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Optical properties of liquid mercury

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Interest in the optical properties of liquid Hg has resulted in numerous studies over the past quarter of a century. Consistent differences have been observed between the optical properties of liquid Hg deduced from reflectance and from ellipsometric spectra, and several models have been proposed which have attempted to explain these differences by the introduction of an inhomogeneous and/or anisotropic surface region. However, a systematic analysis of the previously existing and new ellipsometric data for liquid Hg fails to demonstrate the existence of a surface transition zone having inhomogeneous and/or anisotropic properties. It is further shown that the contradiction between the optical constants obtained from ellipsometric and from reflectance measurements is not real and that the former are representative of liquid Hg while the latter contain large uncertainties because of insufficient sensitivity. The observed deviations of the optical constants of liquid Hg from "Drude" behavior still require theoretical explanation.

I. INTRODUCTION

Over the past 30 years there have been numerous measurements of the optical constants of liquid Hg in the energy range from the ir to the near uv. Of these, reflectance measurements have generally been interpreted as yielding "Drude" values of the optical constants, whereas ellipsometric measurements have led to "non-Drude" values. For the past decade, Rice and co-workers[1–5] have made persistent efforts to explain the differences by introducing inhomogeneous and/or anisotropic surface models. In this paper, we start by discussing the conditions under which properties, such as inhomogeneity and anisotropy, of a transition zone, if present at the surface of liquid Hg, would be detectable in the values of the optical properties obtained from ellipsometric measurements. Previously existing ellipsometric data for liquid Hg are then analyzed in terms of the existence of a surface transition zone. Within the experimental accuracies of the various experiments, no evidence is found for the existence of a surface transition zone. New experimental data, of the reflectances R_p and R_s and the ellipsometric parameter Δ measured simultaneously at a quartz–liquid-Hg interface, are presented. Again, no evidence is found for any surface inhomogeneity or anisotropy for liquid Hg. However, these new data do confirm that the optical properties for liquid Hg obtained by ellipsometry deviate from the Drude expressions. The Drude optical properties which have been deduced from reflectance measurements and which have been thought to be in conflict with those obtained from ellipsometry, are then shown to have very large associated uncertainties. Finally, a Kramers-Kronig analysis of normal-incidence reflectance over a wide energy range shows that the Drude values of the optical properties below ~4 eV are not consistent with the higher-energy values.

II. DETECTION OF SURFACE STRUCTURE BY ELLIPSOMETRY

The high sensitivity of ellipsometry[6] to the presence of surface structure makes ellipsometry a powerful tool in the study of surfaces. This high sensitivity, however, has often led to variable results when ellipsometric measurements have been used to determine the optical constants of a material.[7] Real surfaces usually exhibit irregularities and possibly, just under the surface, inhomogeneities and/or anisotropy. Such surface structures affect the results calculated from ellipsometric measurements much more severely than those obtained from other methods of spectroscopic analysis, e.g., reflectance measurements. The discrepancies found between the optical constants for liquid Hg obtained from ellipsometric and from reflectance measurements is one example that has been attributed to the presence of a surface inhomogeneity and/or anisotropy intrinsic to the clean surface of the material.[1–5,8] To examine the validity of this assumption, we first summarize briefly how the existence of surface structures on what is thought to be an isotropic and homogeneous material can be detected by ellipsometric measurements.

Without knowing the kinds and extent of the structures which actually exist on a surface, the starting point is always the assumption that the surface is nominally smooth, homogeneous, and isotropic. When dealing with a liquid surface, we may accept, *a priori,* the surface to be ideally smooth, but need to examine the data for effects of inhomogeneity and/or anisotropy. After Burge and Bennett[9] we call the dielectric function ϵ, calculated from the measured ellipsometric parameters ψ and Δ for a real surface under the assumption that the surface is smooth, homogeneous, and isotropic, the pseudodielectric function. The calculated value of $\epsilon \equiv \epsilon(n_0, \phi)$ is, in general, a function of the experimental parameters n_0 and ϕ, the refractive index of the ambient medium and the angle of incidence, respectively, if surface structures are present on the real surface. The dependences of ϵ on n_0 and ϕ have been calculated for some simple examples of anisotropic and inhomogeneous surfaces, and these are presented in Figs. 1 and 2, respectively. The results in Fig. 1 were calculated using the optical constants of graphite,[10] a uniaxial crystal, at a photon energy of 3 eV. Shown in Fig. 1 are the values of the real and imaginary parts of $\epsilon(=\epsilon_1 + i\epsilon_2)$ which would be determined from ellipsometric measurements on graphite having the c axis perpendicular to the reflecting surface, on the assumption that the medium is isotropic. For a constant value of n_0, both ϵ_1 and ϵ_2 change only slightly with changing ϕ, and it is thus difficult to get any indication of anisotropy from measurements at various values of ϕ. The dependences of ϵ_1 and ϵ_2 on n_0 obtained at $\phi = 70°$, which is a typical angle of incidence in ellipsometry, are, however, large enough to indicate clearly the existence of some deviation from the assumed conditions. Similar results are found in the case of an inhomogeneous surface. Figure 2 shows the values of ϵ_1 and ϵ_2 obtained from ellipsometric measurements on a liquid-Hg surface which is unknowingly covered with a 10-Å-thick transparent layer. Thus the presence of both anisotropy and inhomogeneity in the vicinity of a surface may be detected by observing the n_0 dependence of $\epsilon(n_0, \phi)$.

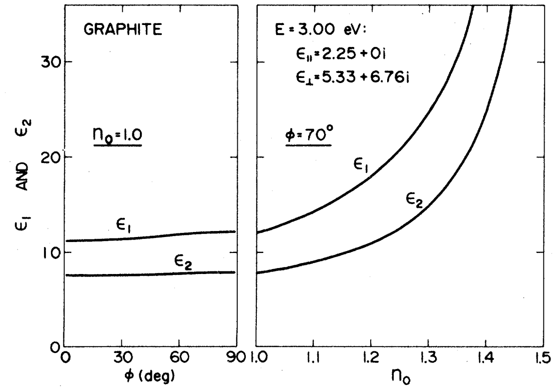

FIG. 1. Pseudodielectric function, $\epsilon = \epsilon_1 + i\epsilon_2$, calculated at 3 eV for a graphite surface with the c axis perpendicular to the reflecting surface as functions of the angle of incidence ϕ and the refractive index of the ambient medium n_0. The values used for the dielectric tensor of graphite are those observed by Greenaway *et al.* (Ref. 10).

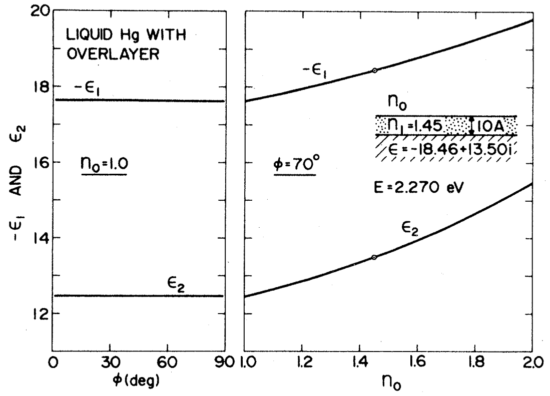

FIG. 2. Pseudodielectric function, $\epsilon = \epsilon_1 + i\epsilon_2$, calculated at 2.270 eV for a liquid-Hg surface covered with a 10-Å-thick transparent layer of refractive index 1.45 as functions of the angle of incidence ϕ and the refractive index of the ambient medium n_0. The dielectric constants used for Hg are those observed by Smith and Stromberg (Ref. 20).

A second way of using $\epsilon(n_0, \phi)$ to detect surface effects associated with a sample is to compare the reflectance $R(n_0', \phi')$ measured for the sample with photons incident at an angle ϕ' through an ambient medium of refractive index n_0' with the reflectance calculated from the pseudodielectric function $\epsilon(n_0, \phi)$ and designated by $R_{\text{calc}}(n_0', \phi'; \epsilon)$. If the surface has associated structure, these two reflectances will, in general, be different. Illustrations of this technique are given in Fig. 3 for the same example of an inhomogeneous surface region that was considered in Fig. 2. For both p- and s-polarized light, the differences between the calculated and observed values of reflectance, $\delta R = R_{\text{calc}}(n_0', \phi'; \epsilon) - R(n_0', \phi')$, are given as functions of ϕ' for three different values of n_0', and for $n_0 = 1$ and $\phi = 70°$. In this example, the values of δR_s are small and would be difficult to detect experimentally. On the other hand, the values of δR_p are large enough to be detected experimentally for $n_0' \neq n_0$ and large values of ϕ'. A δR_p check, with $n_0' \neq n_0$, thus provides a sensitive way of detecting the presence of surface effects. Similar analyses may be made for any other quantities obtainable both directly by measurement and indirectly from $\epsilon(n_0, \phi)$. Examples of such quantities are the ellipsometric parameters ψ and Δ defined by $\tan\psi = r_p/r_s$ and $\Delta = \Delta_p - \Delta_s$, respectively, where r_p and r_s are the reflection amplitudes and Δ_p and Δ_s are the phase changes upon reflection of the incident photons with the electric vector parallel and perpendicular to the plane of incidence, respectively. The values of $\delta\psi$ and $\delta\Delta$ calculated in the same way as δR_p and δR_s and for the same inhomogeneous system are plotted in Fig. 3. It is seen that both quantities are large

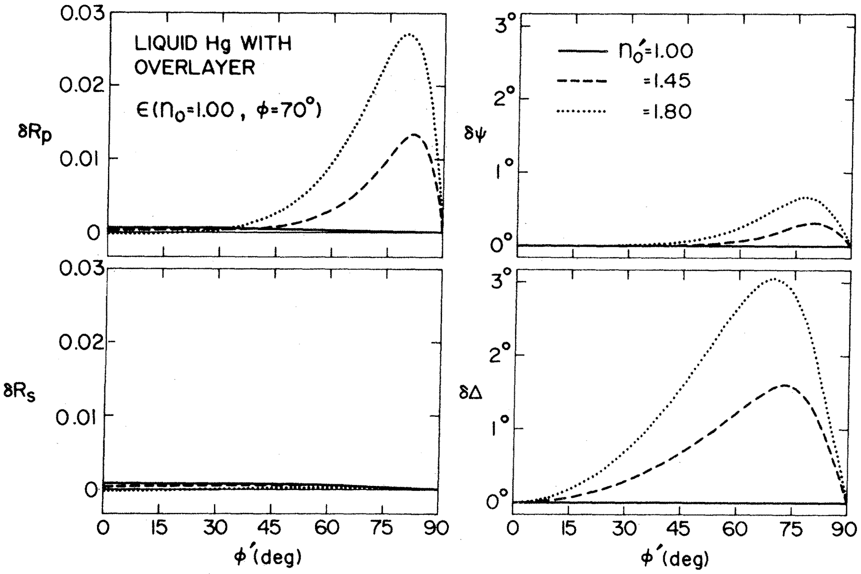

FIG. 3. Differences between the calculated and observed values of R_p, R_s, ψ, and Δ as functions of the angle of incidence ϕ' for the case of the inhomogeneous surface shown in Fig. 2 under an ambient medium of refractive index n_0'. The calculated values were obtained from the pseudodielectric function $\epsilon(n_0=1.0,\ \phi=70°)$.

enough to be detectable experimentally at large values of ϕ' when $n_0' \neq n_0$.

The methods described above for detecting the existence of a surface transition zone associated with a sample involve measurements with different media of refractive indices n_0' and n_0 in contact with the sample. In most cases, however, it is difficult to prepare and make measurements on the same or identical reflecting surfaces in contact with different ambient media. One method of overcoming this difficulty is to check the consistency among the quantities measured simultaneously for the same reflecting surface. A simple, and well-known, test is to measure R_p and R_s at $\phi=45°$. If no surface effects are involved, the measured values of R_p and R_s should satisfy the relationship $R_p=R_s^2$.[11] Simultaneous measurements of R_p, R_s, and Δ on the same reflecting surface are feasible[8] with some types of ellipsometer which are equipped with a photometric detector. These quantities are not independent of each other and, if no surface effects are involved, are connected by the equations[12]

$$R_p/R_s=(b+C^2-2aC)/(b+C^2+2aC)\ ,$$

$$R_s=(b+T^2-2aT)/(b+T^2+2aT)\ ,$$

$$\Delta=\tan^{-1}[2T(b-a^2)^{1/2}/(b-T^2)]-\pi\ ,$$

where $C=\cos\phi$, $T=\tan\phi\sin\phi$, and a and b are parameters which can be determined from any two of the three measured quantities R_p/R_s, R_s, and Δ. Surface effects will therefore be revealed by inconsistencies between the measured values of R_p/R_s, R_s, and Δ; e.g., a difference between the measured value of any one of the three quantities and its value when calculated from the other two. A more indirect check which can be made with the measured values of R_p/R_s, R_s, and Δ is to determine the pseudodielectric function ϵ. The real and imaginary parts of ϵ may be obtained from any two of the three measured quantities using the equations

$$\epsilon_1=2a^2-b+TC$$

and

$$\epsilon_2=2a(b-a^2)^{1/2}\ .$$

The values of ϵ determined in this way generally show inconsistencies unless the measurements involve no surface effects. An example of such an analysis is presented in Table I which shows the values of R_p/R_s, R_s, and Δ which would be observed experimentally for the inhomogeneous surface shown in Fig. 2 for $n_0=1$ and $\phi=70°$. Also shown are the results of calculations involving pairs of these quantities, which demonstrate the apparent inconsistencies in the measured values if it is assumed that there is no surface inhomogeneity.

In the next section we examine the experimental results for liquid Hg in terms of the above discussion.

TABLE I. Values of R_p/R_s, R_s, and Δ which would be observed experimentally for the inhomogeneous surface shown in Fig. 2 for $n_0=1$ and $\phi=70°$, and the apparent inconsistencies in these quantities if it is assumed that there is no surface inhomogeneity.

	R_p/R_s	R_s	Δ	ϵ_1	ϵ_2
Observed	0.6056	0.9189	56.15°		
Calculated from					
R_p/R_s and Δ	⋯	0.9193	⋯	−17.63	12.46
R_s and Δ	0.6040	⋯	⋯	−17.58	12.51
R_p/R_s and R_s	⋯	⋯	56.72°	−17.26	12.11

III. ELLIPSOMETRIC OPTICAL CONSTANTS OF LIQUID Hg

From among the numerous values of the optical constants of liquid Hg obtained so far between 0.2 and 4.0 eV by ellipsometric techniques, the results since 1959 (Refs. 8 and 13–20) are summarized in Figs. 4 and 5. Figure 4 shows the optical conductivity defined by $\sigma=E\epsilon_2/4\pi\hbar$, while Fig. 5 shows ϵ_1, both as functions of the photon energy E. Also shown in the figures by dotted lines for comparison purposes are the Drude values due to nearly-free-electron behavior described by

$$\epsilon_D = 1 - \frac{4\pi\hbar\sigma_0}{(\tau/\hbar)E^2 + iE} ,$$

where τ, the relaxation time, was determined[16] from $\tau=(m/Ne^2)\sigma_0$ using the dc conductivity $\sigma_0=93.87 \times 10^{14}\ \mathrm{sec}^{-1}$ and the density of free carriers $N=8.158\ \times 10^{22}\ \mathrm{cm}^{-3}$ in liquid Hg at 20° C, and e and m are the electronic charge and mass, respectively. Some of the experimental data are given with es-

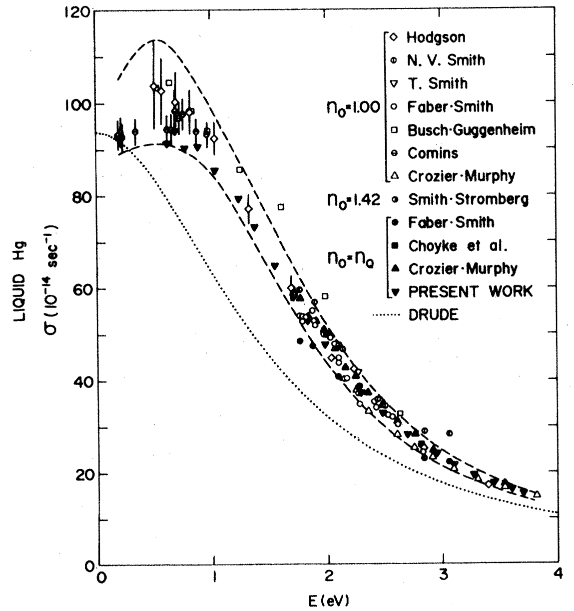

FIG. 4. Optical conductivity σ for liquid Hg observed by ellipsometry as a function of photon energy E. The dashed lines indicate the probable upper and lower limits of the observed values.

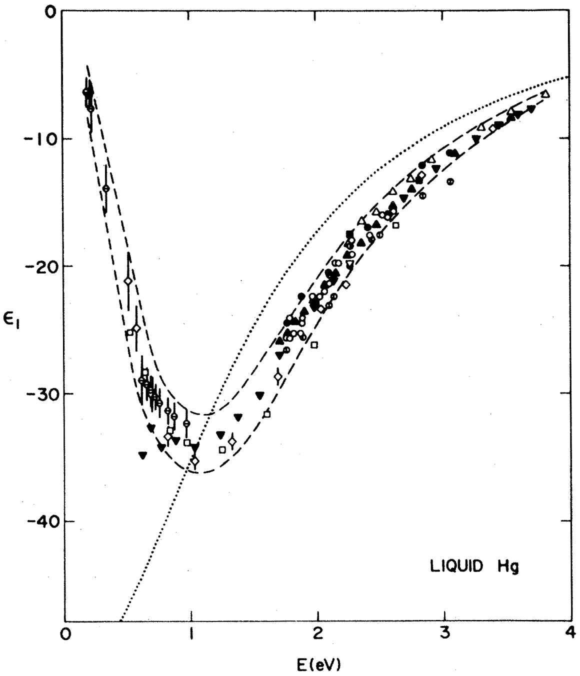

FIG. 5. Real part of the complex dielectric function, $\epsilon=\epsilon_1+i\epsilon_2$, for liquid Hg observed by ellipsometry as a function of photon energy E. The symbol coding is the same as for Fig. 4.

timated error bars, and the probable upper and lower limits of the experimental values are shown by dashed lines. The experimental data presented show a systematic deviation from the Drude values and form, as a whole, spectra showing a general behavior clearly different from that given by the Drude formulas.

All the optical constants summarized in Figs. 4 and 5 have apparently been derived assuming an isotropic and homogeneous reflecting surface, i.e., the basic quantity calculated in each case was the pseudodielectric function ϵ. We start our analysis of the ellipsometric data for evidences of surface structure in liquid Hg, by looking for an n_0 dependence in these results. For this purpose, the data are presented in Figs. 4 and 5 by open and filled symbols for data taken under vacuum (or an inert gas) and in contact with a quartz prism, respectively. No systematic differences are found between the two groups of data for photon energies above ~1.5 eV. Below 1.5 eV, although there are slight differences between the two groups of data, there are also relatively large uncertainties associated with the ellipsometric optical constants. Shown by half-filled circles in the figures at 2.270 eV are the results of measurements by Smith and Stromberg[20] obtained on Hg in contact with cyclohexane ($n_0=1.4198$). They have also performed the measurements at the same photon energy on Hg in contact with liquid benzene ($n_0=1.5084$) and water ($n_0=1.3344$) and found no difference in the values of the optical constants within their experimental accuracy of four significant figures. These observations, taken as a whole, fail to show a definite systematic correlation between the value of the pseudodielectric function and the value of n_0. Thus they fail to prove the existence of a surface transition zone for liquid Hg. In the example given in Fig. 2, the pseudodielectric function has been calculated at a single energy of 2.27 eV for a liquid-Hg surface covered with a 10-Å-thick transparent layer of refractive index 1.45. Similar analyses were performed for other reasonable values of the thickness and refractive index of the hypothesized surface layer on the liquid Hg. These analyses also show, however, that the experimental scatter on the data shown in Figs. 4 and 5 is sufficient to mask any effects resulting from a transparent surface layer $\lesssim 3$ Å in thickness. It is noted here that, in the surface models[1,5] proposed by Rice and co-workers to explain the observed differences between the non-Drude optical properties obtained from ellipsometric measurements and the Drude optical properties obtained from reflectance measurements, their surface parameters do not explain the independence of the pseudodielectric function from the value of n_0.

We next look for evidences of surface structure by performing δR, $\delta\psi$, and $\delta\Delta$ checks, of the kind demonstrated in Fig. 3, using the ellipsometric optical constants presented in Figs. 4 and 5. Of these, the δR_p and $\delta\Delta$ checks at large angles of incidence ϕ' and with $n_0' \neq n_0$ are seen to be the most sensitive to the presence of surface structures. A $\delta\Delta$ check is presented in Fig. 6. Values of Δ measured at a quartz–liquid-Hg interface ($n_0'=n_Q$) for $\phi'=70°$ are compared with the same quantity calculated from the pseudodielectric function $\epsilon(n_0,\phi)$ obtained for liquid Hg in vacuum ($n_0=1$) for various values of ϕ. The measured values of Δ are shown in Fig. 6 by filled symbols and the calculated values by open symbols; the same symbols as in Figs. 4 and 5 being employed to identify the source of the data. Data obtained at a quartz–liquid-Hg interface at angles other than $\phi'=70°$ were converted to the corresponding values for $\phi'=70°$ and were then included in Fig. 6 as "measured values." No systematic inconsistencies between the measured and calculated values of Δ are seen in Fig. 6. Thus this $\delta\Delta$ check on the available data shows no indication of inhomogeneity or anisotropy associated with the surface region of liquid Hg.

To our knowledge, experimental values of R_p measured at an angle of incidence large enough for a δR_p check are not available in the literature, except for the data taken by Crozier and Murphy[8] in their simultaneous measurements of R_p, R_s and Δ at $\phi'=70°$ between 1.7 and 4.1 eV. We have therefore performed similar measurements at $\phi'\approx 60°$ in the energy range from 0.6 to 3.7 eV. Using the results of these measurements, we will show in the next section a δR_p check and the consistency checks among the above three quantities measured simultaneously.

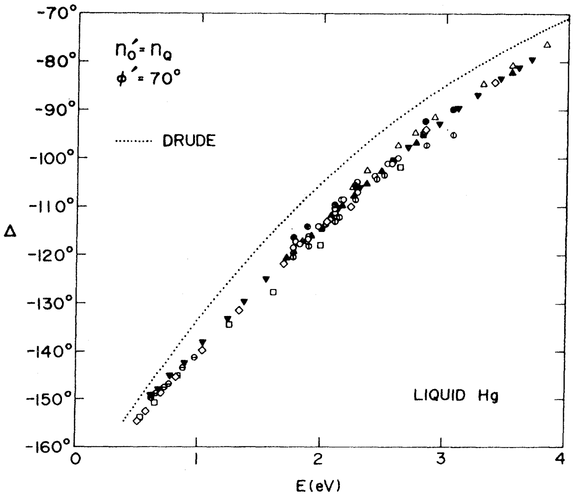

FIG. 6. Δ, measured at a quartz–liquid-Hg interface for an angle of incidence of $\phi'=70°$ (filled symbols) and calculated from the ellipsometric pseudodielectric function ϵ obtained at a vacuum–liquid-Hg interface (open symbols), as a function of photon energy E. The symbol coding is the same as for Fig. 4.

IV. SIMULTANEOUS MEASUREMENTS OF R_p, R_s, AND Δ

New measurements of R_p, R_s, and Δ were made at an interface between a strain-free quartz prism and liquid Hg, employing a conventional-type ellipsometer equipped with a photometric detector. The method used to measure the three quantities at the same interface and at the same time was similar to that employed by Crozier and Murphy.[8] With the azimuth setting of the polarizer fixed at 45° to the plane of incidence, two sets of intensities $I(0°)$ and $I(90°)$, and $I(45°)$ and $I(135°)$ were measured for reflection from the quartz–liquid-Hg interface, where $I(A°)$ is the intensity measured with the analyzer setting at $A°$ to the plane of incidence. The liquid Hg was then removed and the values of the intensities $I_0(0°)$ and $I_0(90°)$, and $I_0(45°)$ and $I_0(135°)$, recorded for total internal reflection at the quartz-air interface. The angle of incidence was determined to be 60.52° ± 0.15° from the value of Δ obtained from these total reflection measurements using the known value of the refractive index of the quartz prism. This result was in good agreement with that determined directly from the instrumental geometry, using a narrow laser beam as a geometrical reference. R_p and R_s for liquid Hg were given by $R_p = I(0°)/I_0(0°)$ and $R_s = I(90°)/I_0(90°)$, respectively, and Δ was determined from[8] $\cos\Delta = -\cos 2\xi / \sin 2\psi$, where $\tan\xi = [I(45°)/I(135°)]^{1/2}$ and $\tan\psi = [I(0°)/I(90°)]^{1/2}$. In this experiment, the surfaces of both the prism and the liquid Hg were visible and could be inspected during the course of the measurements, whereas in the experiments of Crozier and Murphy this was

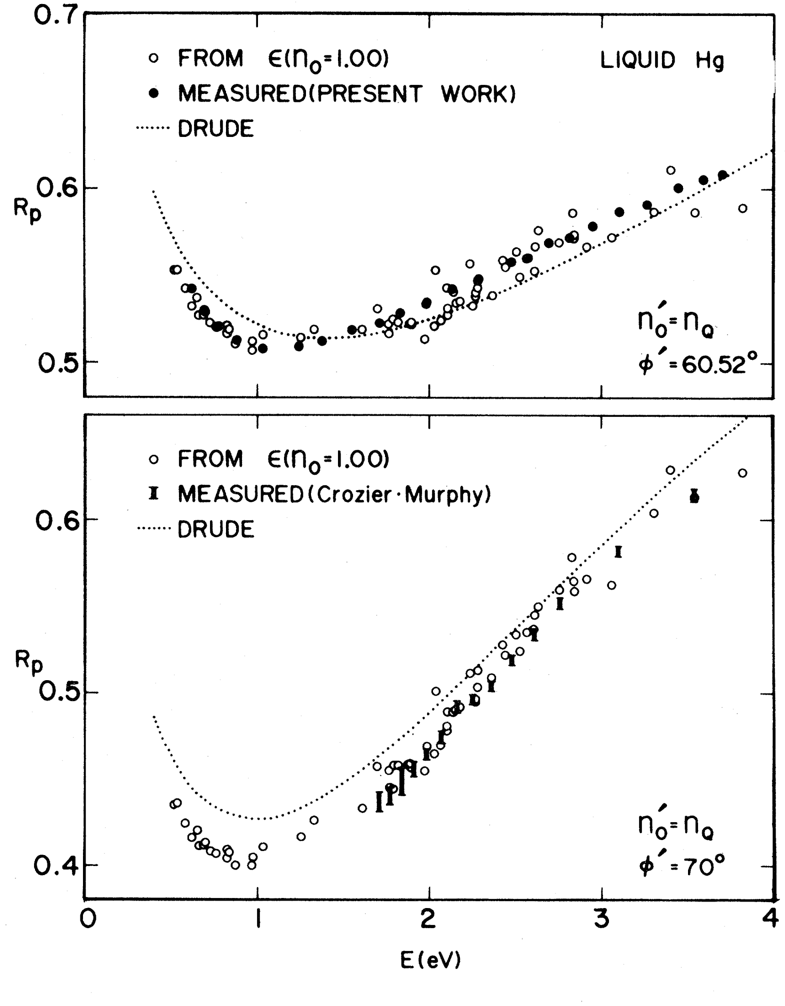

FIG. 7. R_p, measured at a quartz–liquid-Hg interface and calculated from the ellipsometric pseudodielectric function ϵ obtained at a vacuum–liquid-Hg interface, as a function of photon energy E.

prohibited since the system was closed and evacuated. The liquid Hg was cleaned by the overflow method previously used by Hodgson.[13]

The values of the optical constants obtained from the present measurements of $R_p/R_s=(\tan\psi)^2$ and Δ have already been presented in Figs. 4 and 5, and it is seen that they show good agreement with most of the previously published results. A δR_p check on our new data is presented in the upper half of Fig. 7 in the form of the measured values of R_p compared with those calculated from the values of $\epsilon(n_0,\phi)$ in Figs. 4 and 5 obtained under vacuum $(n_0=1)$. Both sets of values, measured and calculated, show a systematic deviation from the Drude values shown in the figure for comparison but are in good agreement with each other. A similar result is seen in the lower part of Fig. 7; the values of R_p measured by Crozier and Murphy[8] at a quartz–liquid-Hg interface at $\phi'=70°$ show agreement with those calculated from $\epsilon(n_0=1,\phi)$. The results shown in Fig. 7 indicate that no surface effects are detected in either our new data or those obtained previously by Crozier and

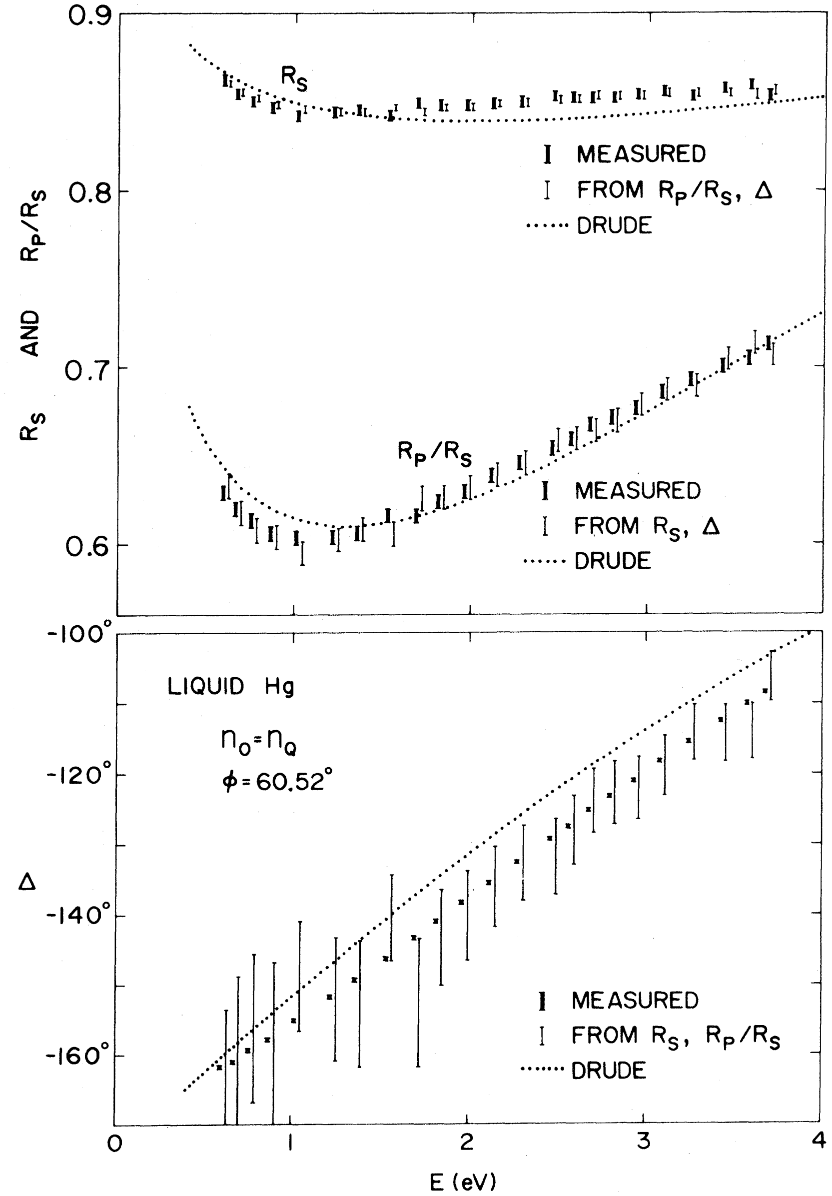

FIG. 8. Demonstration of the consistency among R_p/R_s, R_s, and Δ measured simultaneously at a quartz–liquid-Hg interface as a function of photon energy E.

Murphy. To test this hypothesis further, the next step is to demonstrate consistency among our new measured values of R_p, R_s, and Δ. The first method of consistency analysis is to compare any one of the measured values with that calculated from the other two, and the second is to determine the optical constants from three different pairs of the measured quantities. The first analyses are presented in Fig. 8, and the second in Fig. 9. In Fig. 8 good agreement is found between the observed and calculated values for each of the three quantities, R_p/R_s, R_s, and Δ. In Fig. 9 there is excellent consistency among the optical constants deduced from three different pairs of the measured quantities. (The scatter in σ and ϵ_1 obtained from R_p/R_s and R_s stems from a lack of sensitivity of this pair of observations to the values of the optical constants.) A similar consistency has been reported previously by Crozier and Murphy[8] between the optical constants deduced from R_p/R_s and Δ and from R_p/R_s and R_s when all the measured quantities were obtained at a quartz–liquid-Hg interface. When the measured quantities were obtained at a borosilicate-glass–liquid-Hg interface, they found inconsistencies in the values of the optical constants obtained from different pairs of the measured quantities. However, these inconsistencies seem to be due to an imperfect contact between the glass and liquid Hg. This problem has been pointed out by Smith[15] and Faber and Smith[16] in connection with the ellipsometric results of Lelyuk *et al.*,[21] which were obtained at a glass–liquid-Hg interface and which deviate considerably from the data shown in Figs. 4 and 5.

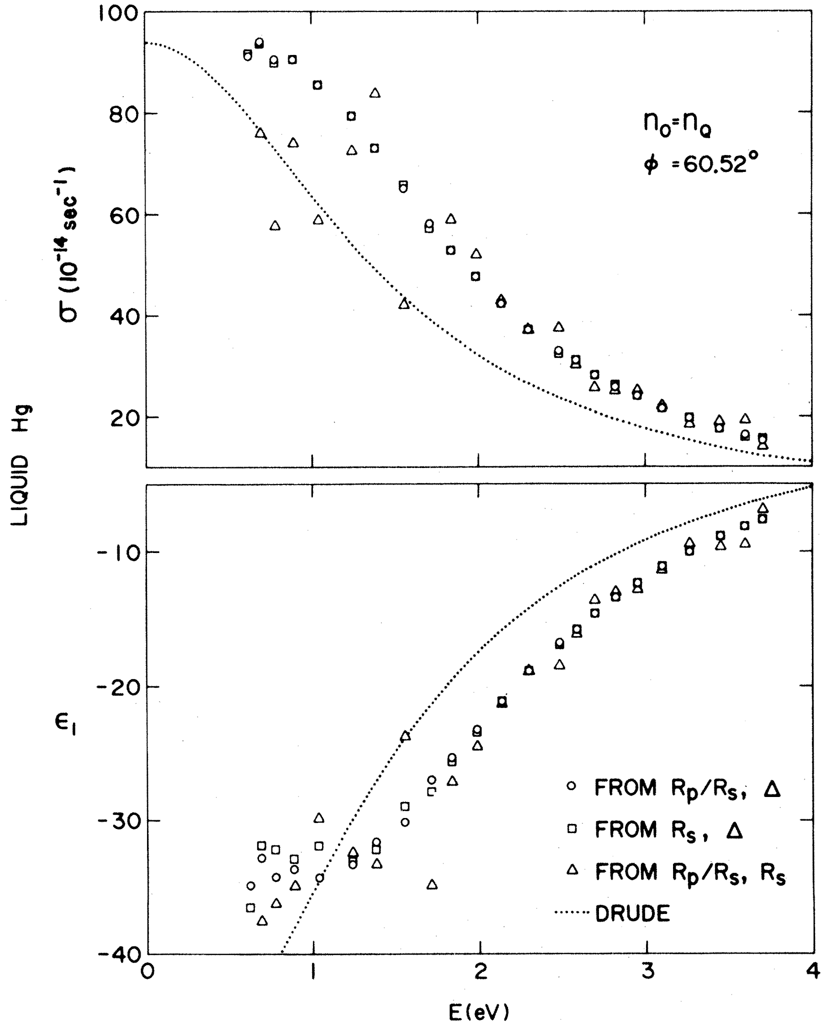

FIG. 9. Optical conductivity σ and the real part of the dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ for liquid Hg, deduced as functions of photon energy E from three different combinations of the measured values of R_p/R_s, R_s, and Δ.

In the series of analyses made above, no experimental evidence suggesting the presence of inhomogeneity or anisotropy associated with the surface region has been found. Rather, we have built a consistent set of evidence indicating, within the sensitivity of these analyses, the nonobservance of any such structure on liquid Hg. In the following sections, we will review the experimental results of several reflectance measurements which have been considered to be in conflict with the ellipsometric results and which suggested the necessity of a surface model for liquid Hg.

V. REFLECTANCE MEASUREMENTS OF LIQUID Hg

Measurements of reflectance made on liquid Hg since 1955 (Refs. 1,5,8,18, and 22–25) are schematically summarized in Fig. 10, which shows the photon energy range of each set of measurements and the contact medium. In addition to measurements of R_N, R_p, and R_s, measurements of two other reflectances, $\bar{R}$ (Ref. 22) and R_p(FTR)[5] have been reported. $\bar{R}$ is the reflectance measured for unpolarized light at $\phi = 45°$ and R_p(FTR) is the frustrated total reflectance measured with p-polarized light for a prism-spacer–liquid-Hg geometry. In each of these studies, the spectral range where observations of Drude values of the reflectances were claimed is indicated by a thick line. For R_N measured under vacuum[24] the stated experimental uncertainty in the reflectance values was ±0.008, while for the rest of the measurements [with the exception of R_p(FTR)] the uncertainties ranged from ±0.002 to ±0.005.

In the δR_p checks in Sec. IV, we have illustrated the consistency between the measured values of R_p and the ellipsometric values of the optical constants. Similar checks may be made with any of the measured reflectances presented in Fig. 10. Since, as has been shown in Fig. 3 for an example of an inhomogeneous surface, δR_p for large values of ϕ' shows the greatest sensitivity to the presence of inhomogeneity or anisotropy in the surface region, even better consistency may be expected when comparing the measured and calculated reflectance values for the other types of reflectance. The values of R_s measured in the present work and shown in the top of Fig. 8 have indeed been found to show excellent consistency with the ellipsometric results. The same results are found for R_s measured by Crozier and Murphy.[8] Inconsistencies have, however, been noted by Rice and co-workers[1,4,5] for R_N and $\bar{R}$. Two such examples are given in Fig. 11, where comparisons similar to those made in Fig. 7 are made between the measured[1,22] and calculated values of R_N and $\bar{R}$ for LiF–liquid-Hg and quartz–liquid-Hg interfaces, respectively. These results have been interpreted as showing the involvement of surface effects in the ellipsometric measurements and led Rice and co-workers to speculate on the presence of inhomogeneous and/or anisotropic surface structures on liquid Hg.[1–5,8] In contrast, we have presented a comprehensive series of analyses demonstrating that surface structures have not been detected through ellipsometric measurements on liquid Hg.

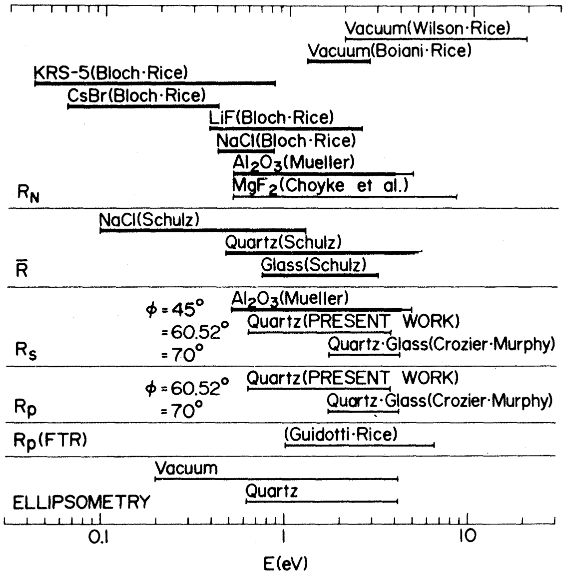

FIG. 10. Schematic summary of reflectance measurements on liquid Hg. Shown above the lines, indicating the photon energy region of each experiment, are the contact medium and the names of the experimenters. Thick lines indicate the spectral region where observations of the Drude reflectance values have been claimed.

In this respect, the fact that the reflectance measurements, which yield results in apparent disagreement with the ellipsometric results, almost all claim agreement with the Drude values seems to be quite suggestive. As can be seen in Figs. 7, 8, and 11, the ellipsometric reflectance values are indeed quite close to the Drude values, but always show small systematic deviations from them. Crozier and Murphy and the present authors confirmed this non-Drude behavior of reflectance by the direct measurements shown in Figs. 7 and 8.

Rice and co-workers,[2–5] employing their surface models for liquid Hg, have recently discussed how the presence of surface structure would affect the R_p(FTR) spectrum. Generally these FTR spectra are interpreted in terms of summations of reflection amplitudes and phases of the multiply reflected beams in the prism-spacer-sample system. FTR spectra have a higher sensitivity to surface structure than ordinary reflectance spectra because of the inclusion of infor-

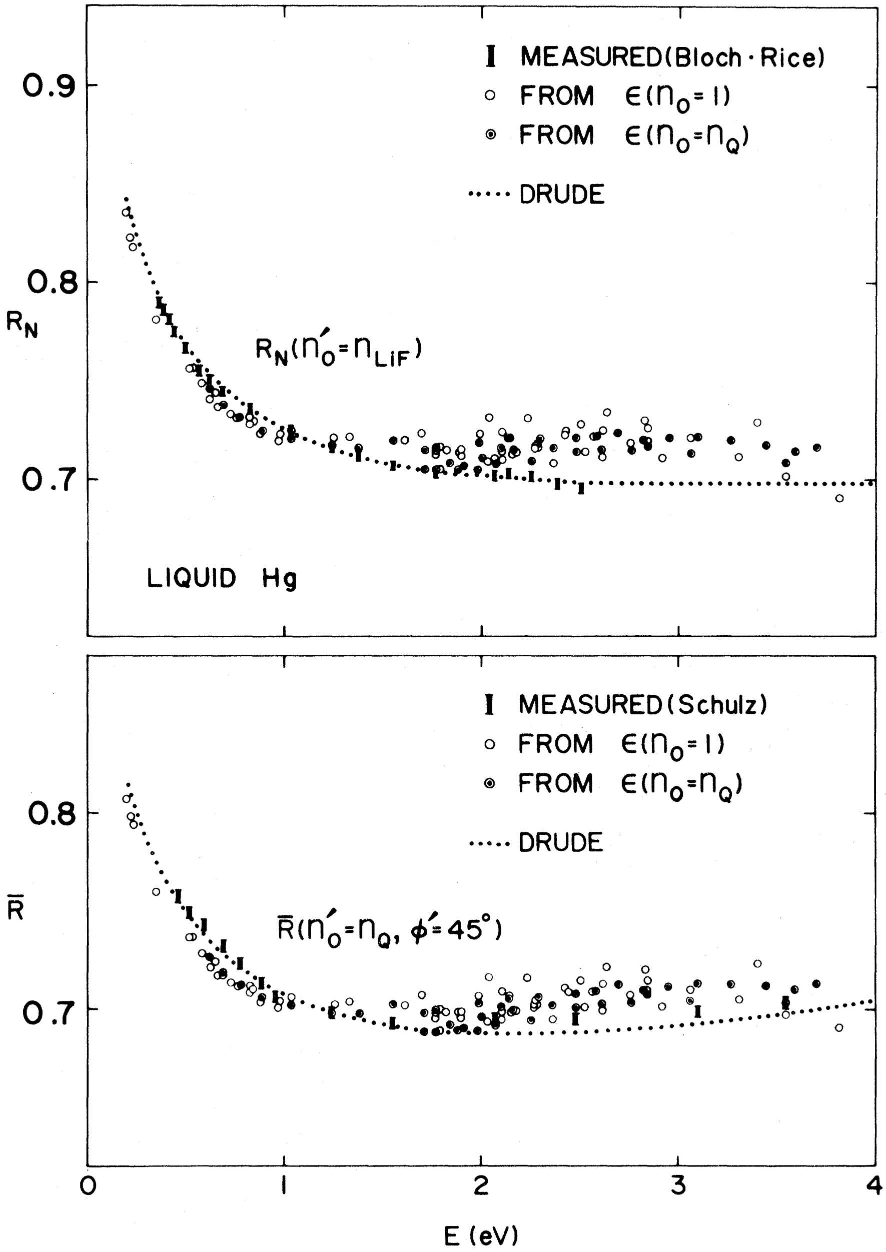

FIG. 11. R_N and $\bar{R}$, observed at LiF—liquid-Hg and quartz—liquid-Hg interfaces, respectively, and calculated from the ellipsometric dielectric function ϵ obtained at a vacuum—liquid-Hg interface, as functions of photon energy E.

mation about the phase shift upon reflection, as well as the use of multiple reflections. They have shown theoretically that a consistency check which compares the ellipsometric optical constants with the FTR values provides a sensitive way to detect surface effects. Rice and co-workers[5] recently attempted such an analysis for liquid Hg. From this analysis they arrived at a semiempirical representation of their hypothesized surface transition region in liquid Hg.

Observations of the Drude reflectance values often led to Drude optical constants for liquid Hg. Before proceeding to our final analysis of R_N which employs a Kramers-Kronig relation, we examine the validity of the extraction of these Drude optical constants from the reflectance measurements.

Bloch and Rice[1] observed Drude values of R_N below 2.50 eV for liquid-Hg surfaces in contact with four different window materials having different values of refractive index. They interpreted their results to be confirmation of the Drude values of the optical constants for liquid Hg. The reason this conclusion is not valid is presented in Fig. 12, where two Drude-value contours of R_N for liquid Hg in contact with KRS-5 (thallium bromide-iodide, $n_0=2.410$) and LiF ($n_0=1.383$) at $E=0.827$ eV are plotted in the $\epsilon_1-\epsilon_2$ plane with the width corresponding to the experimental uncertainty ±0.0025 claimed in their measurements. The two Drude-value contours overlap each other over a wide range of ϵ_1 and ϵ_2; from about −40.2 to −22.5 in ϵ_1 and from 46 to 136 in ϵ_2. These would be the ranges of uncertainties in ϵ_1 and ϵ_2, if they tried to determine the optical constants from these measured reflectance values.

It is to be emphasized that the example presented in Fig. 12 is for the pair of contact media with the largest difference in the refractive index values, and for the highest photon energy in Bloch and Rice's experiments made with different contact media. This is seen in Fig. 10. If we were to show Drude-value contours for other pairs of contact media, and for the lower photon energies used by Bloch and Rice, the overlap between the two Drude-value contours would become larger than shown in Fig. 12, and hence, the uncertainties in ϵ_1 and ϵ_2 inferred from them would also become larger. Furthermore, the values of R_N actually measured by them using KRS-5 at near $E=0.827$ eV are systematically smaller than the Drude value by about 0.005. If this is taken into account, the overlap of two reflectance contours would become even larger.

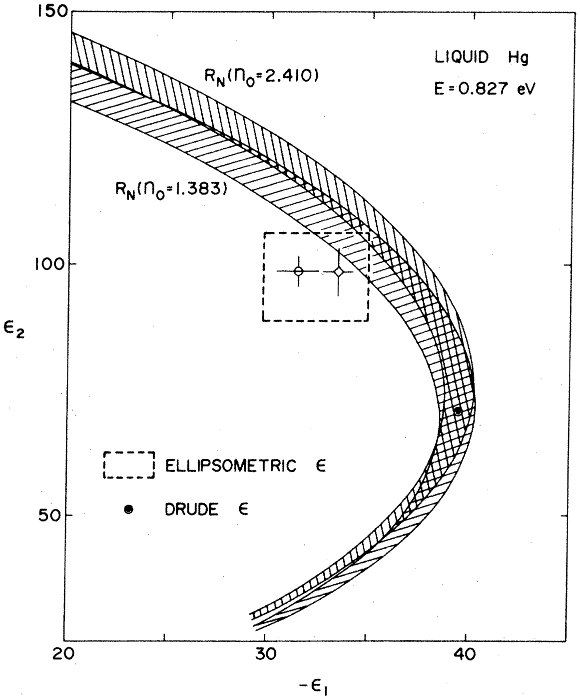

FIG. 12. Drude-value contours of R_N for KRS-5 ($n_0=2.410$)–liquid Hg and LiF ($n_0=1.383$)–liquid-Hg interfaces at $E=0.827$ eV plotted in the $\epsilon_1-\epsilon_2$ plane. The widths (Ref. 1) correspond to the stated uncertainty of ±0.0025 in the value of R_N. The dashed-line rectangle corresponds to the probable upper and lower limits of the ellipsometric values of ϵ_1 and ϵ_2 at this energy as shown in Figs. 4 and 5. Shown inside the rectangle by the same symbols, with error bars, as used in Fig. 4 are the data by Comins (Ref. 19) and by Hodgson (Ref. 13).

Mueller[25] also inferred Drude optical constants from Drude values of reflectances. He observed Drude values of R_N and R_s ($\phi=45°$) for photon energies between 0.5 and 3.8 eV for a liquid-Hg surface in contact with sapphire. He reported the Drude optical constants which had been "calculated" from his observed values of R_N and R_s. However, as can be seen in Fig. 13, the Drude-value contours for two reflectances R_N and R_s ($\phi=45°$) overlap each other over wide ranges of ϵ_1 and ϵ_2 values when allowing for the stated experimental uncertainties of ±0.005 in R_N^2 and R_s^2, implying very large uncertainties in ϵ_1 and ϵ_2 if determined from these reflectances. In ord-

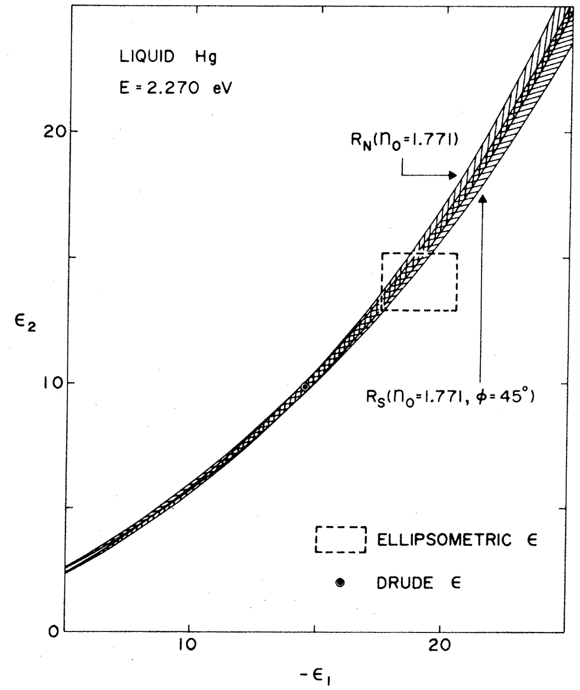

FIG. 13. Drude-value contours of R_N and R_s at $\phi=45°$ for a sapphire–liquid-Hg interface at $E=2.270$ eV plotted in the $\epsilon_1-\epsilon_2$ plane. The widths (Ref. 25) correspond to the stated uncertainty of ±0.005 in the values of R_N^2 and R_s^2. The dashed-line rectangle corresponds to the probable upper and lower limits of the ellipsometric data of ϵ_1 and ϵ_2 at this energy as shown in Figs. 4 and 5.

er to determine the optical constants to an accuracy comparable with that attained by ellipsometry, the reflectances would have to be measured typically ten to a hundred times more accurately than was done by either Bloch and Rice or by Mueller.

Choyke *et al.*[18] determined Drude values of the optical constants below 4 eV from their measurements of R_N at a MgF_2—liquid-Hg interface for photon energies from 0.5 to 8.25 eV. For analysis of their reflectance data they used a method due to Verleur,[26] which employed a fitting procedure to the complex dielectric function, described by an ensemble of classical oscillators, to the observed reflectance spectrum. As noted by Verleur, if this method is used for metals in the region below the plasma energy, the values obtained for the optical constants are very dependent on the initial choice of the trial values of the parameters chosen to describe the classical oscillators. This makes it necessary to determine the value of the dielectric function at at least one photon energy by an independent method in order to normalize the curve fitting. Without doing this, Choyke *et al.* made the reasonable estimate that the accuracy in their Drude optical constants was no better than 50%.

Schulz[22] was the first to report Drude values of the optical constants for liquid Hg. He obtained these values from measurements of $\bar{R}$ and the phase-shift θ upon reflection at normal incidence. The values of $\bar{R}$ were obtained at NaCl—, quartz—, and glass—liquid-Hg interfaces (see Fig. 10). The phase shifts were measured between 1.43 and 3.10 eV at a mica—liquid-Hg interface using a high-resolution interferometer. Since the Drude values of $\bar{R}$ are not in substantial conflict with the ellipsometric optical constants, his Drude values of the optical constants must be ascribed to Drude values of the phase shift. This is demonstrated in Fig. 14, which shows the phase shifts observed by Schulz recalculated for a vacuum—liquid-Hg interface. The uncertainties in his values of θ were typically less than $\pm 0.8°$. By comparison, the values of θ obtained from the ellipsometric optical constants form a quite distinct set which shows non-Drude properties. We have critically examined the experimental techniques employed in the interferometric determination of θ.[22,27–32] The techniques employed by Schulz were excellent, even by present-day standards, and no clear evidence explaining the appreciable difference between his values and the ellipsometric values could be found. One possible source of error, however, could be the Ag film deposited, as a wetting agent, onto the mica surface in order to ensure good contact between the mica and the liquid Hg. Schulz[22] expected the Ag film to be dissolved completely by the liquid Hg, but it is possible that the Ag, once it was in close proximity to the mica surface, remained in contact with the mica and did not migrate away from the surface. We have calculated the normal-incidence phase shift for a mica—Ag—liquid-Hg system and find that the presence of a 60-Å-thick Ag film can account for ellipsometric values of the phase shift close to those found by Schultz, but the calculated variation over the region of Schulz's measurements from 1.43 to 3.1 eV is not fully satisfactory. Thus, Schulz's measurements of the Drude optical constants are the only experimental results which are in real conflict with the ellipsometric results. If this contradiction is real, however, why has it not been observed in the analyses we have made? We will show in Sec. VI from a Kramers-Kronig dispersion analysis that the phase-shift values observed by Schulz do not appear to be consistent with observed normal-incidence reflectance values.

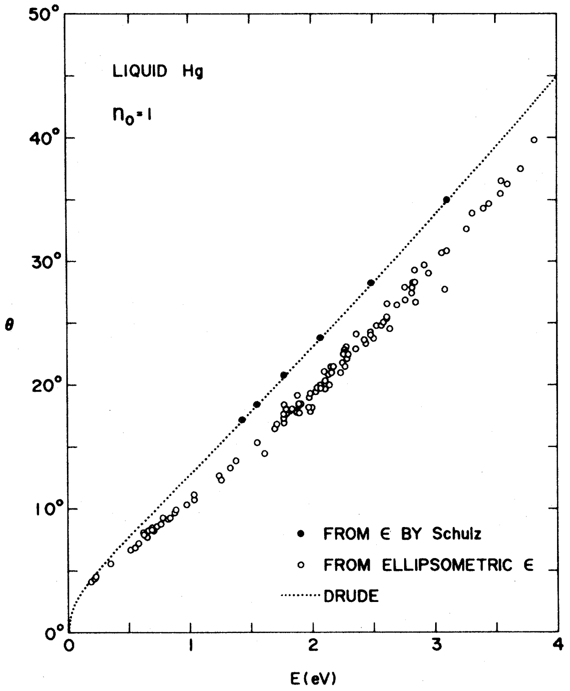

FIG. 14. Phase shift on normal incidence reflection θ at a vacuum—liquid-Hg interface calculated from the ellipsometric optical constants and from the optical constants obtained by Schulz (Ref. 22) as a function of photon energy E.

VI. KRAMERS-KRONIG ANALYSIS OF R_N

The Kramers-Kronig relation

$$\theta(E) = -\frac{E}{\pi} \mathrm{P} \int_0^\infty \frac{\ln R_N(E')}{E'^2 - E^2} \, dE' ,$$

between the real and imaginary parts of $\ln r_N$ where $r_N = R_N^{1/2} e^{i\theta}$ is the amplitude reflection coefficient for normal incidence, is usually employed to determine the optical constants from experimental values of R_N obtained in vacuum over a wide range of photon energies.[11] In this paper we have three reasons for performing a Kramers-Kronig analysis on R_N for liquid Hg. The first is to check whether the Drude values of θ observed by Schulz[22] are consistent with reflectance data, the second is to confirm the Kramers-Kronig consistency of the ellipsometric optical constants, and the third is to determine the optical constants of liquid Hg at energies above those of the ellipsometric measurements.

As indicated in Fig. 10, Wilson and Rice[23] have measured R_N in vacuum over the relatively wide range of photon energies from 2 to 20 eV. Their data are shown in Figs. 15 and 16 on semilog and log-log plots, respectively. Experimental data obtained by Boiani and Rice[24] between 1.24 and 2.76 eV are also included in Fig. 15. Wilson and Rice[23] performed a Kramers-Kronig analysis using their experimental values of R_N together with R_N values obtained by extrapolation of the experimental R_N to lower and higher energies. They obtained results for the optical constants from 2 to 20 eV which are quite close to the Drude values in the region below 4 eV. This result has been interpreted[4,5] as indicating a serious conflict between the reflectance and ellipsometric optical constants for liquid Hg. This interpretation is not justified, however, because their extrapolation of R_N to energies above 20 eV was made in such a way as to yield the Drude value of θ at 2.0 eV. Our analysis showed that the uncertainty involved in their extrapolation of R_N to energies below 2.0 eV was quite small. We have therefore tried, in our analysis, to find possible ways of reducing the uncertainty involved in the extrapolation of R_N to energies above 20 eV.

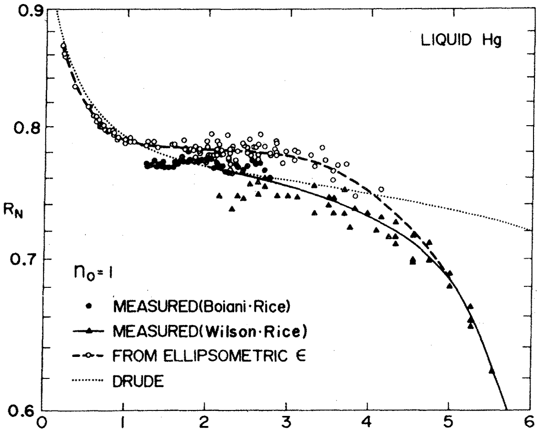

FIG. 15. Measured and calculated values of R_N for a vacuum–liquid-Hg interface as functions of photon energy E.

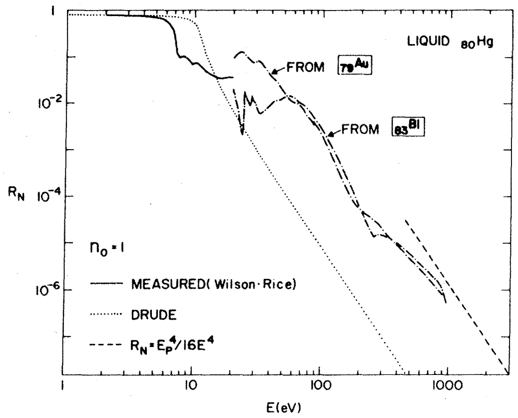

FIG. 16. R_N measured at a vacuum–liquid-Hg interface as a function of photon energy E. The two dash-dotted lines are those calculated from experimental values of the optical constants for solid Au and Bi.

In metals, R_N becomes small at energies above the plasmon energy, and its accurate experimental determination is often not feasible. However, experimental methods of determining the optical constants, and hence R_N, in such cases are well established for solid samples.[33–36] These methods are, however, not applicable to liquid Hg, since they usually involve transmission measurements on samples in the form of thin films. Thus there appears to be no way of determining accurate values of R_N experimentally in the energy region above ~20 eV. We have therefore attempted to estimate approximate values of R_N.

The most obvious procedure would be to use values of R_N for solid Hg after correcting for the differences in the liquid and solid phases. At high photon energies where k, the extinction coefficient, is quite small and n, the refractive index, is close to unity, R_N may be written as[11]

$$\begin{aligned} R &= [(n-1)^2+k^2]/[(n+1)^2+k^2] \\ &\simeq [(n-1)^2+k^2]/4 \ . \end{aligned}$$

Since, at high energies the k spectrum is relatively independent of the phase of the material and the values of both k and $(n-1)$ are approximately proportional to the atomic density, R_N for liquid Hg can be obtained from that for solid Hg by

$$R_{N,\mathrm{liq}} = (D_{\mathrm{liq}}/D_{\mathrm{sol}})^2 R_{N,\mathrm{sol}} \ ,$$

where D_{liq} and D_{sol} are the atomic densities in the liquid and solid phases, respectively. Unfortunately, however, this method could not be employed, since no experimental values of R_N nor the optical constants for solid Hg are available for energies above 20 eV.

We have thus tried a second method of finding approximate values of R_N. This involves the use of known values of R_N for materials whose atomic numbers are close to that of Hg. Since for heavy atoms, like Hg with atomic number $Z=80$, the inner-shell atomic structure differs only slightly from one element to the next in the periodic table, it is to be expected that R_N for Hg in the high-energy region should be given approximately by the values for neighboring atoms if corrections are made for the different atomic densities. We have made two such estimates of the approximate values of R_N for liquid Hg, using literature values[34] of the optical constants from 20 to 900 eV for solid Au ($Z=79$) and solid Bi ($Z=83$). The density factors used in these conversions were $(D_{\mathrm{Hg}}/D_{\mathrm{Au}})^2=0.476$ and $(D_{\mathrm{Hg}}/D_{\mathrm{Bi}})^2=2.077$. The resulting values of R_N are shown in Fig. 16. It is seen that the values of R_N from both Au and Bi show good agreement above ~50 eV, indicating that this is a reasonable method of determining R_N at high enough energies for materials having high atomic numbers.

We have thus significantly reduced the large uncertainty which is inherent in the extrapolation to high energies used by Wilson and Rice. In the region from 50 to 900 eV we have used the average values of R_N obtained from Au and Bi. We have extrapolated these estimated values in the vicinity of 900 eV to higher energies assuming a E^{-4} dependence. R_N in this region should tend to the asymptotic form[11] $R_N=E_p^4/16E^4$ shown in Fig. 16 by a dashed line, where $E_p^2=4\pi Ne^2\hbar^2/m$ and N is the total electron density. The present approximate value at 900 eV is already quite close to that given by this asymptotic form, and it was found that, in the region of our main interest below 20 eV, uncertainties in the results of $\theta(E)$ arising from the form of the extrapolation above 900 eV are negligibly small. The only energy region where the extrapolation of R_N is still uncertain is between 20 and 50 eV, where an average of the values from Au and from Bi could not be assumed. We have performed Kramers-Kronig calculations using values of R_N from both Au and Bi. As may be seen in Fig. 16 these values of R_N may be regarded as upper and lower limits, respectively, of R_N for liquid Hg in this energy region. Our first calculation was performed using the values of R_N below 20 eV which were measured by Wilson and Rice,[23] coupled with R_N from 20 to 50 eV, first from Au and then from Bi. The values obtained for $\theta(E)$ below 5 eV are presented, in the form of $\theta(E)/E$ minus the Drude values, by solid lines in Fig. 17. The Drude values of θ measured by Schulz[22] are clearly outside the region given by the two results from Au and Bi, and the dependence on E is also not consistent with the calculated results.

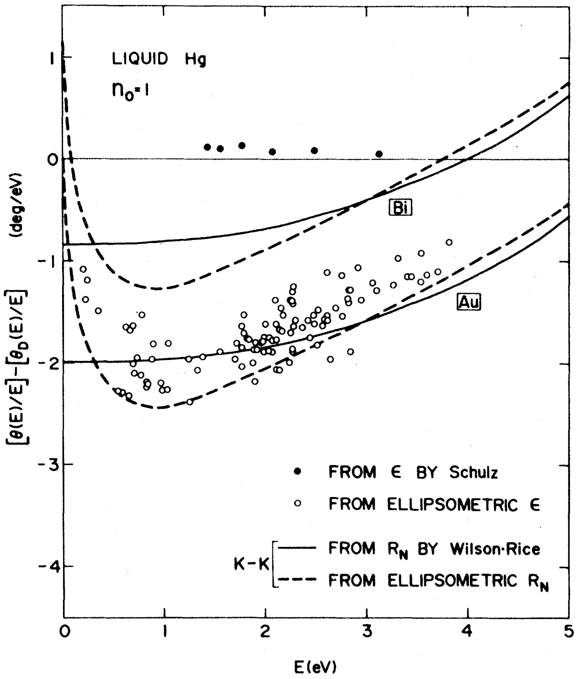

FIG. 17. $\theta(E)/E$ relative to the Drude values, calculated from R_N for a vacuum–liquid-Hg interface using a Kramers-Kronig relation, as a function of photon energy E, and the same quantity calculated directly from the dielectric function ϵ.

Our second Kramers-Kronig analysis was performed to check the consistency of the ellipsometric optical constants. The values of R_N between 0.2 and 4 eV, calculated for this purpose from the ellipsometric optical constants, are presented in Fig. 15. These values of R_N were combined with the experimental values of Wilson and Rice above 5 eV, yielding a complete spectrum of R_N except for the region between 20 and 50 eV. Again calculations were performed using values of R_N from Au and from Bi in this energy region. The values of θ obtained using this second pair of spectra for R_N are presented by dashed lines in Fig. 17. For comparison, values calculated directly from the ellipsometric optical constants are also shown. Nearly all of these values fall between the two dashed lines representing the Kramers-Kronig calculations involving ellipsometric data combined with Au or Bi data. The variation of the plotted function of θ with photon energy E obtained from direct calculation is also consistent with that obtained from the Kramers-Kronig analysis. By a proper choice of the values of R_N between 20 and 50 eV, it is therefore possible to reproduce the ellipsometric values of θ from the ellipsometric values of R_N by means of the Kramers-Kronig dispersion relation linking θ and R_N.

Our last Kramers-Kronig calculation was performed to determine new values of the optical constants for liquid Hg above 4 eV. Values of R_N from 20 to 50 eV were chosen so that, when combined with the ellipsometric R_N values from 0.2 to 4 eV and Wilson and Rice's R_N values from 5 to 20 eV as used in our second Kramers-Kronig analysis, the values of $\theta(E)$ obtained gave a good fit to the experimental points from ellipsometric ϵ values shown in Fig. 17. The values of the optical constants derived from R_N and θ, determined in this way, are presented in Fig. 18 by solid lines and are also tabulated in Table II. Shown by dashed lines in Fig. 18 are the averaged experimental results obtained by ellipsometry between 0.2 and 4 eV. These are almost exactly reproduced by the present Kramers-Kronig calculations. The small discrepancies between the Kramers-Kronig and the ellipsometric results observed below 1 eV seem to be due to a relatively large uncertainty in the ellipsometric optical constants in this region. The average of the Kramers-Kronig and ellipsometric values are tabulated in Table II for energies below 1 eV. The gross features of the spectra are not much different above 4 eV from those obtained previously by Wilson and Rice,[23] though significant numerical differences are found between them.

TABLE II. The real and imaginary parts of the dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ for liquid Hg as functions of the photon energy E.

E (eV)	ϵ_1	ϵ_2	E (eV)	ϵ_1	ϵ_2
0.2	−8.011	398.9	7.0	−0.0380	0.7216
0.4	−18.44	207.4	7.2	0.1732	0.8377
0.6	−27.18	139.3	7.4	0.3375	0.9372
0.8	−32.04	101.2	7.6	0.4411	1.065
1.0	−33.80	75.84	7.8	0.4747	1.158
1.2	−33.76	57.37	8.0	0.4866	1.209
1.4	−31.95	43.59	8.2	0.4895	1.229
1.6	−29.11	33.25	8.4	0.5005	1.216
1.8	−25.94	25.50	8.6	0.5242	1.194
2.0	−22.87	19.67	8.8	0.5630	1.171
2.2	−19.94	15.40	9.0	0.6035	1.147
2.4	−17.50	12.19	9.2	0.6526	1.123
2.6	−15.32	9.701	9.4	0.7173	1.105
2.8	−13.40	7.809	9.6	0.7975	1.129
3.0	−11.71	6.354	9.8	0.8158	1.181
3.2	−10.21	5.258	10.0	0.8052	1.204
3.4	−8.938	4.383	10.2	0.7870	1.200
3.6	−7.764	3.685	10.4	0.7777	1.174
3.8	−6.754	3.141	10.6	0.7815	1.146
4.0	−5.964	2.711	10.8	0.7910	1.114
4.2	−5.225	2.372	11.0	0.8067	1.088
4.4	−4.590	2.091	11.5	0.8616	1.031
4.6	−4.033	1.859	12.0	0.9139	0.9935
4.8	−3.534	1.662	12.5	0.9649	0.9599
5.0	−3.089	1.495	13.0	1.009	0.9384
5.2	−2.684	1.353	13.5	1.046	0.9190
5.4	−2.308	1.235	14.0	1.081	0.9003
5.6	−1.964	1.124	14.5	1.111	0.8855
5.8	−1.650	1.035	15.0	1.142	0.8687
6.0	−1.369	0.9515	15.5	1.174	0.8578
6.2	−1.099	0.8719	16.0	1.207	0.8529
6.3	−0.9604	0.8453	16.5	1.233	0.8592
6.4	−0.8339	0.8262	17.0	1.252	0.8629
6.5	−0.7182	0.8120	17.5	1.268	0.8663
6.6	−0.6166	0.7835	18.0	1.283	0.8745
6.7	−0.5071	0.7315	18.5	1.293	0.8776
6.8	−0.3602	0.6932	19.0	1.306	0.8789
6.9	−0.1975	0.6891	19.5	1.328	0.8794

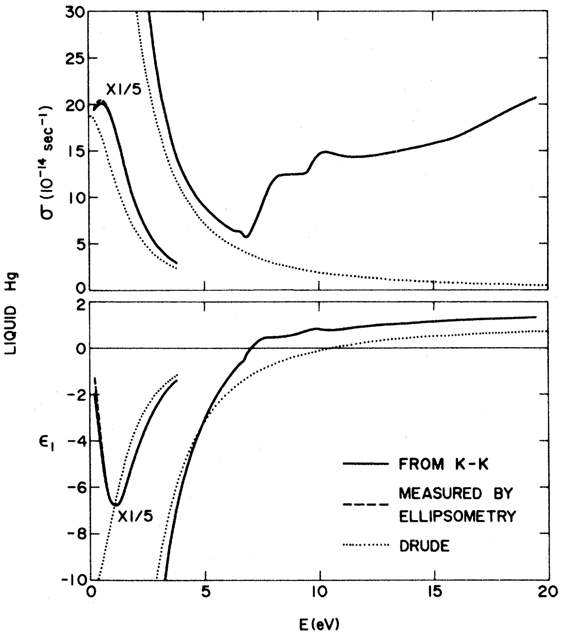

FIG. 18. Optical conductivity σ and the real part of dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ for liquid Hg as functions of photon energy E.

VII. SUMMARY AND CONCLUSIONS

After some general arguments on the experimental aspects of the detection of surface effects in ellipsometry, we have performed a systematic series of analyses of the previous and new experimental ellipsometric and reflectance measurements on liquid Hg. First we showed that there is no positive indication of surface effects in the previously published ellipsometric data. Next, new results have been presented of the simultaneous measurement of R_p, R_s, and Δ obtained at a quartz–liquid-Hg interface. These results have been interpreted as exhibiting consistency between the ellipsometric and reflectance measurements. The published reflectance measurements for liquid Hg have been critically reviewed. Finally, a Kramers-Kronig analysis has confirmed the validity of the ellipsometric optical constants and shown the Drude values to be non-self-consistent. The present analyses establish that, within experimental accuracies, the optical constants obtained from ellipsometric measurements do not seem to involve surface effects and hence are characteristic of bulk liquid Hg.

Since we have been dealing with a liquid surface, it has not been necessary, in this study, to consider the complexities arising from surface roughness. The relative ease in reproducing identical liquid surfaces also simplified evaluations of the experimental data. However, the series of analyses performed in this paper demonstrate a systematic procedure which would apply quite generally, and be useful in the detection of surface structures on homogeneous and isotropic bulk systems in both the liquid and solid phases.

Apparently, the widespread controversy concerning the experimental data for liquid Hg has discouraged theoretical investigations of the optical properties of liquid Hg, especially in the region of free-carrier absorption. To our knowledge, Smith's empirical formulation[37] in terms of strong backscattering of free carriers in liquid Hg is the only attempt which has treated directly the non-Drude behavior of the free-carrier absorption. However, despite the uncertainty over the optical properties, deviations from the nearly-free-electron model have been assumed in studies on various transport properties[38] and on electron density of states[39,40] in liquid Hg. It is hoped that the optical properties determined in the present study will encourage new theoretical efforts to understand the electronic excitations in liquid Hg.

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