Optical properties of liquid Na between 0.6 and 3.8 eV*

T. Inagaki,[†] E. T. Arakawa, R. D. Birkhoff,[‡] and M. W. Williams

Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 17 November 1975)

Ellipsometric measurements have been performed on free surfaces of liquid Na at 120°C between 0.6 and 3.8 eV. The optical conductivity below 2.2 eV agrees well with the classical Drude values, and that above 2.2 eV exhibits a weak absorption analogous to the interband absorption in the solid phase. Analysis of the real part of the dielectric function gives $m*/m = 1.17$ (below 2.2eV) and 1.10 (above 2.2 eV) and a plasma energy of 5.70 ± 0.05 eV.

We report new results for the optical constants of liquid Na obtained by ellipsometric measurements between 0.6 and 3.8 eV of photon energy. Mayer and co-workers[1,2] were the first to measure the fundamental optical spectra of alkali metals in the solid and liquid phases over a fairly wide spectral range from the infrared to the near ultraviolet. Their results on both the solids and the liquids exhibit striking anomalies which cannot be explained by simple theories, and consequently for the last decade a number of theories[3-8] have been proposed going beyond the single-electron picture for electronic excitations to try to account for their results. Later, Smith[9] performed more careful measurements on solid alkalis, and found no anomalous behavior in his results and fairly good qualitative agreement with the predictions of the simple nearly-free-electron model. His results on solid Na have been confirmed recently by us[10] using a somewhat different experimental technique. Little work has been done on liquid alkalis and, to our knowledge, the results of Mayer et al.[1,2] are still the only experimental data available in the literature. The present study was undertaken to reinvestigate the region of the anomalous effects observed in liquid Na.

The basic instrument used in this study was an ellipsometer oriented to measure a horizontal reflecting surface under ultrahigh-vacuum conditions, the details of which have been presented elsewhere.[10] The angle of incidence was set at 60° with an accuracy of ± 5 min, and the alignments of the polarizer and the analyzer relative to the plane of incidence were carried out by the absolute-minimum method of McCrackin et al.[11] The applicability of this method to our instrument has been checked carefully.[10] Among the numerous techniques to determine the two ellipsometric parameters $\tan\psi = r_p/r_s$ and $\Delta = \Delta_p - \Delta_s$ for reflecting surfaces, where r_p and r_s are the reflection amplitudes and Δ_p and Δ_s are the phase shifts upon reflection of the p and s components of the incident photons, respectively, the intensity method due to Beattie[12] was employed in this study because of its relatively high sensitivity[10] in determining ψ. In this method, the anisotropy of the detectors or of any other optical elements is often a source of serious error. Corrections for the anisotropy were made on ψ measured at the liquid-Na surface using the values of ψ measured for total reflection at the interface between a strain-free quartz prism and vacuum. A solid sample of Na metal with the original purity higher than 99.5% was melted at a base pressure of 2×10^{-9} Torr in a tantalum dish in a furnace consisting of a molybdenum heater and a stainless-steel heat shield. After the sample melted, the liquid surface was scraped by a stainless-steel plate, which was movable along guide rails in the horizontal direction, to remove the oxide skin. The measurements for a set of the ellipsometric parameters at a given wavelength were completed within 2 min after scraping, and the scraping was repeated before measurements at each wavelength, although no appreciable change was found in the measured ellipsometric parameters up to at least 4 h after scraping. The liquid temperature was maintained at 120 ± 1 °C, and the pressure was 2×10^{-8} Torr at these temperatures due to the vapor pressure of the liquid sample. At temperatures above 125 °C deposition of Na vapor on the windows of the sample compartment became appreciable during measurements, and below 115 °C the liquid sample solidified onto the edge of the scraper plate when it was placed on the sample surface for scraping. These problems made the measurements quite difficult. One of the difficulties in optical studies on liquid-metal surfaces is that the impurities may diffuse to the surface and affect the results significantly, even though the concentration of impurities in the bulk is quite low. The main impurities in our Na sample were K and Li. The possibility of such an effect was eliminated by removing the oxide layer from the liquid surface after repeated melting and solidification.

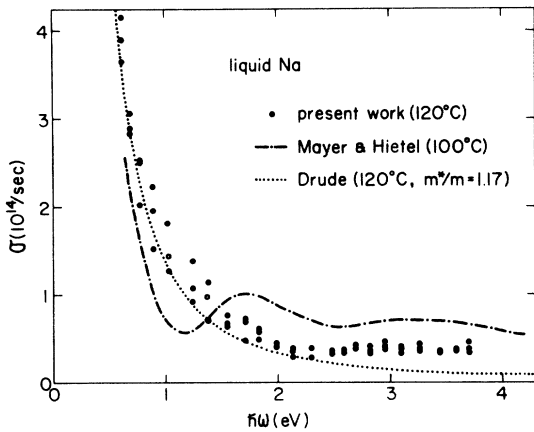The results for the optical conductivity σ defined by $\sigma = \omega\epsilon_2/4\pi$, where ϵ_2 is the imaginary

FIG. 1. Optical conductivity σ of liquid Na vs incident-photon energy.

TABLE I. Optical constants n and k for liquid sodium as a function of photon wavelength λ.

λ (μm)	n	k
2.0	0.31	8.43
1.8	0.23	7.64
1.6	0.18	6.87
1.4	0.15	6.00
1.2	0.12	5.17
1.0	0.087	4.31
0.9	0.072	3.86
0.8	0.059	3.37
0.725	0.048	3.04
0.675	0.041	2.83
0.625	0.034	2.60
0.58	0.029	2.38
0.54	0.026	2.19
0.50	0.028	2.00
0.48	0.030	1.90
0.46	0.032	1.80
0.44	0.033	1.70
0.42	0.034	1.59
0.40	0.035	1.49
0.38	0.036	1.38
0.36	0.036	1.27
0.345	0.037	1.19
0.335	0.037	1.13

part of the dielectric function and ω is the angular frequency of the incident photons, are presented in Fig. 1, together with those of Mayer and Hietel[2] measured at 100 °C. Also shown in Fig. 1 are the Drude values for the conductivity due to the free-carrier absorption defined by

$$\sigma_D = \frac{ne^2\tau}{m^*}\left(\frac{1}{1+\omega^2\tau^2}\right),$$

where n is the density of the free-carriers and τ is the relaxation time. τ was evaluated to be 1.653×10^{-14} sec from the literature values[13] of the dc conductivity $\sigma_{dc} = ne^2\tau/m^* = 8.607\times10^{16}$ sec^{-1} and of the free-carrier density $n = 2.405\times10^{22}$ cm^{-3} at 120 °C. The effective mass m^* of the free carriers was taken equal to 1.17m, where m is the electron mass. This value of m^* was deduced from the experimental values of the real part of the dielectric function, ϵ_1, in the infrared region as described below.
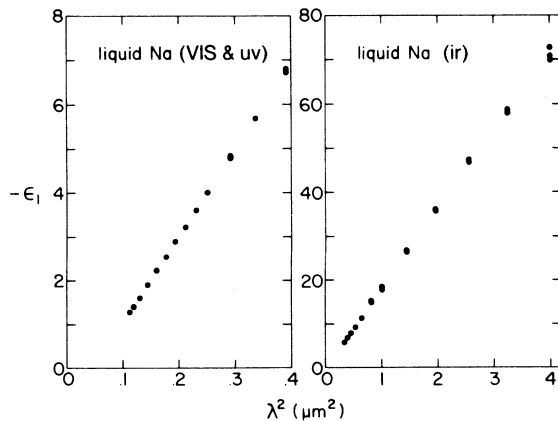

FIG. 2. Real part of the dielectric function of liquid Na at 120°C vs λ^2, the square of the wavelength of the incident photons.

The present results for σ are fairly close to the Drude values and in striking disagreement with those of Mayer and Hietel. In the region below 2.2 eV, quantitative agreement with the Drude curve is quite good, although the scatter of the data points is rather large as compared with that in the higher-energy region. There is no trace in our data of the anomalous peak around 1.7 eV reported by Mayer and Hietel. It thus seems that the absorption properties below 2.2 eV can be described well by the simple Drude model of free-carrier absorption. This result is in contrast to the case of solid Na,[9,10] where the observed conductivity in the free-carrier absorption region is considerably larger than the Drude value. Above 2.2 eV, the observed conductivity exhibits a significant departure from the Drude curve. The discrepancy with the Drude values well exceeds the limit of experimental error, and we could not find any systematic experimental error to account for it. Apparently, this structure above 2.2 eV is a remnant of the interband absorption with threshold at around 2 eV found by Smith[9] and by us[10] in solid Na. The magnitude of this absorption in the liquid is (20–25)% of that in the solid. Smith[14] showed that the interband transition in solid Na should not persist into the liquid phase upon melting. His calculations revealed that in the liquid the Drude and the interband ab-

sorption regions should merge smoothly and that there should be no structure in the conductivity curve. Such behavior has indeed been found most clearly in Al,[15] and Hg,[16] in both of which prominent structures due to interband transitions from the valence band to the conduction band are found in the solid phase, but are absent in the liquid. However, the present data for liquid Na can be separated into two regions, the Drude absorption region and the region of a liquid analog of the interband absorption, and the threshold for the latter is clear at 2.2 eV.

The results for ϵ_1, the real part of the dielectric function, are plotted in Fig. 2 as a function of

λ^2, the square of the wavelength λ in μm. These data were analyzed in a conventional manner using the expression $\epsilon_1 = 1 + 4\pi n_0 \alpha - ne^2\lambda^2/\pi m \text{*}c^2$, where n_0 is the atomic density and α is the ion-core polarizability. This gives $m\text{*} = (1.17 \pm 0.01)m$ below 2.2 eV and $(1.10 \pm 0.01)m$ above 2.2 eV, a plasma energy defined by $\epsilon_1 = 0$ at 5.70 ± 0.05 eV, and $4\pi n_0 \alpha = -0.05 \pm 0.05$. The result for $m\text{*}$ below 2.2 eV is comparable with that from Mayer and Hietel's data at 100 °C, $m\text{*} = 1.19m$, despite the large discrepancies in σ.

Table I shows the best fit values of the optical constants n and k for liquid solium, obtained from this study.

---

†Also at Dept. of Physics, The University of Tennessee, Knoxville. Present address: Dept. of Physics, Osaka Kyoiku University, Osaka, Japan.

‡Also at Department of Physics, The University of Tennessee, Knoxville.

[1]H. Mayer and M. H. El Naby, Z. Phys. **174**, 289 (1963).

[2]H. Mayer and B. Hietel, *Optical Properties and Electronic Structure of Metals and Alloys,* edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 47.

[3]M. H. Cohen and J. C. Phillips, Phys. Rev. Lett. **12**, 662 (1964).

[4]A. W. Overhauser, Phys. Rev. Lett. **13**, 190 (1964).

[5]J. J. Hopfield, Phys. Rev. A **139**, 419 (1965).

[6]K. L. Kliewer and R. Fuchs, Phys. Rev. **172**, 607 (1968).

[7]C. Y. Young, Phys. Rev. **183**, 627 (1969).

[8]N. M. Miskovsky and P. H. Cutler, Phys. Rev. B **5**, 1265 (1972).

[9]N. V. Smith, Phys. Rev. **183**, 634 (1969); Phys. Rev. B **2**, 2840 (1970).

[10]T. Inagaki, L. C. Emerson, E. T. Arakawa, and M. W. Williams, Phys. Rev. B (to be published).

[11]F. L. McCrackin, E. Passaglia, R. R. Stromberg, and H. Steinberg, J. Res. Natl. Bur. Stand. (U. S.) A **67**, 363 (1963).

[12]J. R. Beattie, Philos. Mag. **46**, 235 (1955).

[13]J. W. Mausteller, F. Tepper, and S. J. Rodgers, in *Alkali Metal Handling and Systems Operating Techniques* (Gordon and Breach, New York, 1967), Appendix I, p. 215.

[14]N. V. Smith, Phys. Rev. **163**, 552 (1967).

[15]J. C. Miller, Philos. Mag. **20**, 1115 (1969).

[16]W. E. Mueller and J. C. Thompson, Phys. Rev. Lett. **23**, 1037 (1969).