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Reflection Spectra of Liquid Hg, In, and Bi from 2–20 eV

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The reflection spectra of liquids Hg, In, and Bi have been measured from 2 to 20 eV and the real and imaginary parts of the dielectric constant of Hg obtained from a Kramers-Kronig inversion of the data. For the case of liquid Hg it is found that: (a) The imaginary part of the dielectric constant has a Drude-like contribution and three absorption peaks in the range 2–20 eV. (b) To account for the imaginary part of the dielectric constant in the energy range below 7 eV it is necessary to extend the Drude theory to include more realistically the effects of electron-ion interaction. When this is carried through in the pseudopotential approximation, excellent agreement between theory and experiment is obtained. (c) Both the shape and positions of two absorptions, centered at 8.3 and 10.0 eV, are consistent with the interpretation that the $5d$ levels of Hg are not appreciably broadened in the liquid. The experimental splitting of 1.7 eV is in good agreement with the observed spin-orbit splitting of the $5d^9\,6s^2$ configuration of HgII, which is 1.87 eV. (d) There is a broad absorption centered at about 6.5 eV which at present cannot be unambiguously assigned. The possibility exists that this is an exciton state. Since the real part of the dielectric constant is zero at 7 eV, and thereby $\mathrm{Im}(1/\epsilon)$ has a maximum at 6.95 eV, the position of this absorption is consistent with the extra absorption recently predicted by Hopfield to arise from dynamical screening effects. (e) The data support the conclusion that liquid Hg may be described with the free-electron approximation over a wide range of energies and that the only interband excitations which occur are from the core states to the conduction state. There appear to be no analogs of the interband transitions from the conduction band to higher bands which occur in solids. For the case of liquid In and Bi it was not possible to make a Kramers-Kronig inversion of the data obtained. Nevertheless, it appears that: (a) Liquid In and Bi depart markedly from the free-electron model. (b) The reflectivity of In shows a peak centered at ∼20 eV which, by analogy with the interpretation given of the spectrum of liquid Hg, we believe to be an excitation of a $4d$ core electron. (c) As for Hg, there appear to be no interband transitions of conduction electrons to higher bands, such as occur in the solid on account of the zone structure.

I. INTRODUCTION

ONE of the more striking developments of recent years has been the demonstration that, as far as their properties are concerned, several liquid metals appear to be well described by the free-electron model.[1] For example, the Hall effect in many liquid metals is close to $(n_c e)^{-1}$, the value expected for a free-electron gas with density n_c of conduction electrons,[2,3] and in a number of cases the low-energy reflection spectrum has been shown to be consistent with the predictions of the Drude theory.[4,5] Ziman,[6] and Bradley, Faber, Wilson, and Ziman[7] have developed a model to describe the transport properties of liquid metals. In this model the electrons are considered to be in plane-wave states and to interact with the disordered ions of the liquid through a weak pseudopotential. The conductivity σ_0 is found by the conventional Boltzmann-equation method, in which there is established an equation for the rate of change of occupation probability f_k of the state $|\mathbf{k}\rangle$. As usual, the rate of change of the occupation probability arises from both the imposed electric field and the lattice scattering, and in the steady state the rate of change is zero. The resulting perturbed occupation probability can be regarded as a shift of the Fermi sphere in space. It is found that[6]

$$\frac{1}{\sigma_0}=\frac{m}{n_c e^2\tau}=\frac{m^2}{12\pi^2\hbar^3 n_c^2 e^2}\int_0^{2k_F} a(k)\,|u_k|^2 k^3\,dk\,, \qquad (1)$$

with $\mathbf{k}_F$ the Fermi wave vector, u_k the Fourier transform of the pseudopotential of an ion, and $a(k)$ the liquid-structure factor. In this way Ziman related the scattering of electrons on the Fermi sphere to the scattering of neutrons and x rays, and was able to use data from the latter experiments in his calculation of the conductivity of liquid metals. The model has been used by Bradley *et al.*,[7] to give an account of the transport properties of polyvalent metals, and more recently by Faber and Ziman[8] for liquid alloys.

The time τ is closely related to the time an electron stays in a state of given $\mathbf{k}$ before it is scattered by the ions of the fluid. Thus, one would expect a perturbed occupation probability to relax to the steady-state form in a time of order τ. If it is assumed that the approach of the current density $\mathbf{i}$ to its steady-state value is described by a relaxation-time equation, then it is immediately deduced that the conductivity for a field of angular frequency ω is of the form

$$\sigma(\omega)=\sigma_0/(1+i\omega\tau)\,. \qquad (2)$$

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[1] See, for example, A. I. Gubanov, *Quantum Electron Theory of Amorphous Conductors* (Consultants Bureau, New York, 1965), and N. E. Cusack, Rept. Progr. Phys. **26**, 361 (1963).

[2] A. Greenfield, Phys. Rev. **135**, A1589 (1964).

[3] E. G. Wilson, Phil. Mag. **7**, 989 (1962).

[4] L. Schultz, Advan. Phys. **6**, 102 (1957).

[5] J. N. Hodgson, Phil. Mag. **4**, 183 (1959); **5**, 272 (1960); **6**, 509 (1961); **7**, 229 (1962).

[6] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

[7] C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. **7**, 865 (1962).

[8] T. E. Faber and J. M. Ziman, Phil. Mag. **11**, 153 (1965).

The dielectric constant of the metal is then

$$\epsilon(\omega)=1-4\pi\sigma_0/i\omega(1+i\omega\tau). \tag{3}$$

These equations describe the Drude model for the properties of a metal.[9] The model can be generalized somewhat by introducing an effective mass m^*, different from the free-electron mass: then one can still use Eqs. (1) and (2) although the relaxation-time equation [right-hand side of Eq. (1)] will be changed. According to the Drude model, a particular metal for which n_c is known has optical properties which depend on only two parameters, say σ_0 and m^*. Experiments by Hodgson[5] and Schultz[4] have been carried out on several liquid metals in the infrared and visible range of the spectrum. Their data, with some exceptions, give not only a dielectric constant having the form of Eq. (3), but also values for the parameters σ_0 and m^* close to the dc conductivity and the free-electron mass, respectively. These experiments thus give added support to the nearly-free-electron (NFE) model.

There are several properties, however, which are not described by the NFE model. The Knight shift does not appear to change on melting,[1,10] and recently it has been shown that the Pauli spin susceptibility of lithium does not change on melting.[11] These results imply that there is no change of the density of states on melting, rather than a change to the free-electron value as expected on the basis of the NFE model.

The properties discussed thus far are dependent only on the properties of the electron states close to the Fermi energy, in fact (for other than the low-frequency optical properties), on states within kT of the Fermi energy. This paper describes an experiment to measure the optical properties of liquids Hg, In, and Bi over a wide range of energies, 2 eV–20 eV. This range of energy spans not only the Fermi energy but also the energy of some possible core excitations, It was hoped by this method to investigate electron states over a much greater energy range than any in previous experiments.

II. EXPERIMENTAL DETAILS

Methods of measuring optical constants can be divided into two categories. In the first, one measures two optical properties at each wavelength. In the second, one measures only one property, over a wide range of wavelengths, and uses Kramers-Kronig relations to deduce the optical constants. These relations are of the form of an integral, from zero to infinite wavelength, of some function of the measured property multiplied by a weighting function.

In the far ultraviolet it is difficult to polarize and analyze light beams and to find suitable transmitting windows. On account of these difficulties it proves very inconvenient to measure two optical properties at each wavelength. For example, lacking a simple transparent window material, the liquid sample is of necessity horizontal. Lacking a simple method of polarizing the incident light beam, one must choose a method suitable for any incident polarization. One possibility is to keep a fixed angle of incidence, and measure the reflectivity for incident polarizations of p and $-p$, which can be done by rotating the incident beam by $\pi/2$ about its direction. This in practice means rotating the whole monochromator by $\pi/2$, an operation which, although certainly possible, is extremely undesirable.

It was therefore decided to adopt a Kramers-Kronig method used with success by Philipp and others.[12] In terms of the real and imaginary parts of the refractive index n and k, respectively, the phase and amplitude of the reflection coefficient for light at normal incidence is

$$re^{i\theta}=\frac{n-ik-1}{n-ik+1}. \tag{4}$$

A Kramers-Kronig relation exists between r and θ, namely

$$\theta(\lambda_0)=\frac{1}{\pi}\int_0^\infty \frac{d\ln r(\lambda)}{d\lambda}\ln\left|\frac{\lambda-\lambda_0}{\lambda+\lambda_0}\right|d\lambda. \tag{5}$$

The method consists in measuring the reflectivity r^2 at an angle of incidence α close to normal incidence, over as wide a wavelength range λ as is possible, and using Eqs. (4) and (5) to deduce the optical constants.

There are two obvious limitations to this method. The first is that $r(\lambda)$ is only known for a finite range of wavelengths and to use Eq. (5) it is necessary to assume a plausible form for $r(\lambda)$ outside the measured range. In the case of metals one would expect the low-energy optical properties to be insensitive to the form chosen for r in the long-wavelength extrapolation. For, the reflectivity of metals in the range where $\omega\tau\ll 1$ is insensitive to details of the optical properties, its gross features being determined by the dc conductivity according to the Hagen-Rubens relation. We have concluded that this method alone cannot give good results for the low-energy optical properties. It must be coupled with either low-energy data obtained by methods of the first category or else some definite assumption about the low-energy behavior of the optical properties. These limitations in the case of Hg will be discussed in detail later.

A second limitation is that Eq. (4) is correct only for $\alpha=0$, yet in practice a finite angle of incidence (10°) was used. A Taylor expansion for $\rho(\alpha)$, the observed

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[9] See, for example, M. P. Givens, Solid State Phys. **6**, 313 (1958).

[10] W. D. Knight, Solid State Phys. 2, 93 (1956).

[11] J. E. Enderby, J. M. Titman, and G. D. Wignall, Phil. Mag. **10**, 106 (1964).

[12] H. R. Philipp, W. Dash, and H. Ehrenreich, Phys. Rev. **127**, 762 (1962); H. R. Philipp and E. A. Taft, *ibid.* **113**, 1002 (1959); **120**, 37 (1960); **127**, 159 (1962); H. R. Philipp and H. Ehrenreich, *ibid.* **129**, 1550 (1963); **131**, 2016 (1963). F. C. Jahoda, *ibid.* **107**, 1261 (1957).

reflectivity at angle of incidence α, deduced from the Fresnel relations, is

$$\rho(\alpha)=\rho(0)+p\rho(0)\alpha^2\frac{2n}{n^2+k^2}+O(\alpha^4)\,. \tag{6}$$

The reflectivity depends on the unknown polarization p of the incident beam, defined in terms of the electric vectors parallel and perpendicular to the plane of incidence by

$$p=\frac{e_\perp^2-e_\parallel^2}{e_\perp^2+e_\parallel^2}\,. \tag{7}$$

Thus the fractional error in r^2 due to treating the observed $\rho(\alpha)$ as if it were $\rho(0)$ is

$$\rho\alpha^2\frac{2n}{n^2+k^2}=0.062p\frac{n}{n^2+k^2}\,. \tag{8}$$

It is difficult to estimate p, which depends on the angle of incidence at the grating, the blaze of the grating, and the wavelength. For metals at long wavelengths, $k>n>1$, and the error is negligible. For short wavelengths $n\approx 1$ and $k<1$, and the error tends to 0.062 p. It is in principle possible for the error to be appreciable at some intermediate wavelengths. In the case of Hg it was shown that even for $|p|=1$ the error produces a negligible change in the optical constants.

Figure 1 illustrates the experimental arrangement. The light source was a discharge through H_2 or Ar gas at a pressure of approximately 1–0.1 mm. The source could be run with either a continuous discharge or a repetitive discharge of condensers charged to 10 kV. A 0.5-m Seya-Namioka spectrometer was used as a monochromator, and filters were used to reject the second and higher orders. The light detectors were photomultiplier tubes (EMI 9514B) coated with sodium salicylate. The coating, when hit by the uv light, fluoresced at wavelengths which passed through the tube envelope. These detectors were sensitive over the whole wavelength range used, 600–6000 Å. The intensities of the incident and reflected light beams were measured on different detectors, provision being made for sliding the sample into and out of the beam. Gas from the light source was restricted to flow into the monochromator only through the monochromator slit. With 4-in. diffusion pumps on the monochromator and sample chamber, pressures of 10^{-4} and 10^{-6} mm, respectively, could be obtained in these chambers while the light source was operating. The Hinteregger source and the Seya-Namioka type vacuum spectrometer were manufactured by the McPherson Instrument Corporation.

The sample was first melted under vacuum in a Pyrex tube. Any oxide floated to the surface at this stage. The metal was then pushed, by an overpressure of inert gas, through a fine capillary at the bottom of the tube from where it fell into a stainless steel sample container. In this way a surface of liquid metal was created while the sample chamber was at a low pressure. There was no change of reflectivity of the sample for the duration of an experiment. Moreover, different runs on different samples gave reproducible results. Thus we believe that the procedure described gave clean sample surfaces.

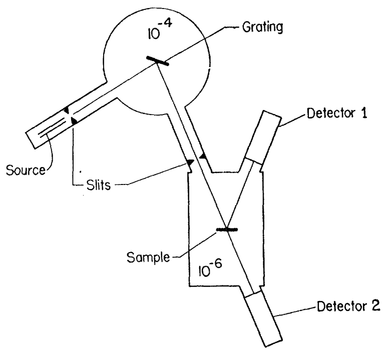

FIG. 1. The vacuum ultraviolet reflectance spectrometer.

The reflectivity of the sample is very small at short wavelengths. Therefore, when nominally working at a short wavelength, any long-wavelength stray light in the incident beam would be an appreciable proportion of the reflected beam intensity. This effect would have led to errors if measurements had been made using the continuum emission of the source. However, all measurements below 1500 Å were carried out using only the line emission of the source. For then, the height of a line above the continuum background is a true measure of the intensity at the wavelength of the line, and is independent of the stray light content which contributes only to the continuum background.

It was necessary to know the relative sensitivity of the two detectors in order to obtain an absolute reflectivity. This was found by measuring the reflectivity of Hg with one configuration of the photomultipliers and then reversing the positions of the detectors and remeasuring the reflectivity. In this way there are obtained two sets of values for the reflectivity, denoted by $\rho_1(\lambda)$ and $\rho_2(\lambda)$ The absolute reflectivity was taken to be $[\rho_1(\lambda)\rho_2(\lambda)]^{1/2}$. For this procedure to be precise it is necessary that a detector have the same sensitivity when observing the reflected and incident beams, i.e., that the detectors be hit in the same position by both the incident and reflected beams. The beam areas and positions were monitored, and great care was taken to ensure that this condition was satisfied. Numerous complete spectra were recorded (e.g., six for Hg), the detectors being reversed on successive runs. The independent sets of data for the absolute reflectivity agreed so well that we conclude that the relative detector sensitivity was constant throughout the runs. We therefore believe our reported reflectivities to be absolute values.

The Hg used was of triple distilled quality, as supplied by the Goldsmiths Company. The In and Bi metals, of 99.99% purity, were supplied by L. Light and Company. The experiments were carried out at temperatures of 25, 170, and 350°C, respectively, for Hg, In, and Bi. Figures 2, 3, 4, and 5 display the results of our experiments.

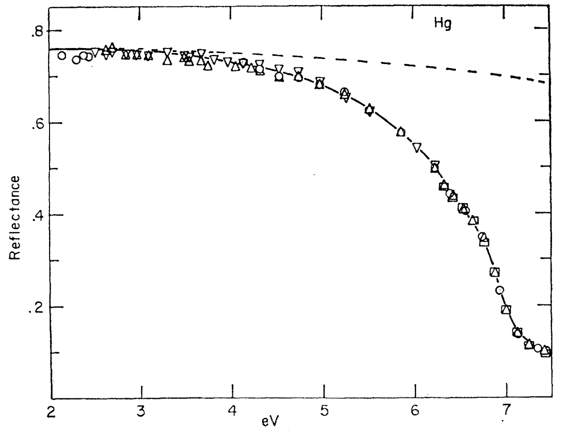

FIG. 2. The reflectance of liquid Hg from 2 to 8 eV. The dashed line is the reflectance predicted by the Drude theory. $T=25°C$.

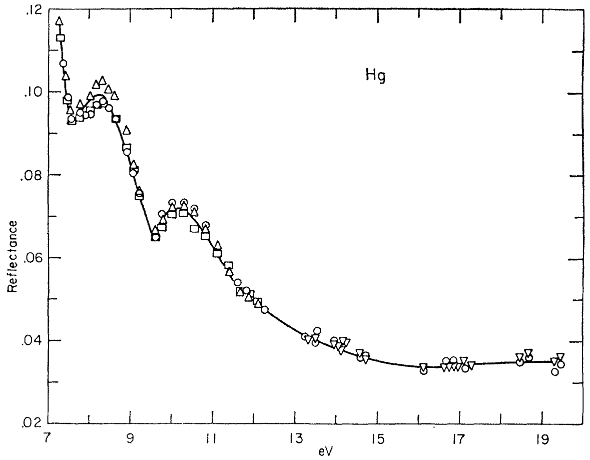

FIG. 3. The reflectance of liquid Hg from 7 to 20 eV.

III. THE OPTICAL CONSTANTS OF Hg

Also displayed in Figs. 2 and 6 is the reflectivity expected from the Drude model assuming an effective mass equal to the free-electron mass and two free electrons per atom. Data obtained by Hodgson[5] and Schultz,[4] by methods of the first category, are shown in Fig. 6. It is seen that Schultz's data agree closely with the Drude model, while Hodgson's is not of the Drude form. It has been pointed out that the normal reflectivity is insensitive to the optical constant at low energies. This is shown up in Fig. 7 where we show the reflectivity calculated from the Hodgson and Schultz data. Our data appear to be in agreement with Schultz and the Drude model. However, if a systematic error of a few percent were present, the conclusion would not be justified. In the absence of unambiguous evidence we have assumed that no systematic error is present in our data.

The optical constants of Hg were deduced from Eqs. (4) and (5) in the following way: For the range $600\,\text{Å}<\lambda<6000\,\text{Å}$ our reflectivity data were used for r^2. For the range $6000\,\text{Å}<\lambda$, the Drude free-electron form for r^2 was used. For the range $0<\lambda<600\,\text{Å}$, two forms for r^2 were used. The first was

$$r^2(\lambda)=r^2(600\,\text{Å})\exp[\beta(\lambda-600\,\text{Å})], \qquad (9)$$

and the value of β was chosen to give agreement of the optical constant with the free-electron value at 6000 Å. The second form chosen was

$$r^2(\lambda)=r^2(600\,\text{Å})(\lambda/600\,\text{Å})^4. \qquad (10)$$

This is the form to be expected at frequencies greater than the plasma frequency. Equation (10), when used in Eq. (5), gave a value for $\theta(\lambda)$. A value $\theta(\lambda)+\beta$ was used in place of $\theta(\lambda)$ in Eq. (4), and the value of β chosen to give agreement at 6000 Å as before. Both these procedures give almost identical optical constants save at wavelengths very close to 600 Å.

The effect of non-normal incidence was estimated as follows. r^2 was first taken to be $\rho(\alpha)$, the data measured

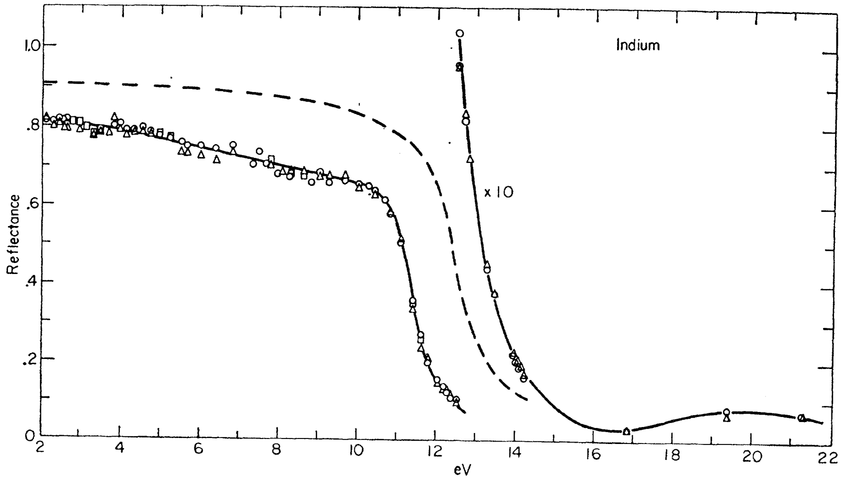

FIG. 4. The reflectance of liquid In from 2 to 21 eV. The dashed line is the reflectance predicted by the Drude theory. $T=170°C$.

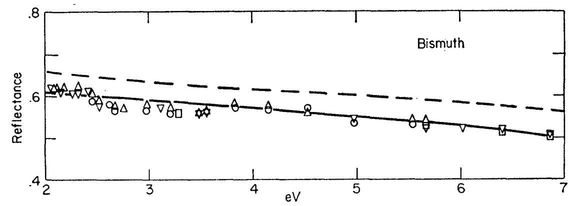

FIG. 5. The reflectance of liquid Bi from 2 to 7 eV. The dashed line is the reflectance predicted by the Drude theory. $T=300°C$.

at a 10° angle of incidence. Then, from the deduced optical constants a correct value of r^2 was found by using Eq. (6) which, in turn, was used to deduce a new set of constants. This procedure, which quickly converged, was carried out for the cases $p=\pm 1$ (completely polarized light). The correction to r^2 and to the optical constants was negligibly small, and so we believe there are no errors introduced in the optical constants deduced because the measurements were not carried out at normal incidence.

IV. INTERPRETATION OF THE SPECTRUM OF Hg

A. Free-Electron Absorption

Figures 8 and 9 show the real and imaginary dielectric constants of liquid Hg, ϵ_1 and ϵ_2, deduced from the data, and compare them to the constants expected from the Drude theory for $(m^*/m)=1$. The excellent agreement at 2 eV exists on account of the way the reflectivity extrapolations were chosen. Figure 6 shows the way our result joins on to that of Schultz. The agreement of ϵ_2 with the Drude value is quite close up to 7 eV. We consider the departure of ϵ_2 from Drude form at higher energies to be due to the onset of further electronic transitions. This rather sudden departure entails, as can be seen from the Kramers-Kronig relations, a more gradual departure of ϵ_1 from Drude form, spread over a range of energies, as is indeed observed. We reserve discussion of these further electronic transitions until a later section.

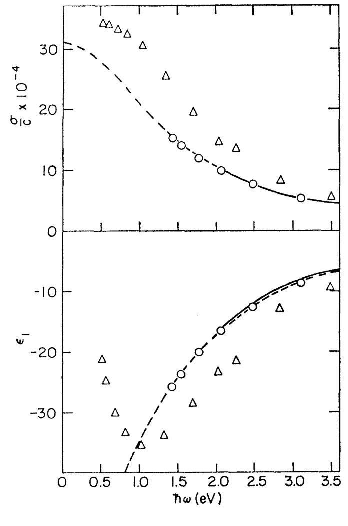

FIG. 6. Comparison of our determination of the real (ϵ_1) and imaginary (σ/c) parts of the dielectric constant of Hg with the data of other investigators. Drude theory (- - -); data of Schultz (○); data of Hogdson (△); this paper (——).

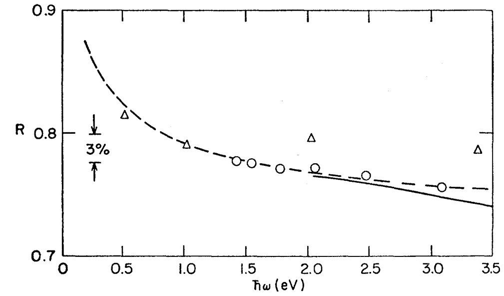

FIG. 7. A comparison of the low-energy reflectance data with the predictions of the Drude theory for liquid Hg. The symbol code is the same as in Fig. 6.

As the energy is increased from 2 to 5 eV, the observed ϵ_2 falls until it is 10% below the Drude value. This discrepancy we believe to be greater than our experimental error. We have studied in some detail one mechanism which can account for the difference, namely an amended Drude (A.D.) theory, which takes better account of the electron scattering by the lattice than does the Drude theory. It may be however, that an equally successful explanation could be found by allowing a departure of the energy-momentum dispersion law from simple parabolic form.

As discussed in Sec. I, a current $\mathbf{i}$ can be regarded as due to a displacement of the Fermi surface. In particular, in the Drude model a current $\mathbf{i}(\omega)$ is due to an oscillation of the Fermi surface at an angular frequency ω. This description neglects, however, the essentially quantum-mechanical nature of the interaction with the electric field. For, a current $\mathbf{i}(\omega)$ is due to absorption of photons of energy $\hbar\omega$ which cause electrons to be excited with energies $\hbar\omega$. When $\hbar\omega$ is approximately the Fermi energy E_F electrons throughout the volume of the Fermi sphere can interact with the light. It is by no means clear that this situation can be described by a small high-frequency oscillation of the Fermi sphere.

Because of the perturbation of the electron motion arising from interaction with the ions of the fluid, the

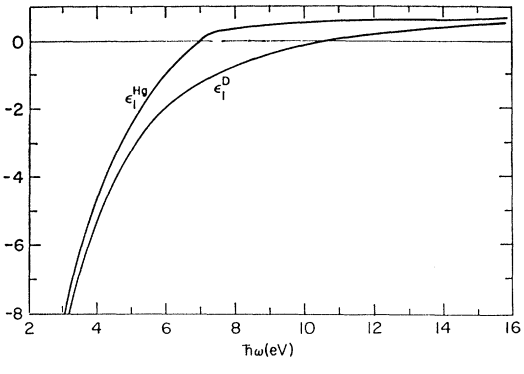

FIG. 8. The real part of the dielectric constant for liquid Hg.

electron energies are uncertain to an extent $\hbar/\tau$. For photon energies $\hbar\omega > \hbar/\tau$ we can envisage an electron to be excited from a state $|\mathbf{k}_1\rangle$ to a quite distinct state $|\mathbf{k}_2\rangle$, such that $E_{k_2} - E_{k_1} = \hbar\omega$. The momentum change of the electron $\hbar(\mathbf{k}_2 - \mathbf{k}_1)$ is due to elastic scattering by the ions of the fluid, and the electronic transition is one of second order (occurring via a virtual intermediate state), the electron gaining its energy from the photon and its momentum from the ions of the fluid. The contribution of this process to the imaginary part of the dielectric constant has been investigated by Dumke[13] in connection with free-carrier absorption in semiconductors.

It may be shown that

$$\frac{\epsilon_2^{\mathrm{AD}}}{\epsilon_2^{\mathrm{D}}} = 2\left(\frac{E_{\mathrm{F}}}{\hbar\omega}\right) \frac{\int_{k_m}^{k_{\mathrm{F}}} k\,dk \int_{K\min}^{K\max} a(K)\,|u_k|^2 K^3\,dK}{k_{\mathrm{F}}^2 \int_0^{2k_{\mathrm{F}}} a(K)\,|u_K|^2 K^3\,dK}, \tag{11}$$

where

$$\begin{aligned} (K_{\min}+k)^2 &= (K_{\max}-k)^2 = k^2 + (2m/\hbar^2)\hbar\omega, \\ k_m^2 &= (2m/\hbar^2)(E_{\mathrm{F}} - \hbar\omega); \quad E_{\mathrm{F}} > \hbar\omega, \\ k_m^2 &= 0; \quad E_{\mathrm{F}} < \hbar\omega. \end{aligned} \tag{12}$$

Thus, for a particular liquid, the departure of ϵ_2 from the Drude form can be computed if u_k and $a(k)$ are known. In Fig. 10 are displayed the values of the ratio $(\epsilon_2^{\mathrm{AD}}/\epsilon_2^{\mathrm{D}})$ for Na and Hg, evaluated with the neglect of the dependence of u_k on $\mathbf{k}$, using the values of $a(k)$ reported by Gingrich and Heaton[14] and Vineyard.[15] Also displayed in Fig. 10 is $(\epsilon_2^{\mathrm{AD}}/\epsilon_2^{\mathrm{D}})$ for a completely random liquid, i.e., for which $a(k) = 1$.

The curve for ϵ_2^{AD} for Hg according to this model is shown in Fig. 9. It is in closer agreement with the data than is the Drude model in the range 2–5 eV, and we believe that even with the neglect of the k dependence of u_k, which is not necessary, this model is a more accurate description of absorption of electromagnetic energy by free electrons that is the Drude model. It is only at energies comparable to the Fermi energy that the predictions of the two models differ.

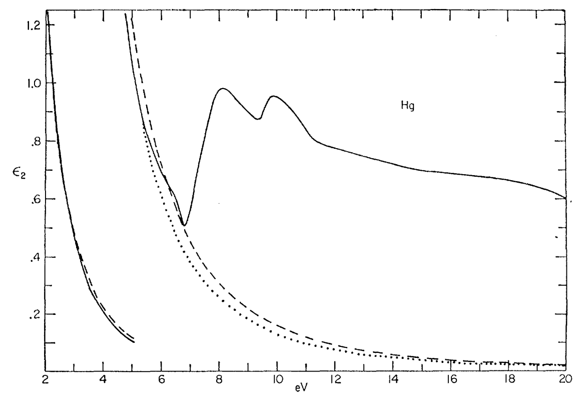

FIG. 9. The imaginary part of the dielectric constant for liquid Hg. Note the change of scale (×10) at 5 eV. Drude theory (····); amended Drude theory (– – –); experimental data (——).

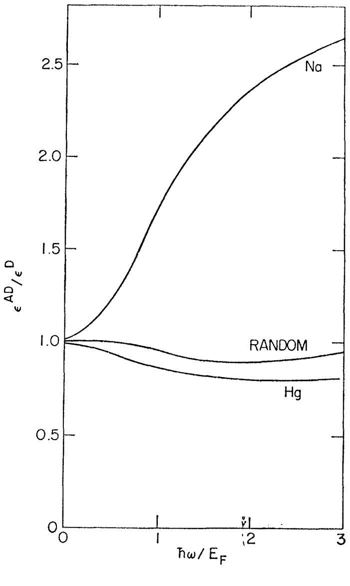

FIG. 10. The ratios of the imaginary parts of the dielectric constant predicted by the Drude and amended Drude theories for three examples.

B. Core Excitation

Considering the dielectric constant to be the sum of a free-electron part ϵ_2^{AD}, and a part depending on further electronics transitions ϵ_2^{c} we write

$$\epsilon_2 = \epsilon_2^{\mathrm{AD}} + \epsilon_2^{c}, \tag{13}$$

so that ϵ_2^{c} can be obtained by subtraction. The result is shown in Fig. 11. We first discuss the structure of ϵ_2^{c} for $\hbar\omega > 7$ eV.

The peaks at 8.3 and 10.0 eV we assign to excitation of core electrons. From available atomic data[16] the lowest energy for excitation of the $5d^9 6s^2 6p$ configuration of Hg(I) is 8.55 eV. The energy difference between the $J = \frac{3}{2}$ and $J = \frac{5}{2}$ states of Hg(II) in the configuration $5d^9 6s^2$ is $E(\frac{3}{2}) - E(\frac{5}{2}) = 1.87$ eV. This is to be compared to a splitting of 1.7 eV for the peaks of ϵ_2^{c}. It is, therefore, plausible that these peaks represent the onset of excitation from a level that is split by spin-orbit interaction.

Further evidence that more than two valence electrons are contributing can be obtained from the application of sum rules. It is shown by, for example, Landau and Lifshitz[17] that

$$\int_0^{\infty} \omega\epsilon_2(\omega)\,d\omega = \tfrac{1}{2}\pi\omega_p^2 = 2\pi^2 N e^2/m, \tag{14}$$

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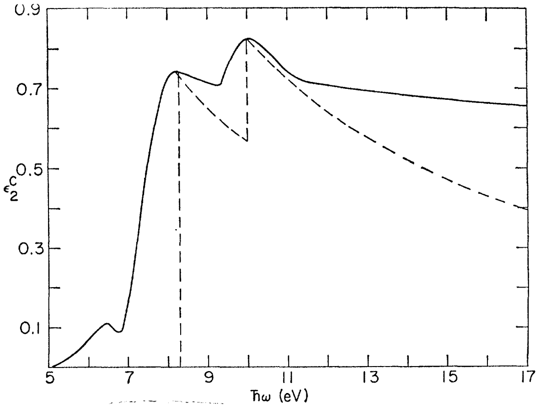

FIG. 11. Excess absorption (imaginary component of dielectric constant) over that predicted by the Drude theory, as a function of photon energy. Experimental data (——); Theory [Eq. (22)] (- - - -).

where N is the *total* number of electrons per unit volume. It is argued by Nozieres and Pines[18] and by Ehrenreich and Philipp[19] that if one writes

$$\int_0^{\omega} \omega\epsilon_2(\omega)\, d\omega = \tfrac{1}{2}\pi\omega_p^2(\eta(\omega)) = 2\pi^2 e^2 \eta(\omega)/m\,, \qquad (15)$$

then $\eta(\omega)$ can be regarded as the number of electrons which contribute to the dielectric constant up to the energy $\hbar\omega$. The value of $\eta(\omega)$ computed from our data, shown in Fig. 12, tends towards 2 electrons/atoms as $\hbar\omega$ increases to 7 eV, but then increases above the value 2. Eventually it would be expected to saturate at 12 electrons/atom provided that the $4p^6$ electrons were not excited at that stage. This is further evidence that d electrons begin to contribute to ϵ_2 when the energy reaches 7 eV.

It should be noted that, in common with the results of other investigators, $\eta(\omega)$ does not quite reach the value 2 in the quasiplateau region around 6 eV. A linear extrapolation of the values of $\eta(\omega)$ at high energy back to the low-energy region shows that the "missing" charge density all appears in the energy range 8–16 eV, and is of exactly the right amount to lead to 2 valence electrons per atom for Hg.

It is convenient to examine a simple model so as to understand the form of dielectric constant to be expected from these transitions. We assume the d levels to have zero width in energy, and also that there is no overlap of d electron wave functions. Of course, there will be some electronic overlap between the wave functions of neighboring ions, the d levels will have nonvanishing width, and a d hole will move through the liquid, but at a very much slower rate than the conduction electrons. Denote the wave function of electron j in the d state of atom j by $\phi(j)$. As an approximation to a conduction-electron wave function we consider a plane wave orthogonalized to all the occupied, localized core states on all sites i. It may then be shown that the contribution to the dielectric constant from excitation of a core electron is just

$$\epsilon_2{}^c(\omega) = \frac{16\pi^2}{V^2}\left(\frac{e}{m\omega}\right)^2 |\langle \mathrm{OPW}, \mathbf{k}_j | \mathbf{p}_j | \phi(j)\rangle|^2 \delta(\hbar\omega - E_{0j})\,. \qquad (16)$$

(OPW = orthogonalized plane wave.) For holes with total angular momentum J, there are $(2J+1)$ degenerate states on each of n atoms/unit volume that can also contribute to $\epsilon_2{}^c(\omega)$. If $|p|^2{}_{J_j}$ is the average of the $(2J+1)$ squares of matrix elements (the average is the same for all atomic sites), then the dielectric constant due to creation of holes of angular momentum J is

$$\epsilon_2{}^c(\omega) = \frac{2J+1}{V} 16\pi^2 \left(\frac{e}{m\omega}\right)^2 \textstyle\sum_j n_c |p|^2{}_{J_j} \delta(\hbar\omega - E_{0j})\,, \qquad (17)$$

the sum being over all vacant states $|\mathbf{k}_j| > |\mathbf{k}_\mathrm{F}|$ of the conduction band. This expression is similar to that derived by Ehrenreich and Cohen.[20] To proceed further we will assume that $|p|^2{}_{J_j}$ is independent of $\mathbf{k}_j$, so that it can be removed from the summation. The summation, which is essentially a measure of the density of final conduction-band states, can then be carried out to give

$$\begin{aligned} \epsilon_2{}^c(\omega) &= 16 \frac{(2J+1)e^2(2m)^{1/2}}{\hbar}\left(\frac{n_c |p|^2{}_J}{2m}\right)\frac{(\hbar\omega - E_G)^{1/2}}{(\hbar\omega)^2}\,; \\ &\qquad \hbar\omega > E_G + E_\mathrm{F}\,, \qquad (18) \\ \epsilon_2{}^c(\omega) &= 0\,; \quad \hbar\omega < E_G + E_\mathrm{F}\,. \end{aligned}$$

It may be reasonably remarked that the approximation in which $|p|^2{}_{J_j}|$ is assumed independent of $\mathbf{k}_j$

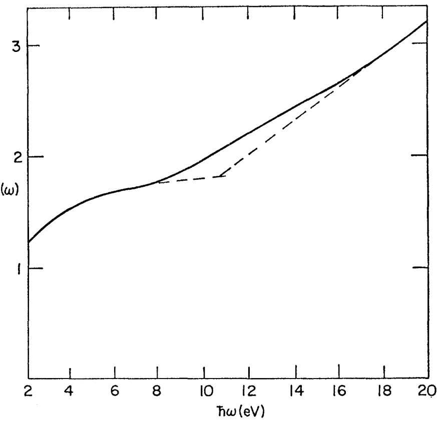

FIG. 12. Test of the Kramers-Kronig sum rule. The dashed lines indicate the extrapolation of the Drude contribution to higher energy, and the linear extrapolation of the d-electron contribution to lower energy.

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[18] P. Nozieres and D. Pines, Phys. Rev. **111**, 442 (1958).

[19] H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).

[20] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

TABLE I. Parameters to fit ϵ_2.

J	E_F(eV)	E_G(eV)	$\left(\frac{n_c\lvert k\rvert^2 J^2}{2m}\right)$
$\frac{5}{2}$	6.48	1.46	0.028
$\frac{3}{2}$	6.84	3.16	0.021

is very crude. This is, indeed, true. If the conduction-electron wave function were a pure plane-wave function and the d-electron wave function were sufficiently localized, then the momentum matrix element would be just the wave vector multiplied into the d-electron wave function in the momentum representation. A calculation of this type leads to a modification of the form of $\epsilon_2{}^c(\omega)$ such that the high-energy tail falls off less rapidly with increasing energy than the case of $|p|^2{}_{J_j}$ independent of $\mathbf{k}_j$. However, there are very important differences between a simple plane wave and the orthogonalized plane wave which is a more accurate representation of the conduction-electron wave function. From pseudopotential theory we find that core effects are very approximately of the form such that a plane-wave state is renormalized by the factor $[1-$(core volume)/(volume per ion)$]$, and such a correction is quite large. In view of the lack of accurate OPW functions for the valence electrons and the inherent lack of accuracy in using a simple plane wave we propose to use the more approximate procedure of regarding $|p|^2{}_{J_j}$ to be independent of $\mathbf{k}_j$.

The form $\epsilon_2{}^c(J=\frac{5}{2})+\epsilon_2{}^c(J=\frac{3}{2})$ is compared to the experimental dielectric constant in Fig. 11. The parameters used for the fit are given in Table I. Consideration of the energy width of the excited states due to their finite lifetime, and of the finite width of the d levels, would cause the simple line shape we have deduced to resemble more that found experimentally. The broadening is, in fact, smaller than the spin-orbit splitting, and this suggests that the d-level widths are less than 1 eV.

Note added in proof. Professor T. Loucks of Iowa State University has kindly sent us some preliminary relativistic calculations of the band structure of crystalline Hg. He concludes that about half of the separation between the $5d(\frac{5}{2})$ and $5d(\frac{3}{2})$ levels arise from the crystal field; and, from the flatness of the bands, concludes that this splitting is relatively insentitive to the detailed crystal structure, arising mainly from the deviation of the potential outside the core from spherical symmetry. In Loucks' calculation the d bands intersect the conduction band. The relevance of these calculations for interpretation of the electronic states of the liquid is not completely clear, but we must conclude that the interpretation we have given may need modification.

C. Other Absorption Mechanisms

An examination of the data displayed in Fig. 11 shows an absorption centered at 6.5 eV which we have not yet examined. It should be pointed out that if $\epsilon_2{}^c$ were found by subtraction of $\epsilon_2{}^{\mathrm{D}}$ rather than $\epsilon_2{}^{\mathrm{AD}}$ from the experimentally deduced ϵ_2, then this absorption would be less pronounced. In this sense, then, the existence of an absorption at 6.5 eV is a less well-substantiated feature of the experimental observations. In the following we shall assume that the absorption is real and must correspond to some as yet unexplored excitation.

Two possible mechanisms immediately spring to mind to explain the extra absorption at 6.5 eV: that it is an exciton or that it corresponds to a dielectric constant effect resulting from dynamical screening of the interactions in the liquid metal.[21] At present we cannot decide which of these alternatives is correct. If the resonance corresponds to an exciton, then the binding energy must be ~1.8 eV. Although the exciton will be degenerate with conduction-electron states, this will shorten the lifetime but not necessarily preclude its existence. A calculation of the exciton binding energy including the effects of interaction screening does not seem possible at present. The other possibility, namely a Hopfield resonance,[21] is predicted to occur when $\mathrm{Im}(1/\epsilon)$ has a maximum. Our data show a maximum of $\mathrm{Im}(1/\epsilon)$ at 6.95 eV, and it is not possible to assert that the broad transition observed may not in fact be centered at higher energy than 6.5 eV. Since the oscillator strength for the Hopfield resonance in Hg is not known, we cannot identify the observed resonance using that criterion. We therefore leave, as an open problem, the identification of the resonance centered at ~6.5 eV.

V. INTERPRETATION OF THE SPECTRA OF In AND Bi

In the cases of In and Bi we have been unable to obtain the dielectric constants from the reflection spectra. This section, therefore, beyond presenting the data, contains only a limited discussion of the optical properties of In and Bi.

Figures 4 and 5 show the results of different measurements on different samples of In and Bi, the surfaces of which were prepared in a vacuum of 10^{-6} mm, as described for Hg. The reflectivity of Hg was periodically remeasured throughout the studies of In and Bi, and the optics calibrated against the Hg reflectivity. The important point is that what was actually measured was the reflectivity of In and Bi relative to Hg. Thus, any systematic error in the absolute reflectivity affects equally each of the metals Hg, In, and Bi.

As discussed previously, to use the Kramers-Kronig relations to compute the optical constants it is necessary not only to have some knowledge of, or assume some form for, the reflectivity outside the wavelength range for which it is measured, but also to have some knowledge of, or assume some form for, the optical constants

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[21] J. Hopfield, Phys. Rev. **139**, A419 (1965).

[22] J. Friedel, Advan. Phys. **3**, 446 (1954).

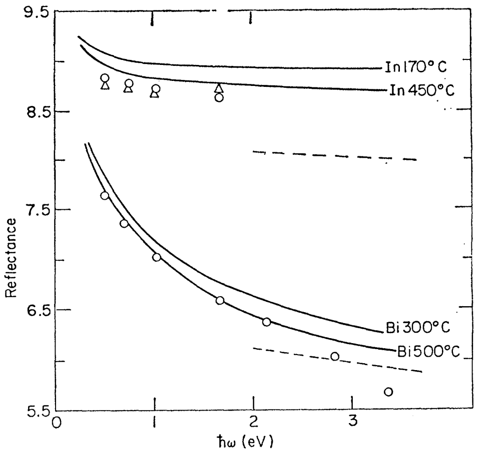

FIG. 13. The low-energy reflectances of In and Bi. Drude theory, $m^*/m=1$ (——); Hodgson's data (○) ($T=500$°C for Bi, 450°C for In); this paper (– – –) ($T=300$°C for Bi, 170°C for In).

at low energies. Displayed in Figs. 4 and 5 are the reflectivities calculated according to the Drude model for $m^*/m=1$. The reflectivity is insensitive to the optical constants at low energy, and the departure of our reflectivity, in absolute magnitude, from the Drude value, is in this sense very large. For example, to make the Drude reflectivity agree with our values at 2 eV requires $m^*/m \approx 0.2$, a value of the effective mass which we regard as extremely unlikely. We thus conclude that our data show that the optical constants at low energy in In and Bi are not of Drude form. Unfortunately, the data give no positive guide whatsoever to the actual form of the optical constants at low energy.

In Fig. 13 we show the reflectivities calculated from the data of Hodgson,[5] obtained at 450 and 500°C for In and Bi, respectively. His optical constants agree quite well, he claims, both in frequency dependence and absolute magnitude, with the Drude theory. We can only conclude that our data do not agree with that of Hodgson. It has to be borne in mind, of course, that our respective experiments were carried out at different temperatures.

Given these conclusions, we have been unable to make any use of Eq. (5) and our data to deduce quantitative information about the optical constants.

We realize, of course, that these conclusions are very sensitive to a systematic error of several percent in our reflectivity, and it is mere semantics to point out that a systematic error cannot be ruled out *a priori*. We believe, however, from the way the experiments were performed, that there is no systematic error in the relative reflectivities of our metals. Table II compares, at 2 eV, our data to Hodgson's data, and also both sets of data to the Drude reflectivity calculated for the appropriate temperature. Scaling of our data by a common systematic error factor cannot bring the reflectivities of all our metals to agree with either Hodgson's data or the Drude theory. A further conclusion, independent of the question of systematic error in our data, is that in some of these metals the optical constants cannot be of the Drude form.

TABLE II. Comparison between present data and Hodgson's data.

Metal		Hg	In	Bi
Percent below Drude-theory value at 2 eV	Hodgson	−4	1	0
	Present work	0	10	7
Percent that present data are below Hodgson's data at 2 eV		4	7	6

The reflectivity of In shows a peak centered at ~20 eV. This we believe is due to excitation of $4d$ core electrons. From available data[16] the energy required to excite the $4d^9 5s^2$ configuration of In(III) is 14.3 eV: The energy required to excite the $4d^9 5s^2 5p^2$ configuration of In(I), although not observed, would be expected to be greater than this. Apart from this peak there appears to be no other structure to the reflectivity.

VI. CONCLUSIONS

The data for Hg suggests that for this liquid metal the free-electron model is valid over a wide range of energies, and that the only interband excitations occuring are from the core states to the conduction state. In contrast, although incomplete, the data for In and Bi suggest that these metals depart from the free-electron model. In all cases there are no analogs of the interband transitions from the conduction band to higher bands which occur in solids on account of the zone structure. At least in this latter sense, the dielectric constant of liquid metals is simpler than that of solid metals.

ACKNOWLEDGMENTS

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