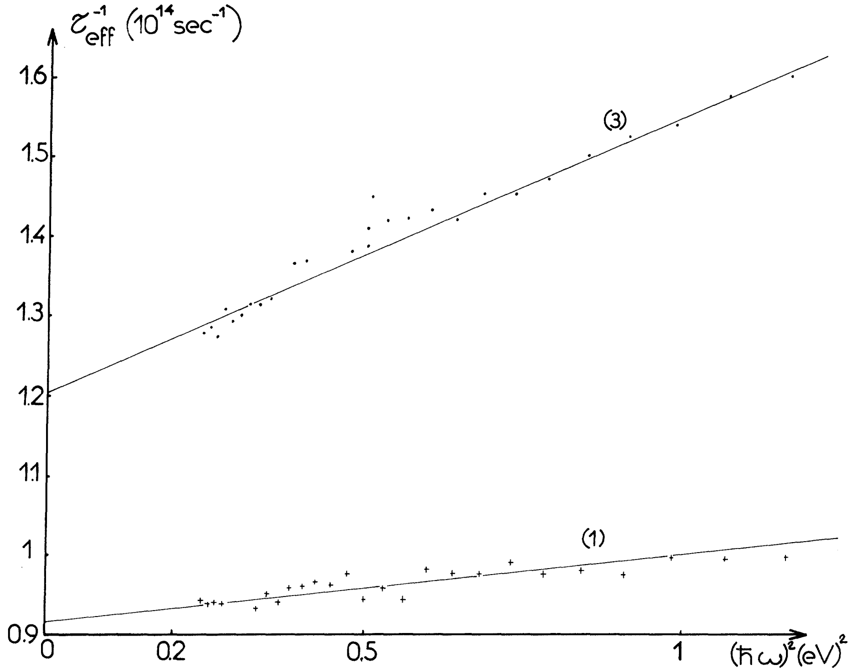

FIG. 6. Reciprocal effective relaxation time $(\tau_{eff})^{-1}$ as defined by relation (3) as a function of $(\hbar\omega)^2$ for films 1 and 3 of Fig. 5.

son.[12] The second value, which corresponds to a nonannealed film, is to be compared with the values obtained on thick films of poor quality by Padalka and Shklyarevskii,[29] $\tau_{ee}^0 = 0.4\times10^{-12}$ sec, and by Dold and Mecke,[30] $\tau_{ee}^0 = 0.5\times10^{-12}$ sec.

The theoretical value of τ_{ee}^0, which would be close to 1×10^{-11} sec for all the films (λ_0 being rather independent of the film structure), would be in any case greater than the experimental ones. Moreover, the variation of the experimental electron-electron interaction relaxation times at zero frequency with the film structure is very difficult to understand in the framework of Gurzhi's theory.

Other interpretations have also been suggested in order to account for the variations of the optical relaxation time with frequency, for example, electron-phonon interaction involving virtual interband transitions,[49] and electron-ion interaction due to the scattering of the electrons by randomly distributed fluctuations of ionic charges.[50] The agreement of these models with the experimental results was shown to be satisfactory in the case of alkali metals[37] and Al,[50] respectively. These theories are interesting attempts at taking into account the influence of various interactions on the optical properties due to the conduction electrons. However, it is still difficult to conclude. At the present time, the electron-electron interaction theory of Gurzhi[44] seems to be the most elaborate one, and to provide the best agreement with our experimental results.

If the variation of τ_{eff} with frequency may be rather large,

for film 1: $\tau_0 = 1.08\times10^{-14}$ sec,

$(\tau_{eff})_{1\,\mathrm{eV}} = 1.00\times10^{-14}$ sec;

for film 3: $\tau_0 = 0.83\times10^{-14}$ sec,

$(\tau_{eff})_{1\,\mathrm{eV}} = 0.64\times10^{-14}$ sec,

it must be noticed that the electron-electron interaction relaxation time at zero frequency τ_{ee}^0 is very long (a few 10^{-12} sec) compared to the total relaxation time at zero frequency τ_0(10^{-14} sec). Thus, τ_{ee}^0 will be neglected in the following discussion of the variation of τ_0 with the film structure.

τ_0, as determined from the slope of the experimental straight lines representing the variations of ϵ_2/λ with λ^2, is different from film to film, decreasing strongly when the film structure deteriorates. Unlike the optical mass, the relaxation time is found to be very sensitive to the presence in the film of structural defects which can be either volume defects (grain boundaries, imperfections and impurities inside the grains) or surface defects. The theory of the anomalous skin effect in thin films allows separation of the surface effect and determination of the relaxation time τ_B corresponding to the scattering of the electrons by phonons and volume defects only. τ_B must be deduced from the experimental value of τ_0 by means of the relation (2) which reads now

$$\frac{1}{\tau_B} = \frac{1}{\tau_0} - \frac{6\pi}{8}\, v\, \frac{1}{\lambda_0}$$

$$\times \frac{\cosh^2(2\pi d/\lambda_0)}{\sinh(2\pi d/\lambda_0)\cosh(2\pi d/\lambda_0)+2\pi d/\lambda_0}(1-p) \quad .$$

This relation involves the scattering parameter p characterizing the film surfaces, which is not known *a priori*. Therefore, the analysis of the optical properties cannot yield more than a relation between the "bulk" relaxation time τ_B and the surface scattering parameter p. τ_B and p cannot be determined both at the same time; a plausible value of one of these parameters has to be assumed in order to determine the other one. We shall give here the values of τ_B corresponding to the two limiting cases $p=1$ and $p=0$ for the films 1 and 3 of Fig. 5, together with the corresponding values of the "bulk" mean free path $l=v\times\tau_B$:

film 1: $d=158$ Å,

$p=1$, $\tau_B=1.08\times10^{-14}$ sec, $l=156$ Å;

$p=0$, $\tau_B=1.83\times10^{-14}$ sec, $l=264$ Å;

film 3: $d=172$ Å,

$p=1$, $\tau_B=0.83\times10^{-14}$ sec, $l=118$ Å;

$p=0$, $\tau_B=1.17\times10^{-14}$ sec, $l=166$ Å.

For each film the measured value of τ_0 depends on both volume and surface scattering. If a specular surface scattering is assumed, then $\tau_B=\tau_0$. If on the contrary, a diffuse surface scattering is assumed, τ_B must have a greater value. It will be shown later that the scattering parameter p is probably close to 1 in most of the investigated films. The decrease of τ_B for the same value of p from film 1 to film 3 must be attributed to the greater amount of structural defects in film 3, as corroborated by electron-microscope studies and electrical-resistivity measurements.

It seemed interesting to compare the values of the relaxation time deduced from optical and dc-resistivity measurements. The zero-frequency value of the "optical" relaxation time τ_0 must be equal to the electrical relaxation time τ_e. In other words, if an "optical" resistivity ρ_0 is determined from the optical microscopic parameters of the conduction electrons by

$$\rho_0=m_0/Ne^2\tau_0 \quad ,$$

the optical and electrical resistivities must be equal. However, this is found experimentally not to be the case. We find

for film 1:

$d=158$ Å, $\rho_e=2.97$ $\mu\Omega$cm, $\rho_0=5.28$ $\mu\Omega$cm;

for film 3:

$d=172$ Å, $\rho_e=4.40$ $\mu\Omega$cm, $\rho_0=7.32$ $\mu\Omega$cm.

In any case, the ratio ρ_0/ρ_e is greater than 1 ($\tau_0<\tau_e$). It seems to be greater (~1.7) for the best films, and to decrease (down to 1.4 or 1.5) when the film structure is worse.

As a matter of fact, in such a comparison, size effects have to be taken into account. As the optical resistivity must be corrected for the anomalous skin effect, so the electrical resistivity must be corrected for size effects since the film thickness is of the order of magnitude of the electron mean free path. According to Fuchs[51] we have

$$\frac{\rho_\infty}{\rho_e}=F\left(p,\frac{d}{l}\right) \quad ,$$

ρ_∞ being the resistivity of the bulk material containing the same amount of volume imperfections as the film of thickness d and resitivity ρ_e; ρ_∞ is related to l by $\rho_\infty=(mv/Ne^2)(1/l)$. As in the case of the optical measurements, a measurement of ρ_e alone for a given film does not allow a determination of both l (or ρ_∞) and p. Only a relation between l and p can be obtained, which is equivalent to the one deduced from optical measurements. From these two relations, it would seem possible to determine both l and p. Figure 7 shows a graphical representation of both relations for film 1 (158 Å). No common solution can be found for any value of p comprised between 0 and 1. The optical value of l is lower than its electrical value for any value of p, their ratio being even smaller when p decreases. (The earlier comparison between ρ_0 and ρ_e corresponded to $p=1$.)

It must be noticed that a minimum value of p can be deduced for each film from its dc electrical resistivity. The mean free path in the film cannot be greater than the value corresponding to phonon scattering only (i.e., in the absence of any impurity scattering) which is equal to 380 Å for Au at room temperature. As l increases for decreasing values of p, this yields a minimum value for p. In the case of film 1, for example, $p\geqslant 0.56$. For most of the films under investigation, p was found to be closer to 1 than to 0, which indicates that the reflection of the electrons on the film surfaces is mostly specular.

Although Greene[52] suggested that the boundary conditions for the electrons at the surfaces depend on the considered transport phenomenon, it seems that, at least for metals, the scattering parameter p must have the same value in optical and electrical experiments. The observed discrepancy definitely comes from a difference between the relaxation times. Such an effect (even a larger one) has already been observed in various cases: bulk electropolished noble metals,[3] Al,[53] alkali metals,[37] even $\mathrm{ReO_3}$[54] (which has a metallic behavior). One may argue that because of surface roughness, the measured value of the film reflectance may be mod-

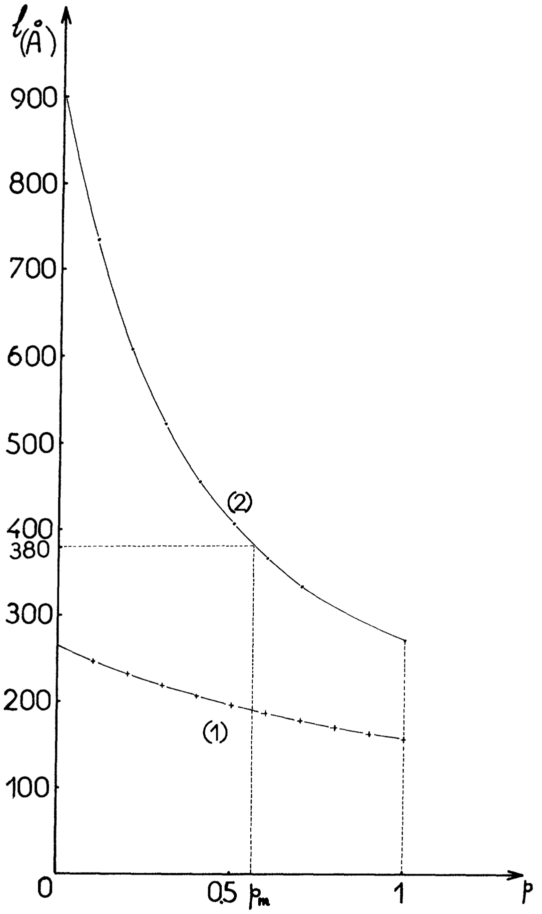

FIG. 7. Mean free path l of the conduction electrons as a function of their scattering parameter p on the film surfaces from the optical (curve 1) and electrical (curve 2) measurements for the well-crystallized film 1 of Fig. 5 (d = 158 Å).

ified by the light scattering and also by the presence of additional fields due to induced extra currents on the surface[55]; therefore, it would be no longer representative of the bulk properties. However, Hunderi and Beaglehole[55] in their experiments on the interaction of light with rough surfaces showed that, as the light scattering decreases for increasing wavelength and as extra fields add coherently to the specular beam, the total decrease of the reflectance due to surface roughness is very small in the infrared. Moreover, as indicated earlier, the surface of the Au films under investigation proved to be very smooth indeed. We have computed in the case of film 1, for $\lambda > 1\ \mu$, the values of the reflectance which would have given a value of τ_0 equal to the value τ_e deduced from the dc electrical resistivity of this film. These values would be 1.5% higher than the measured ones; this difference is certainly much greater than a hypothetic effect of surface roughness.

The discrepancy between the optical and electrical results can tentatively be interpreted as due to an anisotropy of the relaxation time. It can be shown[56] that

$$\rho_0/\rho_e = \langle\tau\rangle_F \langle 1/\tau\rangle_F ,$$

$\langle\tau\rangle_F$ and $\langle 1/\tau\rangle_F$ being mean values of τ and $1/\tau$ over the Fermi surface, respectively. If the distribution of τ over the Fermi surface is not isotropic, this ratio must be greater than 1. Ziman[57] suggested that in noble metals the electrons on the belly and on the necks of the Fermi surface would have indeed different relaxation times, and that this anisotropy would depend on the type of scattering. This statement was confirmed experimentally, for example on Cu by Rayne[58,59] and on Cu and Ag by Dugdale and Basinski[60]; the latter interpreted the observed deviations from Matthiessen's rule in terms of a two-band model for the belly and neck conduction electrons. However, at high temperature, the relaxation time corresponding to phonon scattering must be almost isotropic. There remains a possible anisotropy of the relaxation time corresponding to scattering by imperfections and impurities. This might explain the variations of the ratio of the optical and electrical resistivities with the film structure, i.e., with the nature and amount of defects. Since the scattering mechanism by grain boundaries, which must be predominant, is not yet well known, it is difficult to conclude.

Therefore, from all these observations, it must be emphasized that, although the optical properties of gold due to conduction electrons follow roughly the classical Drude theory, there still remain discrepancies between the experimental results and the predictions of simple theories based on the classical model of independent quasifree electrons. A thorough consideration of interactions between electrons, electrons and phonons, electrons and the lattice, etc., would be necessary in order to interpret these discrepancies. At the same time, similar experiments should be performed at lower energies and lower temperatures.

IV. INTERBAND TRANSITIONS

The optical properties of Au due to interband transitions will be discussed by considering the absorptive part $\epsilon_2(\omega)$ of the dielectric constant, which can be calculated in the random-phase approximation[61] from the electronic energy-band computations. (This has been done indeed in the case of Cu by Mueller and Phillips[62] and by Dresselhaus.[63]) After subtracting from the experimental $\epsilon_2(\omega)$ the contribution due to the conduction electrons as deduced from the infrared measurements, $\epsilon_2^{(i)}(\omega)$ is obtained. For well-crystallized films, the results are reproducible within a few percent. Figure 8 shows the mean values of $\epsilon_2^{(i)}(\omega)$ for a number of films of different thicknesses, together with the data of Hodgson[12] on thick evaporated layers and Cooper *et al.*[4] on electropolished bulk samples. The agreement with Hodgson's results is excellent. Recently, Pells and Shiga[13] obtained from mechanically bulk samples, which were carefully annealed under high vacuum at high temperature, higher values of ϵ_2 in the interband-transition region; however, their ϵ_2 is also surprisingly large below the absorption edge between 1 and 2 eV. In our first experiments on 300–400-Å-thick films, higher values of ϵ_2 were obtained between 3 and 6 eV, but this was found to be due to errors in the determination of n and k because of the inaccuracy of the method itself (cf. Sec. II B).

A problem still remains in the evaluation of the contribution due to the conduction electrons when the observed behavior of ϵ_2 in the infrared is $\epsilon_2 = \epsilon_2^{(c)} = A\lambda^3 + B\lambda$. It seems, however, according to the discussion of III B, that the unexpected term which varies linearly with λ, must be taken into account and subtracted from ϵ_2 in order to obtain the correct values of $\epsilon_2^{(i)}$. When B is large, this decreases slightly the values of $\epsilon_2^{(i)}(\omega)$ with respect to the values indicated on Fig. 8. Such a discrepancy is rather puzzling since the total dielectric constant $\epsilon_2(\omega)$ has very similar values in the interband-transition region for films of different structures, and, as indicated earlier (Sec. II C), it is found to decrease only for films with very small and misoriented crystallites.

Only a few energy-band computations have been performed in the case of Au (the work of Segall[64] at a few symmetry points of the Brillouin zone, and the work of Jacobs[65] and Ballinger and Marshall[66] in more detail). However, the band structure of

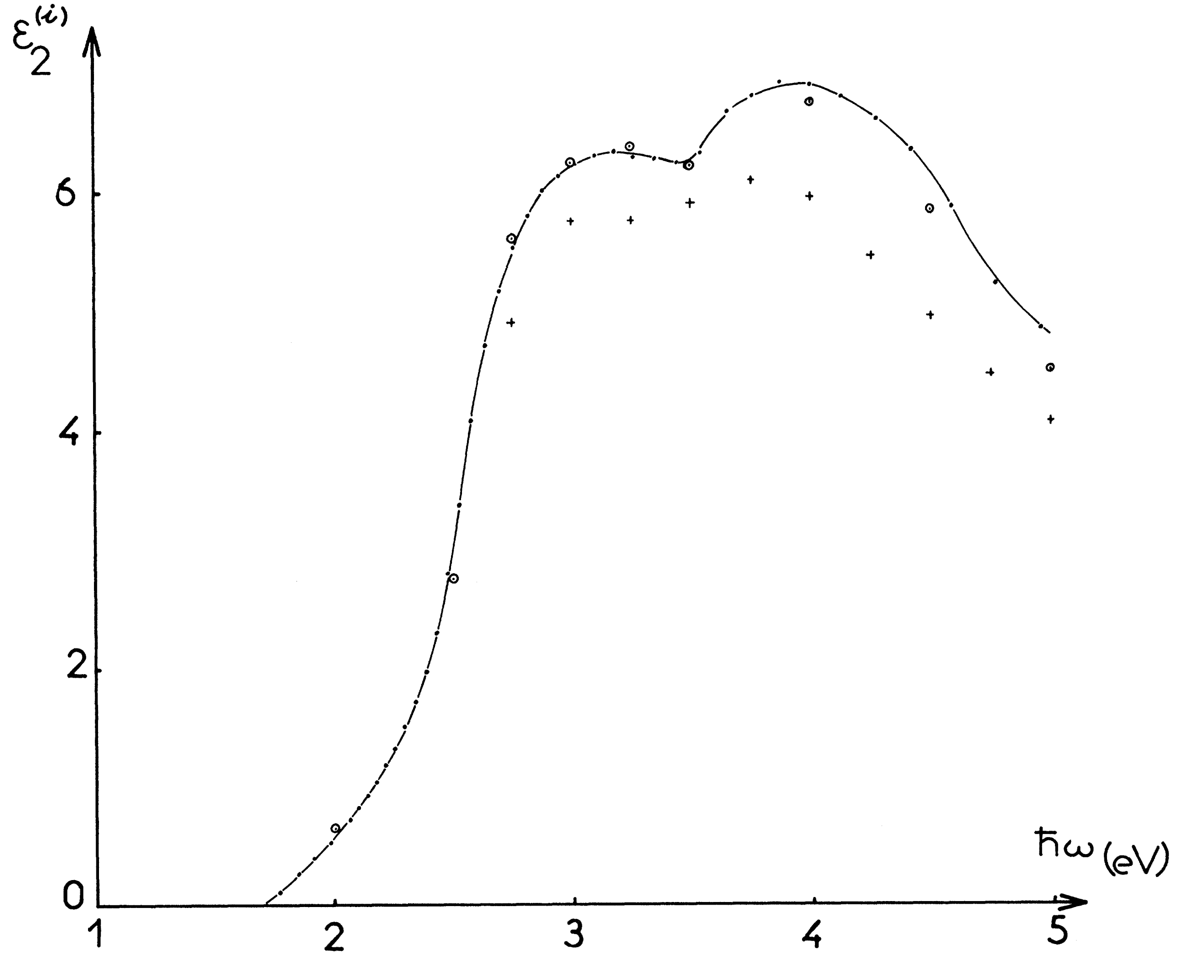

FIG. 8. $\epsilon_2^{(i)}$ (after subtracting the contribution due to the conduction electrons) versus energy $\hbar\omega$: (•) present experiment, (○) Hodgson (Ref. 12), (+) Cooper *et al.* (Ref. 4).

Au must be very similar to that of Cu which is now rather well known. The optical properties are dominated by the presence of a flat narrow *d* band located at only a few eV below the Fermi level. The absorption edge corresponds to transitions from the top of this *d* band to the conduction band at the Fermi level in the vicinity of *L*. At higher energies, various transitions can contribute to the optical absorption and it is very difficult indeed to decide what type of transition is responsible for the second maximum in $\epsilon_2^{(i)}(\omega)$. The situation is quite clear now in the case of Cu, particularly since the significant piezoreflectance experiments of Gerhardt.[8] The main transitions which take place as the energy increases are from the top of the *d* band to the Fermi level at *X*, from the conduction band at the Fermi level to the upper conduction band at *L* (this transition seems to have a much greater oscillator strength), from the bottom of the *d* band to the Fermi level in the vicinity of *L*. Recently, Pells and Shiga[13] observed by varying the temperature a splitting of the ϵ_2 curve for Cu into three distinct contributions which would correspond to these various transitions. The interpretation of similar data for Au is not as clear as for Cu. In Au, the energies of such transitions must be even closer to each other and nothing very definite can be said.

The present experiments, which give only the values of $\epsilon_2^{(i)}$ as a function of frequency at room temperature, do not bring any new argument about the nature and exact location of the involved transitions. However, the accuracy of the results allows a very precise and detailed analysis of the $\epsilon_2^{(i)}(\omega)$ spectrum. Moreover, the possibility of modifying the crystallographic structure of the samples may give additional information about the absorption processes.

It appeared interesting to investigate not only the variations of $\epsilon_2^{(i)}(\omega)$, but also those of the quantity

$$J(\omega) = (\hbar\omega)^2\epsilon_2^{(i)}(\omega),$$

which in the one-electron approximation is proportional to the associated density of states for the transitions contributing to $\epsilon_2^{(i)}(\omega)$:

$$D(\omega) = \int_{\mathrm{BZ}} [2/(2\pi)^3]\delta[\hbar\omega_{if}(k) - \hbar\omega]\, d_3k,$$

with $\hbar\omega_{if} = \hbar\omega_f - \hbar\omega_i$, i and f denoting the initial and the final energy band, respectively. This is, of course, valid only if the momentum matrix elements can be assumed to be constant in the considered *k* region. Figure 9 shows $J(\omega)$ for Au as a function of energy. Because of the simultaneous contribution of various transitions, the analysis of such a curve is difficult. However, four different parts can clearly be distinguished.

(a) From 2.5 to 3.5 eV, a parabolic part corresponds to the absorption edge and to the first maximum in $\epsilon_2^{(i)}(\omega)$. Figure 10 shows the straight lines obtained when plotting J^2 as a function of energy in this energy range. An extrapolation down to $J = 0$ gives the value of the onset of interband transitions $\hbar\omega_0$. Therefore, $J(\omega)$ is strictly parabolic over a wide energy range (1 eV) above the onset:

$$J(\omega) = \alpha(\hbar\omega - \hbar\omega_0)^{1/2} .$$

This behavior was observed for all films regardless of their structure, even for films of type (3) (cf. Sec. II C) for which $\epsilon_2^{(i)}$ has much lower values (as shown by the line 3 on Fig. 10). The onset energy $\hbar\omega_0$, which can be determined very accurately in this way, was found to be the same for all the films under investigation:

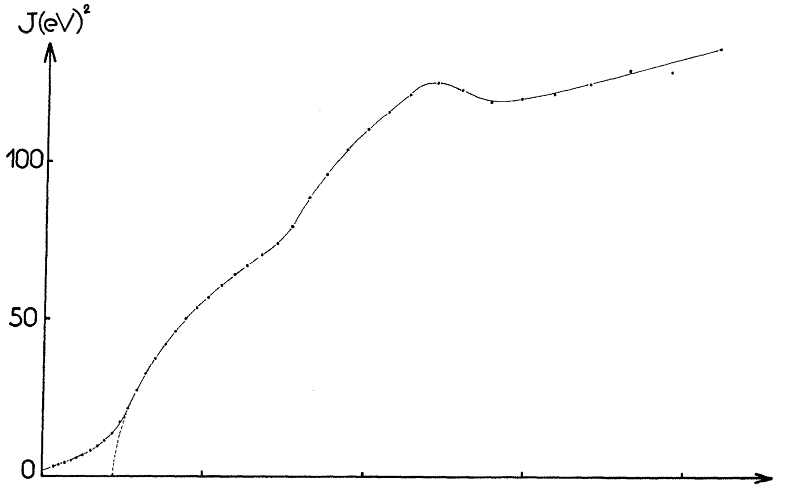

FIG. 9. $J(\omega) = (\hbar\omega)^2\epsilon_2^{(i)}$ as a function of energy $\hbar\omega$ for Au films.

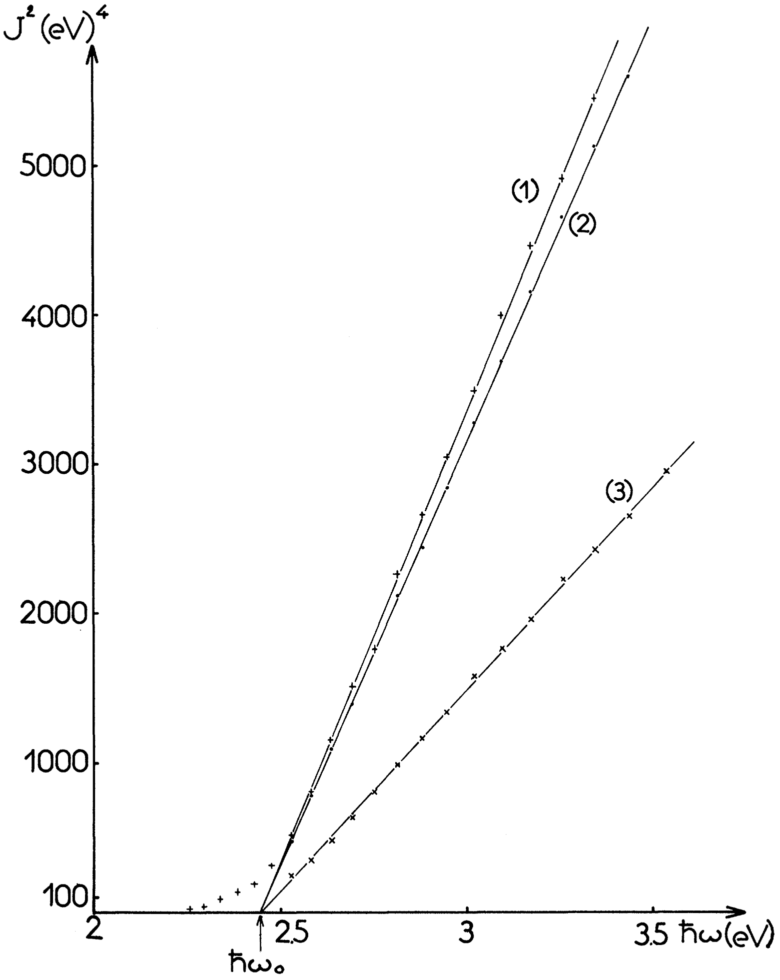

FIG. 10. J^2 as a function of energy $\hbar\omega$ for films of different structures: (1) well-crystallized film, (2) less annealed films, (3) film with very small and misoriented crystallites.

$$\hbar\omega_0 = 2.45 \pm 0.01 \text{ eV} \ .$$

Only the slope of the experimental lines varies from film to film according to its structure. For rather well-crystallized films, the slight variation (a few percent) is correlated to the existence of a $B\lambda$ term in the evaluation of the conduction-electron contribution. For nonannealed films, the difference in α may be important as shown in Fig. 10.

Therefore, neither the nature of the optical absorption near the edge, nor the energy of the onset of interband transitions are modified by the presence of a great amount of structural defects and the lack of long-range order. Only the intensity of the absorption decreases, which may be interpreted as a decrease of the oscillator strength of the transitions. Moreover, it is apparent from the shape of $J(\omega)$ that the leading transitions which contribute to the optical absorption between 2.5 and 3.5 eV are the same as those which take place at the absorption edge; in other words, there is no significant contribution of other transitions up to 3.5 eV.

It must be noticed that the absorption edge in the $\epsilon_2^{(i)}$ curve of Au is not very steep, and that it is therefore very difficult to determine the exact value of $\hbar\omega_0$ when looking at $\epsilon_2^{(i)}$ only. (The value deduced by Cooper *et al.*[4] is, for example, too small, $\hbar\omega_0 = 2.35$ eV.) From this point of view, the difference between the three noble metals is striking; the absorption edge becomes steeper from Au to Ag, then to Cu. In the case of Cu, the theoretical computation of $\epsilon_2^{(i)}$ by Mueller and Phillips,[62] using the energy-band structure of Burdick[67] together with the combined interpolation scheme of Mueller,[68] was not able to reproduce the shape of the experimental absorption edge; the theoretical increase of $\epsilon_2^{(i)}(\omega)$ is definitely slower and lower than the experimental one. It was suggested[62,69] that this discrepancy was due to an additional enhancement of the oscillator strengths by the attractive interaction of an exitonic type (like, for example, the model proposed by Mahan[70]) between the excited electron and hole. However, it was recently shown[71] that the effect of electron interaction on the interband optical properties in simple metals would not exceed 10 to 20%. On the other hand, Dresselhaus,[63] by a phenomenological approach to the energy-band structure, obtained a better agreement between the theoretical and the experimental values of $\epsilon_2^{(i)}(\omega)$ in the region of the absorption edge. The concerned interband transitions take place, as indicated above, between the top of the *d* band and the Fermi level. They are not associated with a critical point of the density of states, and are not localized in *k* space; the *k* conservation rule is not very stringent and one can speak of "nondirect" transitions.[72] The steep rise of $\epsilon_2^{(i)}(\omega)$ is related to the fact that, because of the flatness of the *d* band, the Fermi level almost coincides with one of the constant $\hbar\omega_{if}$ curves.[73] Therefore, one can infer that the shape of the absorption edge mostly depends on the curvature of the upper *d* band, which is connected with the spin-orbit coupling. This coupling decreases from Au to Cu,[74] which means that the top of the *d* band must be quite flat for Cu and more curved for Au, in agreement with the experimental results.

(b) Below 2.5 eV, an exponential part appears as an absorption tail below the onset of interband transitions. It can be observed down to 1.5 eV. This tail is strictly exponential as shown by Fig. 11, does exist for all the films, and is exactly identical regardless of the film structure. When a supplementary absorption takes place between 1 and 2 eV, its contribution to ϵ_2 is only additive and the tail is not modified.

An absorption tail may generally be correlated to the existence of phonon-aided indirect interband transitions, which are possible at energies lower than the onset of direct transitions since the wave vector is not conserved. However, the tail observed here extends too far for such an interpretation. It cannot be related either to defects or some kind of lack of order since it is insensitive to the film structure. It appears rather to be an intrinsic property connected with the direct interband transitions. The most probable interpretation is that it is due to a lifetime broadening of the absorption edge of Auger type, i.e., due to the finite lifetime of the hole created by the excitation of a *d* electron at the top of the narrow flat *d* band.[75]

Many observations have been made recently about the excitation of surface plasmons by light in metals because of surface roughness. In Au, the surface plasmon energy is about 2.7 eV. Hunderi and Beaglehole[55] in their measurements of the reflectivity of rough gold surfaces indeed observed an additional decrease of the reflectivity in this region, peaking at 2.40 eV. As already emphasized, the surface of the films under investigation here was very flat and smooth, and no similar effect was observed. However, in one case only (a 184-Å-thick film) we noticed an unexpected behavior of $\epsilon_2^{(i)}$ around 2.2–2.3 eV, which appeared as a supplementary absorption. This film had been measured optically before and after annealing, and the anomaly observed only after annealing; by comparing the x-ray reflection-interference fringes, it was found that their contrast had drastically decreased after annealing (the values of the film thickness were the same) indicating the existence of an un-

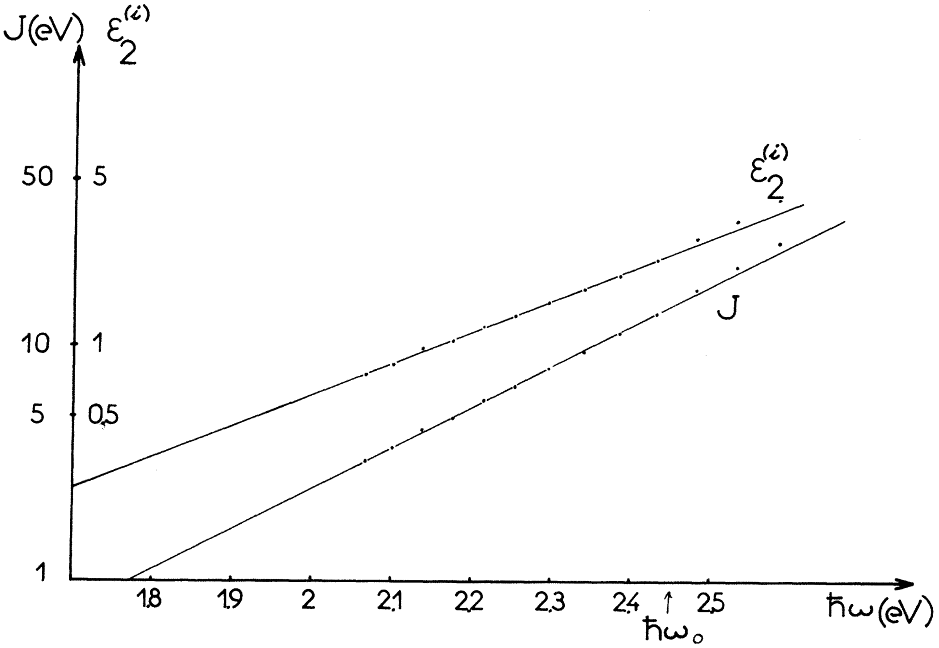

FIG. 11. Exponential behavior versus energy of the absorption tail below the absorption edge.

usual surface roughness. The observed behavior of $\epsilon_2^{(i)}$ was very similar to that mentioned by Garfinkel *et al.*[76] on thick Au films. The piezoreflectance measurements on their samples showed that an important negative structure in the $\Delta\epsilon_2$ due to strain corresponded to the faint structure in ϵ_2 at 2.30 eV. According to our conclusions, this effect can definitely be attributed to surface roughness.

(c) Two distinct parts, for $3.5 < \hbar\omega < 4.8$ eV and for $\hbar\omega > 4.8$ eV, seem to correspond to two different types of interband transitions. The part between 3.5 and 4.8 eV, with its parabolic behavior between 3.5 and 4.4 eV and its maximum at 4.4 eV, is very similar in shape to the $J(\omega)$ curve at energy higher than 4 eV observed by Gerhardt[8] in the case of Cu. Gerhardt suggested that such a shape was typical of transitions at an M_2 saddle point of the density of states when only that part of the initial energy band which is below the Fermi level can contribute to the transitions. According to this suggestion, the second maximum in $\epsilon_2^{(i)}$ would be due essentially to transitions from the conduction band below the Fermi level to the upper conduction band at L. One cannot identify the nature of the transitions of different type which take place at $\hbar\omega > 4.8$ eV. They are probably transitions from the bottom of the d band to the Fermi level in the vicinity of L. No evidence of transitions at X is found in the present data.

When the crystallites of the films are small and misoriented, the second maximum in $\epsilon_2^{(i)}$ still remains centered at 3.9 eV, but its intensity strongly decreases (more than the intensity of the first maximum) and the peak is smeared out. This observation is consistent with a blurring of the critical point due to defects.

V. SUPPLEMENTARY "ANOMALOUS" ABSORPTION

It has already been pointed out that a supplementary absorption appeared for some films between 1 and 2 eV, i.e., well below the absorption edge. This was also observed on rather poor nonannealed Au films by Shklyarevskii and Yarovaya[77]; they showed that the absorption decreases strongly after annealing the films. On the other hand, Hodgson[12] reported faint supplementary absorption bands centered at 1.4 eV in well-annealed thick Au layers, and tentatively attributed them to indirect transitions, because their intensity increased when increasing the temperature. This "anomalous" absorption seemed to us related to some kind of imperfections and impurities in the samples rather than to an intrinsic property of Au. We then looked systematically at the shape, location, and intensity of these bands in relation to the film structure. Figure 12 shows the results obtained for $\epsilon_2(\omega) - \epsilon_2^{(c)}(\omega)$ in three typical cases; also represented is the absorption edge $\epsilon_2^{(i)}$ for a well-crystallized film without supplementary absorption (curve 1). The dotted lines represent what is left in each case when the absorption edge and its tail have been subtracted from $\epsilon_2 - \epsilon_2^{(c)}$.

The supplementary absorption thus appears like an absorption band, in general, symmetric, centered at approximately 1.4 or 1.5 eV. Its intensity strongly depends on the film structure and is much greater when the film has not been annealed; it decreases after annealing. Its width is always very large (1 eV) but varies from film to film.

Such bands are not observed for well-crystallized films but do exist for all the films which contain a large amount of defects (structural imperfections or impurities). The achievement of the recrystallization process, which usually takes place during annealing, was shown to be crucial in order to prevent the appearance of an anomalous band. In particular, it was noticed that a faint band very similar to those reported by Hodgson[12] (curve 2 in Fig. 12) was observed for all the films deposited at high temperature (100 °C), although their structure seemed to be comparable to that of annealed films deposited at room temperature (which did not present such an anomaly). As a matter of fact, it was proved[78] that when a film is deposited at high temperature it becomes continuous at a greater thickness. Consequently, the individual grains are already large and cannot grow much more during the annealing. The recrystallization process, which consists of a displacement of grain boundaries across the film because of the preferential growth of some grains, is very limited. This is the reason why such films contain inside the grains a larger amount of imperfections and impurities.

From these observations, we attributed the anomalous absorption bands to the presence of some kind of point defects, like vacancies, or impurities, like gas atoms. The proportion of these defects or impurities would be 0.1 to 1% depending on the film (as calculated by considering the experimental absorption band as due to bound oscillators with strength nearly equal to 1). In such very thin polycrystalline films, the number of vacancies must be extremely low. Therefore, the only possible origin for the anomalous absorption bands seems to be impurity atoms. It must be noticed that these bands appear to be surprisingly similar to the supplementary absorption bands observed in dilute noble-metal–transition-metal alloys[79,80] and due to the existence of virtual bound states on the impurity atoms.

There is apparently no correlation between the anomalous bands and the deviation from the Drude theory (B term in ϵ_2/λ) which is observed for some

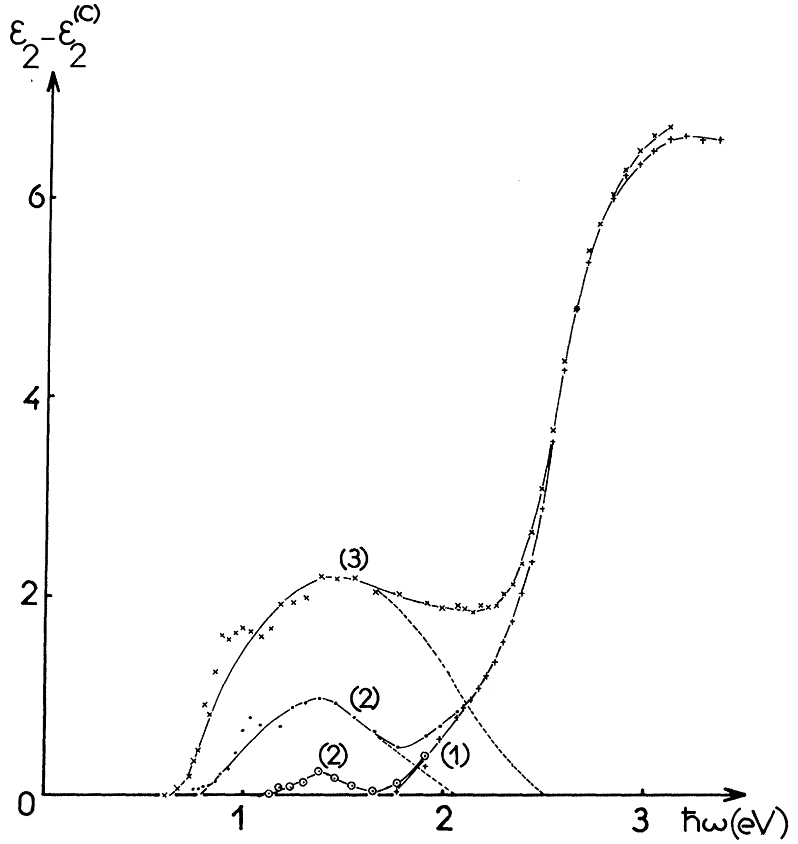

FIG. 12. $\epsilon_2-\epsilon_2^{(c)}$ (contribution due to the conduction electrons) versus energy $\hbar\omega$, showing the appearance of "anomalous" absorption bands for films of different structure: (1) well-crystallized film, (2) films deposited at high temperature and annealed, (3) nonannealed film.

films. The two phenomena seem to occur quite independently, although both are connected with the film structure and may coexist for the same film. However, in the presence of an anomalous band, the absorption due to the conduction electrons is somewhat perturbed. It is smaller than what is expected from the structure, electrical resistivity, etc., of the film; in other words, the apparent optical relaxation time is greater than the value which one would expect. Consequently, the ratio of the optical to the electrical resistivity is smaller than usual. Such a case is represented by line 5 in Fig. 5; films 1 and 5 have similar structure and electrical resistivity, almost the same thickness but film 5, deposited at 100 °C, presents a strong anomalous band.

One finds for $p=1$ that

$$\tau_0=1.08\times10^{-14}\text{ sec and }\rho_0/\rho_e=1.77\text{ for film 1,}$$

$$\tau_0=1.66\times10^{-14}\text{ sec and }\rho_0/\rho_e=1.19\text{ for film 5.}$$

On the contrary, the value of the optical mass is the same. This fact may be another argument in favor of a resonant interaction between the bound states of the impurities and the electronic states in the conduction band of the Au matrix.

In the case of very discontinuous or "island" films, the absorption due to interband transitions is drastically decreased, while a strong supplementary absorption centered at about 1.7 eV appears (Fig. 3). These anomalous bands are very similar to those reported for a variety of very thin films[81] and must be interpreted in relation with the scattering of light by the granular films; their origin is thus quite different from that of the above-mentioned bands observed on continuous films. It must be emphasized that even in the case of island films which are made of very small crystallites (100 Å) the shape of the absorption due to interband transitions remains the same, indicating that neither the electronic band structure nor the nature of the transitions are strongly modified.

VI. CONCLUSION

The use of thin semitransparent films proved to be very suitable to the investigation of the optical properties of Au. The present method not only allowed an accurate determination of both the real and imaginary parts of the dielectric constant, but the possibility of modifying the crystallographic structure of the samples also gave additional information on the absorption processes. The results obtained in the 0.5–6-eV range were interpreted in terms of intra- and interband transitions. That part of the dielectric constant due to the conduction electrons was found to present deviations from the Drude theory, even after correction for surface effects. These discrepancies were tentatively attributed to a dependence on frequency and an anisotropy of the optical relaxation time. Obviously, electron-electron interaction has to be taken into account in order to interpret the present data correctly. Although the present method is not as powerful in the interband transition range as derivative techniques, its accuracy allowed a detailed analysis of the absorption spectrum. In particular, the onset of interband transitions was determined accurately, and an Auger broadening of the edge clearly showed up. Neither the nature nor the location of the contributing interband transitions were found to be modified by important structural changes of the films. Lastly, the supplementary absorption often observed in Au below the absorption edge was definitely attributed to the presence of impurities in the samples.

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Equivalence of Expanding in Localized or Bloch States in Disordered Alloys*

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Calculations are made of the configuration-averaged density of states and the electrical conductivity of a binary disordered alloy by two quite distinct techniques, namely, by beginning with the Bloch states of a perfect crystal and making a cluster expansion in the scattering off imperfections, and by beginning with localized atomic states and making a cluster expansion in the interatomic hopping matrix elements. The two techniques are shown to give the same results when all irreducible single-site diagrams are included in the self-consistent field approximation and multiple-occupancy corrections are made self-consistently; it is conjectured that this equivalence holds at each level of the cluster expansion. In the process, the connection between the recent calculation of transport properties by Velický in the coherent potential approximation, the diagrammatic technique of Edwards, and the diagramatic technique of Matsubara and Toyozawa is established.

I. INTRODUCTION

It has recently become clear that formally, at least, the general problems of determining the nature of electron, phonon, magnon, and exciton states in disordered alloys are the same. Perhaps the most widely used approaches to the problem have been to calculate the Green's functions averaged over an ensemble of all configurations of the atoms by perturbation-expansion techniques. The usual technique, which was introduced by Edwards,[1] is to begin with the states of a perfect crystal and make a cluster expansion in the scattering due to the imperfections, which can with sufficient scattering lead to states localized about the imperfections. Another technique, first used for the configurationally averaged crystal by Matsubara and Toyozawa,[2] is to begin with localized states, whose energies vary from site to site and make a cluster expansion in the hopping matrix elements between localized states which, with sufficient hopping, can

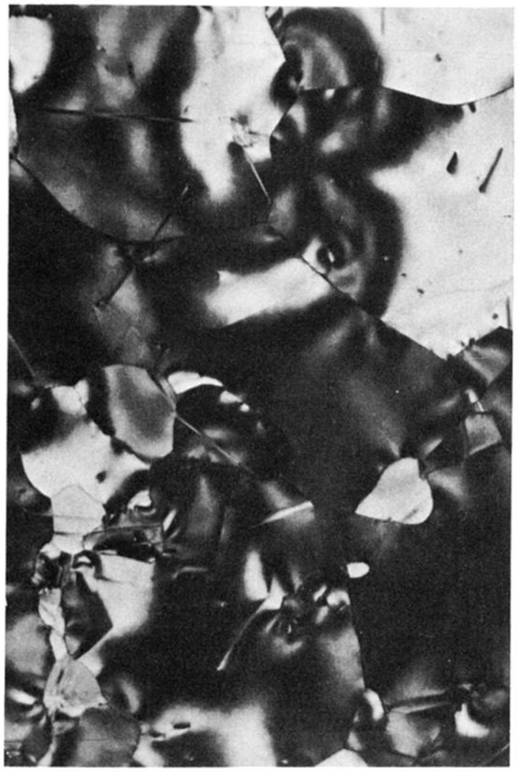

FIG. 1. Transmission electron micrograph of a well-crystallized Au film ($d = 158$ Å).

FIG. 2. Transmission electron micrograph of a nonannealed Au film ($d = 232$ Å).