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# Optical properties of liquid aluminum in the energy range 1.2–3.5 eV

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The optical properties of clean liquid aluminum were investigated in the energy range 1.2–3.5 eV using pulsed-dye-laser spectroscopic ellipsometry. Aluminum specimens were electromagnetically levitated and melted, and any residual aluminum oxide and nitride phases were vaporized at high temperatures ($T > 1850$ K). An automated dual-detector rotating analyzer ellipsometer that moved to a set of fixed azimuths was employed to measure the optical constants, using a nitrogen laser-pumped dye laser as the light source for wavelengths from 360 to 990 nm. Measurements were obtained over the full wavelength range at ca. 1550 K and at five wavelengths over the temperature range 1200–1800 K. Liquid aluminum exhibits an absorption peak near 1.4 eV (ca. 885 nm) like that of the solid which arises from interband transitions in the same energy range. This existence of an absorption peak at 1.4 eV is supported by the results of previous electron-induced x-ray emission, electron energy loss, and NMR experiments as well as theoretical analyses of the structure of liquid aluminum. The reasons that this peak was not observed in the previous ellipsometric work are discussed.

## I. INTRODUCTION

The optical properties of liquid metals and alloys are of considerable interest in connection with radiative heat transfer, thermophysical property measurements, and electronic structure. The latter interest has led to ellipsometric measurements on several liquid-metal systems, which were reviewed by Arakawa, Inagaki, and Williams.[1]

The optical properties of clean liquid aluminum are the subjects of this paper. Their behavior is of particular interest in the near-infrared spectral range, where solid aluminum exhibits a characteristic absorption peak at ca. 1.5 eV photon energy. This peak has been observed for the liquid in this work and was not found in earlier ellipsometric studies,[2,3] but has been predicted to occur on the basis of x-ray-emission data.[4]

The available sources of optical-property data and band-structure calculations for solid aluminum were reviewed by Smith, Shiles, and Inokuti.[5] They describe the effects of temperature, crystallinity, and sample preparation methods on the prominent 1.5-eV absorption peak exhibited by clean aluminum. The original data for the solid in this energy range are provided by Mathewson and Myers,[6] Shiles *et al.*,[7] Bennett, Silver, and Ashley,[8] and others. Properties in the vicinity of the 1.5-eV peak have been determined at temperatures up to 600 K.[9]

There are only three reported ellipsometric studies of the optical properties of liquid aluminum. The measurements by Miller[2] were at 0.8–4 eV, those of Comins[10] were at 0.15–0.35 eV, and Havstad[3] has recently provided data in the 0.13–2.6-eV range. Miller[2] reported a nearly Drude-like behavior for the liquid, with $n^*/n = 1.03$ and no evidence of an absorption peak in the 1.5-eV range. Havstad[3] also found no absorption peak in his data for the liquid.

On the basis of soft-x-ray spectra measured on the $L_{23}$ emission for both solid and liquid aluminum, Catterall and Trotter[4] proposed that the liquid structure resembled a basically ordered lattice having randomly arranged defects. Additional support for this view was provided by Knight, Berger, and Heine,[11] who suggested, on the basis of theoretical considerations as well as NMR, spin susceptibility, and x-ray-diffraction data, that the electronic properties and the short-range structure of aluminum were expected to undergo little change upon melting.

The x-ray-emission experiments were sensitive to the presence of oxide on the metal surface. Catterall and Trotter[4] reported that the structure in the x-ray-emission spectrum of liquid aluminum disappeared when their specimens contained oxide impurities on the surface. Also, in studies of the $K\beta$ emission, Fischer and Baun[12] found that the linewidth decreased from 13.4 to 5.6 eV when the liquid temperature was increased considerably above the melting point. Baun (cited by Powell[13]) also reported that the change in the $K\beta$ emission linewidth was reversible with temperature. These changes in the nature of the $K\beta$ emission could be explained by oxide contamination effects, such as those observed by Catterall and Trotter. That is, aluminum oxide would precipitate from the metal at low temperatures and interfere with the observation of emission from the metal. At high temperatures the oxide would dissolve or evaporate to allow measurements on the metal surface.

Measurements on vapor-quenched aluminum[9,14] show the 1.5-eV peak in specimens deposited at higher temperatures. For deposition at room temperature or above, the peak is characteristic of solid aluminum. The magnitude of the 1.5-eV absorption decreased at lower deposition temperatures and was practically absent in films deposited at 25 K. The optical properties of films formed at 25 K were quite different from either the solid or the liquid, but did display evidence for the 0.5-eV interband absorption of solid aluminum.

In light of the literature, it was considered appropriate to eliminate oxides from the aluminum specimens investi-

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gated in the current work. This was done by conducting the optical-property measurements on electromagnetically levitated liquid aluminum and by heating the specimens to temperatures sufficient to vaporize oxides, decompose nitrides, and also reduce the oxygen and nitrogen content of the metal well below the solubility limits. The thermodynamic basis for this cleaning procedure was first presented by Brewer and Rosenblatt,[15] and its successful application was described in our earlier paper.[16] In this earlier work, we obtained ellipsometric measurements of the optical properties of clean liquid aluminum at $\lambda=632$ nm and at temperatures from 1000 to 1800 K.

In this work we have obtained ellipsometric measurements of the optical properties of liquid aluminum over the 1.2–3.5-eV photon energy range. The experiments were unique in two respects. First, the liquid was levitated and heated in an electromagnetic field to eliminate container interactions and contamination. Second, a pulsed-dye laser was used as a light source which allowed high spectral resolution to be obtained. We also report measurements on the temperature dependence of the optical properties at five selected wavelengths over a temperature range 1200–1800 K. We provide an examination of the potential sources of error in the measurements, as well as a complete description of the experimental apparatus.

## II. EXPERIMENTAL DETAILS

The present study was conducted on electromagnetically levitated specimens. Optical properties were determined using a pulsed-dye-laser spectroscopic ellipsometer. The following sections describe first the electromagnetic levitation and heating apparatus and the optical design for measurements on specimens in this apparatus. Then the purification of specimens and conditions used for optical-property measurements are described. Finally, the spectroscopic ellipsometric system is described in some detail. A schematic drawing of the apparatus is given in Fig. 1.

### A. Electromagnetic levitation and optical systems

One of the unique features of the present work is the use of *no containers* in the study of liquid metals at high temperatures. Electromagnetic levitation and heating were used to suspend and melt the liquid-aluminum specimens. The system consisted of a high-vacuum chamber, a 5-kW radio-frequency generator that operated at ca. 250 kHz with a 4:1 step-down transformer that supplied power to the levitation coil. Aluminum-metal specimens of ca. 5 mm diameter were readily levitated in a 4–5-mm-wide gap between the two sets of upper and lower turns of the levitation coil. Further details of the electromagnetic levitation system including work with pure aluminum and with liquid-Ti-Al alloys can be found in two earlier publications.[16,17]

Specimens weighed about 0.150 g, which formed 5-mm-diam liquid droplets. Once a specimen was levitated, melted, and purified of oxide and nitride by heating to high temperatures, the spectroscopic ellipsometric measurements could be conducted over an extended period of time. Levitation of the specimens was possible for periods up to 12 h limited only by deposits of aluminum on the electromagnetic coil due to vaporization at high temperatures. The levitated specimens were stirred by the electromagnetic field and exhibited a 20–30-Hz rotation rate and small-amplitude surface oscillations. These motions led to an averaging of the ellipsometric measurements over all of the material in the specimen.

The system was designed to operate with a horizontal optical plane. The incoming laser beam illuminated approximately 50% of the curved specimen surface where it was reflected into a large cone. The angle between the incoming source and the ellipsometer axis was fixed. The ellipsometer analyzer was positioned by translating it to the spatial location where light reflected at the known angle of incidence was collected and analyzed.

The instrument employed an optical system with an $F$ number of 30 to collect light over a small cone. By ray tracking the optical system, the typical reflecting spot size from a 5-mm-diam liquid (sphere) was calculated to

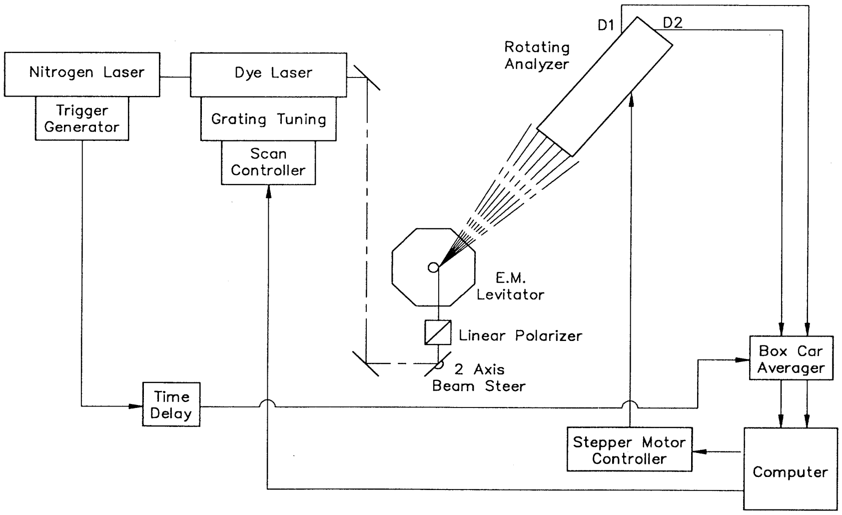

FIG. 1. Schematic diagram of the pulsed-dye-laser spectroscopic ellipsometer, the electromagnetic levitator, and the data-acquisition and control apparatus.

be an approximately elliptical shape with dimensions of 600 $\mu$m × 200 $\mu$m.

Apparent specimen temperatures were measured using a calibrated optical pyrometer (Pyro Photo II, Pyrometer Instrument Company, Northvale, NJ) whose operating wavelength was 650 nm. Spectral emissivity corrections to the apparent temperatures were obtained from an earlier study[16] and from additional measurements of the spectral emissivity obtained in this work.

### B. Specimens and purification

The aluminum specimens were obtained from Ventron-Alfa, Beverly, MA and were stated to contain $< 10$ ppm metallic impurities. Mass spectrometric analyses of the bulk material for oxygen gave about 10 ppm oxygen in the as-received materials and in specimens which had been purified by levitation heating. The as-received material contained some surface oxide which was not measured by the analysis. The analytical results on processed specimens showed that the surface oxide was removed by the purification procedure, which is described below.

Highly emissive aluminum oxide was always observed on the surface of the liquid upon initial melting of the aluminum specimens in the levitation coil. This indicated that, because of the presence of surface oxide, the total initial oxygen content of the specimens was on the order of 1000 ppm, the estimated solubility of oxygen in liquid aluminum at the process temperature.[18] The areas covered by the oxide phase were easily distinguished from the duller low-emissivity liquid-metal surface. They remained until the specimens were heated and processed for several minutes at high temperatures and then did not reappear when the specimens were cooled to lower temperatures.

The mechanism by which the oxide phase was removed has been described.[15,16] Under the reducing conditions of an oxide-metal mixture, the oxide evaporated as the gaseous suboxide $Al_2O$. A vapor pressure of $Al_2O$ on the order of $10^{-6}$ bar was required to remove the oxide in a few minutes, and this resulted in a process temperature requirement of 1430 K or greater. A temperature of approximately 1800–1900 K was actually used. Under these conditions the oxygen-metal ratio in the vapor phase was much greater than that in the condensed phase and rapid vaporization of the oxide occurred. After this was complete (as shown by a uniform specimen brightness), the process was continued to reduce the concentration of dissolved oxygen to about 10 ppm, well below the solubility limit. The removal of oxygen was facilitated by the intense electromagnetic stirring of the specimens [typical fluid-flow velocities are 20–50 cm/s (Ref. 19)].

Thermodynamic calculations were performed[16] to determine the conditions for removal of any aluminum nitride (AlN) which may have been present on the surface. The maximum temperature used to remove oxygen from the specimens, 1900 K, was estimated to be adequate to also remove AlN by decomposition to gaseous nitrogen. It is recognized that oxygen impurities are predominant. Once the initial high specimen temperatures were reached, substantial Al vapor was released (and condensed onto the chamber surfaces) to serve as a getter for gaseous impurities in the chamber atmosphere.

All of the experiments were conducted under ca. 0.4 bar of pure helium. This resulted in a sufficient convective-heat-loss rate that the specimens could be maintained in the desired temperature range while also being levitated. The inert-gas atmosphere also minimized vaporization of aluminum during the extended duration of the experiments.

Once the specimen was heated to the high initial temperature, the flow of He gas into the levitation chamber was stopped, and the optical-property measurements were initiated. Changes in the specimen temperature in the range 1200–1800 K were made by adjusting the radio-frequency power. The optical properties of liquid aluminum were measured vs wavelength at a temperature of $1550 \pm 10$ K and vs temperature at several selected wavelengths. It was determined that the temperature dependence of optical properties was sufficiently small that errors due to $< \pm 10$ K temperature fluctuations between measurements at different azimuths of the analyzer were negligible. Surface temperature gradients in the levitated sample were measured with the optical pyrometer to be $\pm 5$ K in agreement with the predictions of Ref. 19.

### C. Ellipsometry

A high-intensity laser source was used to achieve good precision in the ellipsometric measurements despite the high intensity of incandescent radiation from the hot specimens. A Molectron UV-24 nitrogen laser pumped a Molectron DL-II dye laser to provide laser radiation in the wavelength range 360–990 nm (3.44–1.25 eV). The laser had a pulse width of 7 ns and was operated at a repetition rate of 20 Hz. A total of 22 different dyes were required to obtain laser radiation over all but a few narrow wavelength regions of the spectrum, with a spectral resolution of approximately 10 GHz. Incident laser-pulse energies were adjusted to 1 mJ or less in a 0.5-cm-diam beam.

The incident source optics included a two-axis beam steering device followed by a 2-mm aperture and two Glan Thomson linear polarizers. The second polarizer was fixed at +45° with respect to the plane of incidence, and the first could be rotated to adjust the light intensity incident on the specimen. Small variations in the beam location ($\pm 1$ mm) occurred when different dyes (and dye cuvettes) were used and were steered to place the intense portion of the beam onto the aperture. The first polarizer and the defining aperture were also located on two-axis translators to facilitate alignment of the laser beam incident on the specimen. The second polarizer was of the Glan Thomson design with a clear aperture of 18 mm and was fixed in place.

The method used for ellipsometry was based on the work of Beattie[20] and a modification of Beattie's technique developed by Krishnan *et al.*[21] A beam-splitting Glan Thomson prism was used as the analyzer to provide the orthogonal components of the polarization for simultaneous detection. This analyzer provided a beam deviation (45°) between the two orthogonal components which was independent of wavelength. Measurements of the light intensities could simultaneously be recorded for individual azimuth pairs of {0°,90°} and {45°,−45°} or {135°,45°} by rotating the analyzer to three fixed orientations.

The analyzer optics consisted of a strain-free fused-silica lens that focused the image of the specimen onto a 1-mm-diam aperture. A second lens placed behind this aperture collimated the beam through the beam-splitting Glan Thomson analyzer crystal. A pair of lenses were used to refocus the light onto the active surface of the two photodetectors. The analyzer prism, detector assembly, and secondary optics were all rigidly mounted to a motorized rotation stage which had a precision of ±0.002° and an absolute accuracy of ±0.01° in rotation. A set of 15 narrow-band interference filters (70–100 nm bandwidth) were used to reduce incandescent radiation incident on the detectors.

Light-intensity measurements were made using a pair of high-speed Si photodiodes (Hamamatsu S1722-02). The output of these detectors was ac coupled to an EG&G model 165 boxcar averager with two model 162 gated integrators. The detector electronics converted the incident 7-ns laser pulses into electronic pulses of width approximately 150 ns. Gate widths of approximately 50 ns centered on the electronic pulses were used in signal processing. Outputs of the boxcar averager were measured with a laboratory computer with the aid of a 16-bit analog-to-digital plug-in card. The computer also operated motors which rotated the analyzer and operated the dye-laser monochromator between measurements.

In practice, it was necessary to operate the boxcar such that the input signals averaged no greater than 20% of full scale. This prevented momentry overloads and nonlinearities when the reflected laser intensity fluctuated due to specimen motion.

The intensity ratios $I(0°)/I(90°)$ and $I(135°)/I(45°)$ and/or $I(45°)/I(-45°)$ were determined by allowing the analyzer to rotate to fixed positions. Equations given in previous papers[20–22] were used to obtain the ellipsometric parameters, $\psi$ and one or two values for $\Delta$, from these intensity-ratio measurements. No systematic differences in the equivalent measurements of $\Delta$ were observed.

The method used to calibrate the ellipsometer has been described by Hunderi and Rydberg.[23] The ellipsometer was first placed in a straight-through configuration with its axis colinear with the incident dye-laser beam. The zero azimuth of the analyzer in the polarizer frame of reference was determined by extinction through one of the exit paths of the analyzer. The source polarizer was then rotated to 45° while keeping the analyzer at 0°. The intensity ratios were recorded for dye-laser wavelengths from 375 to 990 nm. The source polarizer was then rotated to 0° and the procedure repeated with the analyzer at both ±45° positions.

Under ideal conditions, intensity ratios for all of the calibration measurements would be unity. In practice, the ratios differed from unity by a few percent, as a result of variations in detector sensitivities, polarizer defects, transmission errors, and small residual birefringence that may have been present in the optical components. For given wavelength the calibration intensity ratios for the three analyzer positions were equal within experimental error. They were fit to a wavelength-dependent function which was used to correct detected intensity ratios.

The angle of incidence used for all of the ellipsometric measurements was 67.38°±0.16°. This angle was set by adjusting the incident laser beam and the analyzer axes perpendicular to the entrance and exit windows of the chamber. The angle was measured with the help of a pentaprism used to reflect the incident beam through an angle of exactly 135°.

## III. RESULTS

### A. Analysis of errors

The precision of the measurements was influenced primarily by two factors. First, specimen rotation and oscillations caused fluctuations in the collected light intensities. This required the gated integrators to be operated at 10–20 % of full scale in order to prevent momentary signal overload conditions. Second, small drifts on the order of 0.1% of full scale, but occasionally larger, occurred in the dc offsets of the two boxcar output channels. Since the integrators were operated at small fractions of full scale, errors in the measured intensities typically as large as 1% were possible. Consecutive measurements of intensity ratios at a fixed wavelength were in approximate agreement with this estimate. Other sources of random error in the measured intensities were negligible.

Small changes in the specimen temperature (less than 25 K) between intensity-ratio measurements at different analyzer settings contributed a further source of random error. These errors were analyzed on the basis of measured values for the temperature dependence of the intensity ratios.

Absolute accuracy was influenced by two factors. First, because a cone of light was analyzed for its polarization, an error resulted because the properties were calculated using the mean angle of incidence. The laser-beam divergence, less than 1 mrad, was negligible. Second, the ellipsometer calibration function was estimated to have errors as large as ±1%, which varied with wavelength.

A final source of error was evident in the fact that a set of data obtained for a single laser dye would sometimes exhibited a larger deviation from the complete set of data than the analyzed errors would allow. Also, measurements in the overlapping wavelength range for two laser dyes sometimes exhibited small systematic differences, of magnitude expected for 1% errors in intensity measurements. Both of these sources of error were attributed to drift in the dc offsets between the dc-offset and optical-property measurements. Separate measurements confirmed that the offsets were sensitive to changes in the ambient laboratory temperature and could change by the amounts required to explain these additional deviations in the results.

Table I summarizes the error analysis in terms of its

TABLE I. Errors in the measurements of $\varepsilon_1$ and $\sigma$ at 1500 K.

| | $-\varepsilon_1$ | | | $\sigma$ $(\Omega\,\text{cm})^{-1}$ | | |
|---|---|---|---|---|---|---|
| Wavelength (nm) | 420 | 625 | 970 | 420 | 625 | 970 |
| Mean values | 19.3 | 40.6 | 73.5 | 1750 | 4200 | 5800 |
| Random errors | | | | | | |
| Intensity measurement (±1%) | 0.04 | 0.18 | 0.49 | 67 | 130 | 190 |
| Temperature variation (25 K) | 0.03 | 0.05 | 0.13 | 21 | 32 | 32 |
| Systematic errors | | | | | | |
| Calibration (±1%) | 0.06 | 0.28 | 0.74 | 100 | 190 | 280 |
| Incidence angle (±0.9°) | +0.08 | +0.17 | +0.31 | +7 | +18 | +24 |
| Maximum error | | | | | | |
| Random | 0.05 | 0.19 | 0.51 | 70 | 130 | 190 |
| Total | 0.11 | 0.37 | 0.95 | 120 | 230 | 340 |
| | 0.6% | 0.9% | 1.3% | 6.8% | 5.5% | 5.9% |

effects on the measured polarization ($\varepsilon_1$) and optical conductivity ($\sigma$) values at three wavelengths. The last two lines of the table give the analyzed total uncertainties for the optical properties.

### B. Optical-property results

The preliminary optical-property experiments on aluminum were the first experiments conducted with the new apparatus. They were used to develop operating procedures which would yield accurate and precise measurements, to obtain data used to evaluate errors, and to determine the laser dyes required to establish adequately the wavelength dependence of optical properties for liquid aluminum. The results from these preliminary experiments are not presented because they were not conducted with the care used to obtain the final results. In the final experiments, the offsets were frequently measured, the intensities were limited to less than 20% of full scale, the incident laser beam was carefully aligned and centered on the optical components, the electromagnetic levitation chamber was purged overnight for each experiment, the specimens were always purified by heating to high temperatures prior to the optical-property measurements, additional laser dyes were used to fill gaps in the data, measurements at sufficiently small wavelength intervals were obtained for each dye, and the laboratory temperature was more stable, which reduced offset drifts.

The final results presented here were collected in separate experiments on five different specimens. Figure 2 shows the optical conductivity $\sigma=4\pi\varepsilon_0 nk\nu$, and Fig. 3 gives the polarization $\varepsilon_1=n^2-k^2$ for liquid aluminum plotted as a functions of photon energy; $n$ and $k$ are the indices of refraction, $\varepsilon_0$ is the permittivity of vacuum $(8.854\times10^{-12}$ F/m), and $\nu$ is the frequency of the light. Also presented in the figures are the data for the solid at room temperature which were recommended by Smith, Shiles, and Inokuti,[5] shown as a solid line, and the results

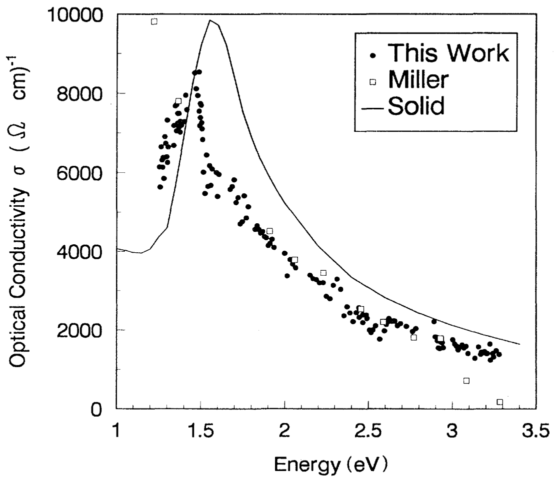

FIG. 2. Optical conductivity of liquid aluminum at 1550 K vs photon energy. Data of Miller (Ref. 2) are given by open squares. Data for the solid at room temperature (Ref. 5) are given by the solid line.

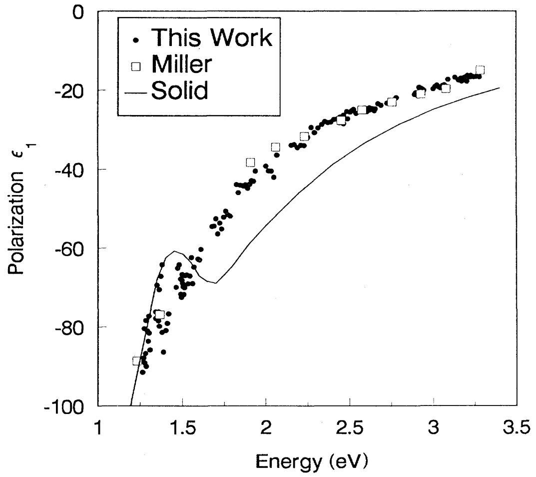

FIG. 3. Polarization $\varepsilon_1$ of liquid aluminum at 1550 K vs photon energy. Data of Miller (Ref. 2) are given by open squares. Data for the solid at room temperature (Ref. 5) are given by the solid line.

of Miller[2] for liquid aluminum, given by the open squares.

The durations of the experiments were such that, for each specimen, data were obtained over a limited set of wavelength ranges with a few laser dyes. In compiling the results, six data points were rejected because the light intensities were too large or because large specimen temperature variations occurred during the measurements. The results of one entire experiment, obtained on a particular specimen, were rejected. Contamination of this specimen was suspected, perhaps as a result of contact with deposits that had formed on the electromagnetic levitation coil in a previous experiment. During the optical-property measurements, a laser dye was acquired for measurements at 3.37–3.40 eV, outside the range of the analyzer calibration. The results of measurements with this dye were rejected because the optical-property results [$\varepsilon_1 \approx -14.3$, $\sigma \approx 550$ ($\Omega\,\mathrm{cm}^{-1}$)] were inconsistent with the remaining data.

An outstanding result demonstrated by these data is that the liquid has an absorption peak at 1.4 eV similar to that found for the solid. The magnitude of the optical-conductivity maximum is comparable to that for the solid. Its position is shifted to lower energy, as also occurs for the solid at higher temperatures.[9,24] The present and earlier results are in good agreement at energies greater than 1.6 eV, but the absorption peak at 1.4 eV was not observed by Miller[2] or by Havstad[3] in their measurements on liquid aluminum.

Gaps in our data exist in the wavelength ranges 840–875 nm, near the absorption peak, and at 740–770 nm, as a result of the lack of suitable laser dyes. The initial detection of the absorption peak was in fact uncertain because laser dyes for the wavelength range 840–925 nm (1.48–1.34 eV) were not yet available.

Figures 4(a)–4(d) show the temperature dependence of the optical properties measured at five wavelengths. Values for the index of refraction, *n*, and the extinction coefficient *k* are given in Figs. 4(a) and 4(b), respectively. Values for $\sigma$ and $\varepsilon_1$ are given in Figs. 4(c) and 4(d), respectively. Linear regression lines are drawn through the data to indicate the trends in the values with temperature. The wavelengths for these measurements were 381, 422, 500, 625, and 968 nm, designated by the symbols stated in the legend. The temperature range was approximately 1200–1800 K. The data display a slight tempera-

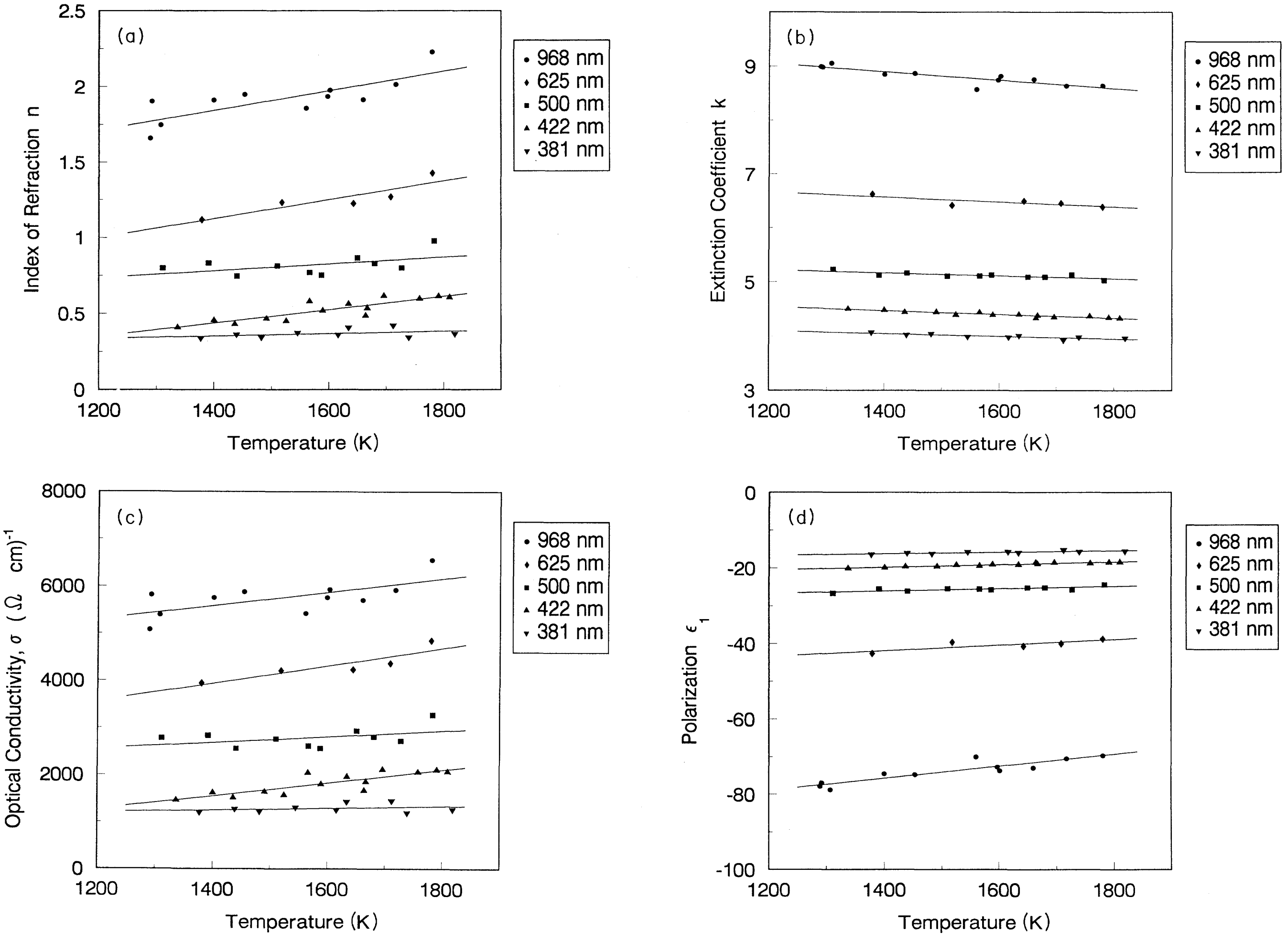

FIG. 4. Plots of *n*, *k*, $\sigma$, and $\varepsilon_1$ vs temperature for liquid aluminum. The solid lines are least-squares fits to the data.

ture dependence in these properties, which tends to become greater with increasing wavelength. The changes with temperature are small enough that the present results obtained over the full wavelength range at 1550 K can be compared directly with the results of Miller[2] at 1173 K and Havstad[3] at 950–1130 K.

Figure 5 shows the wavelength dependence of the normal spectral emissivity ε at a temperature of 1550 K. The curve drawn in the figure shows values for the solid at room temperatures.[5] These values and the normal spectral reflectivity $R$ were calculated using the expression

$$\varepsilon = 1 - R = 1 - \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} . \qquad (1)$$

It can be seen in Fig. 5 that, despite the large variations with wavelength that occur in the optical constants of liquid aluminum, the radiative properties show little wavelength dependence except in the vicinity of the 1.4-eV (885-nm) absorption peak.

## IV. DISCUSSION

The qualities which distinguish the present experimental investigation of the optical properties of liquid aluminum from the two other reports[2,3] on this subject were that (i) containerless conditions were used, (ii) oxides and nitrides were removed by vaporization at high temperatures, and (iii) pulsed dye lasers (rather than continuum sources) were used to provide high spectral resolution *and* high signal-to-noise levels in the presence of incandescent radiation from the hot specimens.

There is no doubt that the process for removing oxygen and nitrogen from the specimens was successful. Chemical analysis on specimens demonstrated approximately 10 ppm oxygen on processed specimens which exhibited oxide on their surface upon first heating and melting. The concentration of oxygen was reduced by processing to about 0.01 of the estimated solubility limit[18] of 1000 ppm.

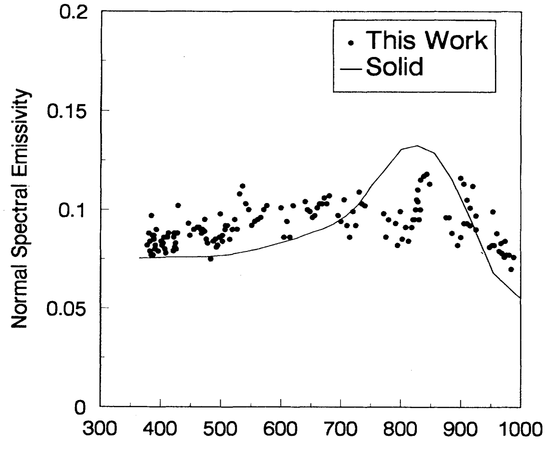

FIG. 5. Normal spectral emissivity vs wavelength at 1550 K for liquid aluminum. Data given by the line, for solid aluminum at room temperature, were calculated from the optical constants (Ref. 5).

The light intensities during the 7-ns laser pulses were very large, on the order of $10^6$ W/cm$^2$. About 10% of the 1 mJ of energy incident on the specimen for each laser pulse was absorbed and heated the illuminated 5-mm-diam area. The electronic-to-thermal energy conversion occurs on a time scale of $10^{-14}$ s, and the heat diffused to a depth approximately 260 nm in 7 ns, assuming a thermal diffusivity of 0.1 cm$^2$/s. The average temperature rise for the volume of liquid heated during the 7-ns pulse was thus calculated to be 7 K, using a heat capacity equal to 32 J/(mol K).[25] Since the optical properties exhibited negligible variations over this temperature interval, it was concluded that nonlinear effects of the high laser intensities did not occur.

For the reasons just given, we conclude that the strong absorption peak at 1.4 eV detected in this work is an intrinsic property of liquid aluminum. This confirms the electronic structure of liquid aluminum detected by soft-x-ray-emission spectra which were reported by Catterall and Trotter.[4] The reasons that this structure was not detected in the previous ellipsometric work of Miller[2] and of Havstad[3] are not entirely clear.

In inspecting the data of Miller[2] and Havstad,[3] one finds that their data in the vicinity of the absorption peak are, in fact, consistent with the present findings. For example, there is greater scatter in the data obtained by Havstad near 1.3 eV than at nearby energies, which may have resulted from the absorption peak. Also, Miller's datum at 1.35 eV agrees with our measurements (as do all of her results in the visible). However, at 1.23 eV, just outside our energy range, the optical conductivity reported by Miller is nearly twice that obtained by slight extrapolation of the present results.

There are extrinsic factors which may contribute to the differences between our results and those of Miller and Havstad. The levitation and high-temperature processing techniques that we used enabled exceptionally pure liquid-aluminum specimens to be obtained. In contrast, the liquids investigated by Miller[2] and Havstad[3] were saturated with aluminum oxide and niobium, respectively, as a result of reaction with containers. The aluminum-oxygen phase diagram[18] shows an estimated solubility limit approximately 0.05 mol. % oxygen in liquid aluminum at 1000 °C. The aluminum-niobium diagram[18] shows that about 4 mol. % niobium will dissolve in liquid aluminum at the temperatures investigated by Havstad.[3]

The x-ray-emission studies have also identified anomalous behavior associated with oxygen contamination. Catterall and Trotter[4] observed the peak in the $L_{23}$ x-ray-emission spectrum of the liquid in an aluminum oxide crucible. They reported that the absorption peak disappeared when the liquid occasionally became contaminated with an oxide layer. Also, Fischer and Baun[12] reported that the $K\beta$ x-ray-emission linewidth narrowed when liquid aluminum was heated several hundred degrees above the melting point in a zircon crucible.

On the basis of their $L_{23}$ x-ray-emission spectra, Catterall and Trotter[4] concluded that "... the peak observed in the spectrum of liquid aluminum indictates the presence of a 'zone structure' in the liquid, which in turn appears to imply a pseudo-crystallinity or instantaneous short range order with the atom positions showing a resemblance to those in the solid." This view was consistent with the subsequent work of Powell,[13] who reported a close similarity in the electron-energy-loss spectra for liquid and solid aluminum. Knight, Berger, and Heine[11] had already predicted on the basis of NMR, magnetic susceptibility, electrical conductivity, and other results that several metals, including aluminum, would undergo little change in their physical structure and electronic properties upon melting. These predictions have been confirmed for sodium[1] and others. The present work adds further experimental support to this description of the electronic structure for liquid aluminum.

Knight, Berger, and Heine[11] calculated that the effective mass $m^*/m$ of liquid aluminum was equal to 1.5, based on spin-susceptibility measurements. On the other hand, when the optical properties of the liquid were fit to the Drude theory,[2] a value of $m^*/m$ of approximately unity was obtained. The corresponding result for the effective carrier density was $n^*/n = 0.88$, which is much less than the values typical of liquid metals. Thus it is now clear that the visible–near-infrared optical properties of liquid aluminum cannot be fit with a Drude model. Instead, a model such as that which has been successful for the solid[26] may be required, in which both Drude and parallel-band absorption are taken into account.

It should be remarked that our own earlier measurements[16] on aluminum obtained at a wavelength of 633 nm by He-Ne laser ellipsometry gave values for $\sigma$ that were 30% smaller than those from the present work. We believe now that the earlier measurements may have been made on slightly contaminated specimens. Although bright and clean aluminum surfaces were obtained in the earlier work, tarnish on zirconium specimens could not be removed because of residual nitride contaminants. Since then, the gas purity has been improved such that untarnished zirconium is readily obtained.

The temperature dependence of the optical properties show that, for all wavelengths, $n$ increases and $k$ decreases with temperature, which was already known for $\lambda = 633$ nm.[16] It is evident also that $\varepsilon_1$ increases (becomes less negative) with temperature at all wavelengths. The optical-conductivity data show that $\sigma$ is approximately constant at the smaller wavelengths and increases slightly with temperature at the longer wavelengths. This is the same trend that occurs for the solid,[9] where the temperature coefficient is negative at wavelengths less than the absorption peak and positive at longer wavelengths.

These are the first results from a program to investigate the optical properties of liquid metals and alloys in containerless high temperature conditions by pulsed-dye-laser spectroscopic ellipsometry. Under containerless conditions high-temperature liquids are ideal objects for ellipsometric investigations. They provide very pure and clean, specularly reflecting surfaces which can be investigated over a wide temperature range, including undercooled liquids at temperatures as low as 80% of the melting point. It has been found that liquids display a perhaps unexpected degree of structure in their optical-property vs wavelength functions which will be of further theoretical interest. Measurements on liquid zirconium are nearly complete and will be reported in the future. Work is also in progress on liquid nickel and zirconium-nickel alloys and to extend the measurement capabilities to a wavelength of approximately 220 nm.

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