LA-UR- *00-98*

Title:	The Optical Properties of Liquid Cerium at 632.8 nm
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Submitted to:	Materials Science and Engineering

Unclassified/Not UCNI

LANL Class. Group   date   JAN 1 8 2000

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The Optical Properties of Liquid Cerium at 632.8 nm

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Abstract

The normal, spectral emissivity, $\varepsilon_\lambda(T)$, and optical constants, n and k, of liquid

cerium were measured at 632.8 nm over a temperature range of 1702 – 2171 K using

rotating analyzer ellipsometry. The cerium was electromagnetically levitated and melted

to prevent contamination of the liquid metal by contact with a container. The emissivity

at 0.9 μ and 1900 K was determined from the brightness temperature. The solubility of

oxygen in liquid cerium at 1786 K was estimated and the effect of oxygen on the optical

properties was demonstrated. Using available thermodynamic data and assumptions of

ideal solution behavior, the volatilization of oxygen and nitrogen impurities is discussed.

1. Introduction

The optical properties, index of refraction, n, and extinction coefficient, k, of liquid

metals are difficult to measure because of their chemical reactivity and opacity. In

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recent years, a containerless technique has been developed [1,2] in which metals can be electromagnetically levitated and melted thus eliminating potential contamination of the liquid by the container. The optical properties are determined using rotating analyzer ellipsometry, RAE. In this method, linearly polarized light is reflected from the specimen at a known angle of incidence and the polarization state of the reflected light is determined from intensity ratio measurements at different azimuths of a Glan-Thompson analyzing prism. The reflection is specular because the liquid metal surface is smooth. In general, the reflected light will be elliptically polarized and the optical properties may be determined from the change in polarization state upon reflection.

Although the optical properties of metals are of interest in their own right [3,4], a more practical application is the non-contact, radiometric temperature measurement of non-blackbodies [5]. The brightness temperature, T_B, obtained from an optical pyrometer of sufficiently narrow bandwidth centered on the wavelength λ is related to the true temperature, T, by

$$\frac{1}{T} = \frac{1}{T_B} + \frac{\lambda}{C_2} \cdot \ln[\varepsilon_\lambda] \qquad (1)$$

where C_2 is the second radiation constant. In general, the normal, spectral emissivity, ε_λ, is a function of the temperature. For opaque materials, ε_λ and the normal, spectral reflectivity, R_λ, are related by assuming Kirchhoff's law, $R_\lambda + \varepsilon_\lambda = 1$. R_λ can be calculated from the optical constants, n and k, using the Fresnel relations, which are well known in optics. Application of the Fresnel relations when one medium is a conductor

requires the use of the complex index of refraction, n^*, for that medium. The optical properties are related to n^* by $n^* = n - ik$ and the reflectivity is calculated using equation (2).

$$R_\lambda = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2}$$ (2)

In the present application of equation (2), n_0 is the index of refraction of the low pressure gas surrounding the levitated liquid metal and its value will be very close to unity.

Previously, Mulford et al. [6] obtained high temperature, thermophysical properties of liquid uranium using an isobaric, rapid pulse heating method. In these experiments, brightness temperatures were measured using high speed, optical pyrometry. The brightness temperatures were subsequently corrected [7] to true thermodynamic temperatures using the emissivity obtained from RAE on levitated uranium liquid [8]. In order to extend optical property measurements to liquid plutonium and other actinide metals and alloys, it was necessary to build a levitation/RAE apparatus within a glovebox enclosure because of the radio-toxicity of these materials. Before performing experiments on plutonium, it was deemed prudent to insure proper operation of the equipment on non-radioactive samples. Nickel and cerium were chosen because the optical properties of nickel have been reported [1,9-11] and, as noted by Ackermann et al. [12], cerium has certain striking similarities to plutonium, particularly with respect to its oxidation and oxide vaporization behavior. When finely divided, cerium and plutonium are both pyrophoric and considerable care is required to prevent oxidation of the liquids.

The optical constants have not been reported for liquid cerium, but the normal, spectral emissivity has been measured by Baria et al. [13] at 645 nm over a temperature range of 1150 – 1820 K by application of equation (1). The cerium was melted in a tantalum crucible which contained a blackbody hole. Optical pyrometry was used to obtain both T and T_B by sighting the pyrometer on the blackbody and liquid metal surface, respectively. Using the same technique, Won Dokko et al. [14] measured the normal, spectral emissivity of a series of liquid cerium-copper alloys as well as the pure components. It was of interest to compare the emissivity of liquid cerium derived from the optical constants measured in this work using RAE with the emissivity obtained from the brightness and true temperatures using equation (1) in the work of Baria et al. and Won Dokko et al.

2. Experimental Description

2.1 Samples

The 6.35 mm diameter, cast cerium rod used in these experiments came from two sources, Goodfellow Corporation, Cambridge, England, lot number CE007910/10 and Electronic Space Products International (ESPI), Ashland, Oregon, USA, lot number Q637. The stated purity of both samples was 99.9% by weight. Impurities levels greater than 10 ppm are given in Table 1. These were determined by glow discharge mass spectrometry with separate combustion analyses for C and S to form CO_2 and SO_2, respectively, and inert gas fusion analyses for N and O in the case of the ESPI cerium. Separate analyses for C, N, O and S were not performed on the Goodfellow material and the stated impurity levels for these four elements have large uncertainties.

Table 1. Cerium impurities greater than 10 ppm

	C	N	O	Al	P	S	Mn	Fe	Cu	Ta	La	Pr	Nd	Tb	Ho	Yb
Good-fellow	130		340		12					74	93	11		12		
ESPI	1400	20	110	200		110	16	200	24		85	20	24	20	65	14

Even though the cerium was stored in a vacuum desiccator, tarnish formed within a day. It was necessary to remove surface oxidation by mechanical polishing before cutting samples for optical property measurements. Samples cut from the cerium rod were typically 0.6 to 0.7 grams. Once cut, samples were loaded into the levitation chamber within a few minutes and the chamber was evacuated and purged three times with helium or argon. The inert gas was passed through a Supelco high capacity, zirconium chip furnace, model 23802, to reduce oxygen and water contaminates to sub ppm levels.

Nickel samples were cut from a 5 mm diameter rod and treated similarly to the cerium. The nickel rod, AESAR batch number NM25708, had a stated purity of 99.995%. An analysis using dc arc emission spectroscopy detected 5 ppm silicon and 5 ppm silver by weight. The only other elements detected were Mg, Al, Ca, Fe, and Cu, each less than 5 ppm.

2.2 Equipment description

A schematic drawing of the apparatus is shown in Fig. 1. The specimen, stainless steel levitation chamber, incident beam polarizer, video camera and beam steering optics are located inside the stainless steel glovebox. The volume of the levitation chamber is 31 liters. The 15 mW, He-Ne laser, incident beam attenuator, chopper, ellipsometer, computer and electronics are located outside of the glovebox for ease of maintenance. Strain free, non-birefringent glovebox and chamber windows are adjustable so that the laser beam passes through at normal incidence. This was done to avoid unwanted changes in the polarization state at these interfaces. Radio frequency, RF, power is brought in through the bottom of the glovebox using a Los Alamos designed, water cooled RF feedthrough. A Pillar Industries, 50 kW generator, not shown in Fig. 1, supplies RF power to the glovebox through a water cooled, coaxial copper transmission line. The generator operates at a frequency of 270 kHz. A 12:1 voltage step down transformer is used for impedance matching of the generator to the load. The water cooled, levitation coil was made of 1/8" diameter copper tubing and consisted of three lower turns and two upper turns wound in the reverse sense to provide lateral stability to the sample. The outer diameter of the coil was 13.8 mm.

The chamber top can be lifted from its baseplate using an electric hoist to allow sample loading and recovery. Up to three samples can be loaded at a time on ceramic pedestals placed on a carousel mechanism. A particular sample can be positioned within the coil from outside the glovebox using rotary and linear motion feedthroughs. Once a sample was levitated, but before it melted, the pedestal was lowered to avoid contact with the molten specimen. The carousel also contains three recovery cups which can be positioned directly under the coil to catch the sample when the experiment is terminated.

The carousel is designed to shield new and recovered specimens from vaporization from the levitated sample to avoid cross contamination.

Brightness temperatures were measured with a Pyrometer Instrument Co., Photo II Automatic Pyrometer which had an effective wavelength of 650 nm. The pyrometer was calibrated by sighting on a tungsten strip lamp certified by the National Institute of Standards and Technology. Temperature corrections for reflection and absorption by chamber and glovebox windows were determined by sighting on a blackbody radiator with and without the windows in the optical path. A Mikron Instrument Co., model M190H, infrared pyrometer was used to measure the brightness temperature of liquid cerium at an effective wavelength of 0.9 μm.

2.3 Experimental procedure

Samples were levitated and melted in helium, argon or a mixture of both. The gas pressure and composition were used to control the sample temperature. Typical pressures ranged from 80 to 250 torr providing a temperature range of about 400 K. Helium was used to achieve the lowest temperatures because of its higher thermal conductivity. The inert gas also suppressed vaporization and helped protect the windows from condensation. Known quantities of reactive gases could also be metered into the chamber using an MKS, model 647, mass flow controller calibrated for 0.1 to 10 standard cubic centimeters per minute of oxygen.

For polarimetry measurements, the plane of incidence, defined by the incident and reflected rays, was horizontal. By repositioning the incident beam steering mirrors at fixed positions on the optics table, three different angles of incidence, nominally 67.5°,

73.0° and 78.75°, could be selected and the beam could also be sent directly through the sample position into the ellipsometer. The actual angle of incidence was determined using a prism containing an interfacial angle close to the compliment of the angle of incidence and known to within 0.03°. The angle of incidence was measured by first sending the beam through the apparatus in the straight through configuration and marking the exit position at some known distance from the sample position. The prism was then placed at the sample position such that the straight through beam was reflected back on itself. The beam steering optics were then moved to the desired polarimetry configuration. The displacement of the straight through beam and the beam reflected from the prism were used to relate the prism interfacial angle and the actual angle of incidence. For the present experiments, a single angle of incidence, 72.84°, was used. Of the three available angles of incidence, this was chosen to give the best sensitivity for determining the optical constants.

The incident beam polarizer produced linearly polarized light whose plane of polarization made an angle of 45° with the plane of incidence. The incident beam was mechanically chopped at 1000 Hz to allow lock-in detection of the reflected light. Using suitable optics, the light reflected from the sample was collimated and filtered before passing through a Glan-Thompson analyzing prism which separated the beam into orthogonally polarized components. A laser line filter placed before this prism was used to block most of the light radiated by the incandescent sample. The ordinary and extraordinary rays from the analyzing prism were focused onto two, United Detector Corp., model UDT020D, silicon photodetectors and the photocurrents were measured with two Stanford Research, model SR 530, lock-in amplifiers. The Glan-Thompson

prism could be rotated about the reflected ray direction allowing orthogonal components of the reflected light to be measured simultaneously at different azimuths. Acquisition of intensities and brightness temperatures and setting of the ellipsometer analyzer azimuth were performed under computer control. The optical constants, emissivity and true temperature were calculated and displayed in real time.

2.4 RAE Theoretical Basis

Based on a method described by Beattie [15], the ellipsometric parameters $\tan(\psi)$ and Δ were determined from reflected light intensity ratios measured at three azimuths of the analyzer, $0°$ and $\pm45°$ with respect to the plane of incidence. The parameters $\tan(\psi)$ and Δ are the ratio of the reflectivities and relative phase difference, respectively, of the p- and s-components, where p- and s- refer to components parallel and perpendicular to the plane of incidence. If the intensities I_1 through I_6 correspond to azimuths of $90°$, $0°$, $135°$, $45°$, and $-45°$, respectively, then $\tan(\psi)$ and $\cos(\Delta)$ can be calculated from equations (3) - (5)

$$\tan(\psi) = \sqrt{I_2 / I_1} \tag{3}$$

$$\cos(\Delta) = \frac{1}{2}\left[\sqrt{I_2 / I_1} + \sqrt{I_1 / I_2}\right] \times \frac{\left[1 - \dfrac{I_3}{I_4}\right]}{\left[1 + \dfrac{I_3}{I_4}\right]} \tag{4}$$

$$\cos(\Delta) = \frac{1}{2}\left[\sqrt{I_2 / I_1} + \sqrt{I_1 / I_2}\right] \times \frac{\left[1 - \dfrac{I_6}{I_5}\right]}{\left[1 + \dfrac{I_6}{I_5}\right]} \tag{5}$$

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In practice both equations (4) and (5) were used to calculate Δ and the two results were averaged. The two intensities in each of the intensity ratios in equations (3) – (5) were measured simultaneously and thus the ratios were not affected by variation of the laser power or variation of the reflected intensity due to sample translation and oscillation. The optical constants, n and k, are related to the ellipsometric parameters, ψ and Δ, by

$$n^2 - k^2 = \sin^2(\phi_0)\tan^2(\phi_0)\frac{\cos^2(2\psi) - \sin^2(2\psi)\sin^2(\Delta)}{(1 + \cos(\Delta)\sin(2\psi))^2} + \sin^2(\phi_0) \qquad (6)$$

$$2nk = \frac{2\sin(2\psi)\cos(2\psi)\sin(\Delta)}{(1 + \cos(\Delta)\sin(2\psi))^2} \cdot \sin^2(\phi_0)\tan^2(\phi_0) \qquad (7)$$

where ϕ_0 is the angle of incidence.

Before making optical property measurements, a calibration procedure was employed in which a highly attenuated, linearly polarized beam was sent directly into the ellipsometer. At each of the three azimuths of the analyzer, the plane of polarization was set to give equal intensities for the ordinary and extraordinary rays. The deviations of the these intensity ratios from unity were used to correct the measured intensity ratios during optical property measurements. The correction factors take into account mismatches in the photodetectors and electronics as well as slight alignment errors which cause the beams to hit different spots on the detectors at different azimuths. Typically, the corrections were on the order of 10%.

The ellipsometer contained two mirrors which could be inserted into the optical path for alignment purposes. One mirror allowed the sample to be viewed through a

telescope for rough alignment. While viewing the sample using this mirror, the ellipsometer was manually translated horizontally and vertically to center the sample on a crosshair. The exact sample levitation position varied slightly between experiments. This was due, in part, to inadvertent movement of the coil while cleaning it, to different sample sizes and properties, and to different RF power levels. The second mirror was inserted into the optical path for precise automatic alignment under computer control. In this mode, the beam reflected from the sample hit a United Detector Corp., model SC-4D, position sensitive detector. The output from this detector was used as an error signal to drive two orthogonal, stepper motor translators attached to the ellipsometer. The alignment could be performed occasionally during an experiment to compensate for changes in sample height due to vaporization losses.

3. Results

3.1 Nickel

Optical property data were collected on Ni at a mean temperature of 1868 K. During the experiment, the temperature was lowered by 183 K by increasing the helium pressure. However, the optical properties were constant within the random scatter of the data over this small temperature range. The average of fourteen measurements yields 2.52±0.02, 3.76±0.01, and 0.380±0.001 for n, k and ε_λ, respectively, at 632.8 nm. The uncertainties are the sample standard deviations.

3.2 Cerium

Optical properties for liquid cerium at 632.8 nm are shown in Figs. 2 and 3 as a function of temperature. Measurements were performed on two Goodfellow samples and one ESPI specimen. Small systematic differences in the results for the three samples are apparent in the figures. For example, at 1900 K there is about a 2% difference in the emissivity for the Goodfellow 1 and 2 samples. The lower emissivity for Goodfellow 2 is attributed to the use of purifying chip furnaces on the inert gas lines. The furnaces were deliberately not used for Goodfellow 1 in order to see the effect of small concentrations of gaseous impurities. Since chip furnaces were used for both the Goodfellow 2 and ESPI measurements, the small systematic differences in their properties are believed to be intrinsic to the samples. The most obvious sample difference is the 1400 ppm carbon impurity for the ESPI sample. Fig 4. shows the temperature and emissivity history for the ESPI sample. The temperature was lowered or raised by increasing or decreasing the inert gas pressure in the levitation chamber. These results show that the emissivity reproducibly tracks the temperature.

Least squares fits were performed on the combined data from the Goodfellow 2 and ESPI samples. Data from Goodfellow 1 were excluded because of the less pure atmosphere. The results from the least squares fits for ε_λ, n and k for the temperature range 1702 – 2171 K are given in equations (8), (9), and (10), respectively.

$$\varepsilon_\lambda(T) = 2.17 \cdot 10^{-5} T + 0.280 \tag{8}$$

$$n(T) = -7.75 \cdot 10^{-5} T + 2.52 \tag{9}$$

$$k(T) = -2.84 \cdot 10^{-4} T + 4.80 \tag{10}$$

From a measurement of the true temperature, T, and the brightness temperature, T_B, in equation (1), it was possible to obtain the normal, spectral emissivity of liquid cerium at a second wavelength. The emissivity at 0.9 μ and 1900 K is 0.351±0.002. The brightness temperature of the levitated sample was measured with the Mikron infrared pyrometer. Simultaneously, the true temperature was measured with Photo II pyrometer and the RAE. The Mikron pyrometer was calibrated against the Photo II pyrometer by comparing readings on blackbody radiator.

3.3 Effect of oxygen on the optical properties

The effect of dissolved oxygen on the emissivity of cerium is shown in Fig. 5. The mean temperature of the experiment was 1772±5 K. The initial mass of cerium was 0.6475 g. For the first 200 seconds, the emissivity was constant at 0.319. At about 250 seconds, 6 standard cubic centimeters, scc, of oxygen mixed with 10 scc of argon were added to the levitation chamber over a period of 1 minute. This was followed by the addition of 50 scc of argon, also inlet over a period of 1 minute, to flush residual oxygen from the lines. Following the addition of oxygen, the emissivity increased steadily as oxygen was transported to the sample. As the emissivity increased, both n and k steadily decreased by 2.4 and 3.5%, respectively. During this period, the surface of the liquid cerium was featureless with no indication of a second phase as viewed through the pyrometer telescope. After 1045 seconds, a solid phase formed on the sample surface, which was interpreted to be oxide. Data points collected after the appearance of the second phase are beyond the ordinate scale used in Fig. 5 and are not included.

Additional cerium oxidation experiments are summarized in Fig. 6 in which the product nk is plotted as a function of temperature. As discussed below, the product of n and k is sensitive to impurities such as dissolved oxygen. The line labeled "Pure Ce" was calculated from equations (9) and (10). Pure cerium refers to metal which has been previously heated to temperatures greater than 2100 K. The line labeled "Start of oxidation" shows nk values from oxidation experiments, but before any oxygen was added to the chamber. In order to minimize vaporization, temperatures in the oxidation experiments were deliberately kept below 1900 K because one of the goals was to estimate the solubility of oxygen in liquid cerium. The "Start of oxidation" line is representative of the as received cerium. The data labeled "Oxygen saturated" includes nk values measured after the addition of oxygen and just before a second solid phase appeared floating on the surface of the liquid metal. Since enough oxygen was added to eventually precipitate a thin, but finite layer of oxide, the curve should, perhaps, be more properly labeled "Oxygen supersaturated".

The line representing the as received material in Fig. 6 lies below the pure cerium line indicating the presence of sample impurities, most probably oxygen. Combustion analyses to form CeO_2 were performed on the as received cerium, which was assumed to have an initial composition CeO_x. Samples were heated in air at 1125 K until constant weight was achieved. The results for the Goodfellow and ESPI material were $CeO_{0.0282}$ and $CeO_{0.0298}$, respectively. A combustion analysis was also performed on a 0.680 gram Goodfellow sample which was levitated and melted at 1884±6 K for 3412 seconds without any addition of oxygen to the chamber. The final composition was $CeO_{0.022}$.

3.4 Sample cleaning

Removal of impurities from cerium sample Goodfellow 2 at high temperature by volatilization is illustrated in Fig. 7. The product of n and k is plotted as a function of temperature. The initial temperature was also the highest and the temperature decreased monotonically during the experiment. The high temperature points at the beginning of the experiment, which deviate from the line, were not included in Figs. 2 and 3. The change in nk at temperatures above ≈ 2100 K is due mainly to removal of impurities by vaporization.

3.5 Oxygen solubility in liquid cerium

The solubility of oxygen in liquid cerium was estimated from the amount of oxygen required to precipitate a second phase. By steadily decreasing the amount of oxygen added to the chamber for a series of identical size samples held at the same temperature, 1786 ± 10 K, a point was eventually reached where a second phase did not form. By observing whether a second phase did or did not form, the solubility was bounded by $0.0797 \geq X_O \geq 0.0628$ where X_O is the mole fraction of atomic oxygen. These limits were calculated from the initial mass of cerium, the initial oxygen content of cerium measured by combustion analysis, and the volume of oxygen added to the chamber. A combustion analysis on the recovered single phase sample yielded $X_O = 0.0648$. The agreement of 3% between the calculated, 0.0628, and measured, 0.0648, composition of the homogeneous sample indicates that all of the added oxygen reacted. For this sample, the initial mass of cerium and added oxygen were 0.6470 and 0.0029 gram, respectively. The mass of the recovered sample was 0.6378 gram. The difference

in initial and final mass is presumably due to small vaporization losses. A combustion analysis on the recovered two phase sample yielded $X_O = 0.0698$. This number is smaller than the calculated composition, $X_O = 0.0797$, indicating not all of the added oxygen reacted by the time a second phase formed and the experiment was terminated.

4. Discussion

4.1 Nickel

Krishnan [1] previously reported the normal, spectral emissivity of Ni at 632.8 nm over the temperature range 1822 – 2143 K. A value of 0.397 ± 0.010 is calculated from the fit to Krishnan's data at 1868 K. Krishnan et al. [9] reported the complex dielectric constant for Ni at 1800 K and 632.8 nm from which the optical constants can be calculated from relationships given in Born and Wolf [3]. The resulting values for n and k are 2.56 ± 0.13 and 3.63 ± 0.12, respectively. The agreement of 2 to 4% between this work and Krishnan et al. for n, k and ε_λ indicates that the equipment is working satisfactorily. In another study [10] of the emissivity of liquid nickel alloys, the emissivity of pure nickel was given as 0.356 at 1868 K and 632.8 nm. Finally, the optical properties of pure nickel were reported [11] in the energy range 1.2 – 3.5 ev at a temperature of 1764 K. The emissivity at 632.8 nm was read as 0.394 from the graphical data. Averaging the emissivity from [1,10,11] at 632.8 nm and ignoring the somewhat lower temperature in [11] yields 0.382 which is in good agreement with the present work.

4.2 Cerium

Over the range 1150 – 1820 K, Baria et al. [13] reported a temperature independent emissivity for liquid cerium of 0.322±0.004. The determination was made at 645 nm, the effective wavelength of the pyrometer, using a method based on equation (1). Although no temperature dependence of the emissivity was reported by Baria et al., in a previous study [16] a slight tendency of the emissivity of the liquid to increase with temperature was noted. This was attributed to oxidation of the surface. Ignoring the small difference in the wavelength and the question of temperature dependence, the agreement of the present work with Baria et al. is better than 1.6% for the overlapping temperature range. In a study of a series cerium-copper alloys, Won Dokko et al. [14] reported the normal, spectral emissivity of liquid cerium as 0.292±0.009 for the temperature range 1157 – 1802 K. The equipment was essentially the same as used by Baria et al. [13]. This low value of the emissivity is surprising since the oxygen content of the cerium used by Won Dokko et al. and Baria et al. were 525 and 52 ppm, respectively. As shown in Fig. 5, the emissivity of cerium increases with increasing oxygen content. Won Dokko et al. stated that their measured emissivities for the pure liquid components, cerium and copper, were lower than all previously reported values. A subsequent measurement [9] of the normal, spectral emissivity of liquid copper at 632.8 nm also yields an emissivity larger than reported by Won Dokko et al. for overlapping temperatures.

An analysis of the random and systematic errors associated with the electromagnetic levitation RAE technique have been discussed by Krishnan et al. [10,17]. In addition, the long term stability of the equipment was estimated by recalculating the optical properties for the ESPI sample using repeated measurements of

the calibration factors taken over the course of all of the cerium experiments. These calculations reflect the effects of condensate on the windows, stress induced birefringence as the beam passes through different window positions, slight rotations of the ellipsometer during alignment, changes in detector efficiency and drift in the lock-in amplifiers. The variation in emissivity calculated with calibration data collected over four months was about 0.6%. Including the errors in the analysis of Krishnan et al., the estimated accuracy in the emissivity is 1.5%.

4.3 Effect of oxygen on the optical properties and sample cleaning

Fig. 5 demonstrates that the emissivity is sensitive to dissolved oxygen. Krishnan et al. [18] have shown that the effect of dissolved oxygen and nitrogen in zirconium is to decrease the number of free electrons that are available in the conduction band in a manner proportional to their respective valances. The product of n and k is directly related to the density of conduction electrons. A similar effect is seen here. As cerium is oxidized the value of nk is reduced.

The difference between pure cerium and the as received metal represented by the "Start of oxidation" line in Fig. 6 indicates that heating the metal to temperatures >2100 K results in removal of impurities. This is further confirmed by results shown in Fig. 7 for the Goodfellow 2 sample. The value of nk increases at the highest temperature, which was achieved at the beginning of the experiment. The ESPI cerium was initially held at >2100 K three times longer than Goodfellow 2, but its nk value is only 0.2% higher than Goodfellow 2 following the cleaning period. This shows that additional cleaning would not be achieved by maintaining the metal at >2100 K for longer times.

The combustion analyses of Goodfellow and ESPI cerium indicate a much higher oxygen content than given in Table 1. The reason for this discrepancy is not known. The samples were exposed to the air briefly after polishing and before loading into the chamber. If all the oxygen measured in the combustion analysis were present as a surface layer, it would only be about 3 microns thick and would probably not be visually detectable.

The data representing oxygen saturated cerium in Fig. 6 show that nk is further reduced from the pure and as received metal by the addition of oxygen. The difference in the three curves in Fig. 6 is consistent with the oxygen content of as received cerium, measured from combustion analysis, and the amount of oxygen added to the chamber to further oxidize the metal. The reduction of nk with increasing temperature for "Oxygen saturated" cerium reflects the higher solubility of oxygen at higher temperature. If the dependence of nk on composition were known, then the oxygen saturated curve would give the liquidus phase boundary, or more precisely, an upper bound for the solubility because some supersaturation is inevitable.

The effectiveness of the removal of oxygen and nitrogen impurities by volatilization from liquid cerium can be estimated from calculations similar to those suggested by Brewer et al. [20]. The results of these calculations for the Ce-O and Ce-N systems are summarized in the pressure-composition phase diagrams shown in Figs. 8 and 9, respectively. The interpretation of these diagrams has been discussed by Gilles [21]. At 2200 K, Fig. 8 indicates that the vapor in equilibrium with cerium liquid is richer in oxygen than the condensed phase. Continued vaporization under vacuum conditions will tend to remove oxygen and purify the metal. The vapor species included

in the calculations were Ce(g), CeO(g), CeO$_2$(g), O(g), and O$_2$(g), but Ce(g) and CeO(g) are the most important. The equilibrium pressures of Ce(g) and CeO(g) over Ce(liquid, O saturated) + Ce$_2$O$_{3-x}$(s) have been measured by Ackermann et al. [12]. The equilibrium pressures of the other species were calculated using data from [12, 19, 22]. The solubility of oxygen in liquid cerium at 2200 K was calculated from the cerium pressures over pure cerium and the over Ce(liquid, O saturated) + Ce$_2$O$_{3-x}$(s), assuming Raoult's law. Pressures over the Ce(liquid) phase were calculated by assuming that Henry's law applies from the oxygen solubility limit to pure cerium. Ackermann has shown that no intermediate phases exist between Ce(liquid, O saturated) and Ce$_2$O$_{3-x}$(s) and his results have been used to extend Fig. 8 to include the sesquioxide. The qualitative features Fig. 8 remain the same at lower temperatures, but the total equilibrium pressure is lower. At 1800 K, the total pressure over Ce(liquid, O saturated) and Ce$_2$O$_{3-x}$(s) is smaller by a factor of 140 than the pressure at 2200 K. For the same size sample, removal of oxygen impurity will be 140 times slower at 1800 K.

Thermodynamic data for the calculation of the Ce-N pressure composition diagram were taken from [19,22-26]. The solubility of nitrogen in cerium was taken from Massalski et al. [27]. Of the gaseous species Ce(g), CeN(g), N(g) and N$_2$(g) included in the calculation, Ce(g) and N$_2$(g) are the most important. Lacking partial molar free energies, Ce(liquid) was treated as an ideal solution. At 2200 K, the calculations indicate that nitrogen cannot be completely removed by volatilization. Compositions of the liquid to the left or right side of the minimum in Fig. 9 will preferentially lose metal or nitrogen, respectively. Continued vaporization will eventually produce a condensed phase whose composition coincides the with the vapor

composition at the minimum total pressure. Further vaporization will produce no change in composition of the liquid.

4.4 Oxygen solubility in liquid cerium

At 1786±10 K, the solubility of oxygen in liquid cerium appears to be about 6 to 7 mole percent atomic oxygen. Because the extent of supersaturation is unknown, this estimate must be considered an upper bound. Ackermann et al. measured the vapor pressure of pure liquid cerium [19] and the pressures over cerium liquid saturated with oxygen in equilibrium with $Ce_2O_{3-x}(s)$ [12]. At 1786 K, the pressures over the pure liquid and saturated liquid and oxide are 5.04×10^{-7} and 4.89×10^{-7} atm, respectively,. Assuming Raoult's law, the solubility of oxygen in liquid cerium at 1786 K is $X_O = 0.030$ which is somewhat smaller than the bound given above.

5. Conclusions

The optical properties of liquid cerium have been measured on samples which were cleaned in situ. The purity levels reported in Table 1 were found to be overly optimistic, probably due oxidation upon brief exposure to the atmosphere. However, it has been demonstrated by experiment and thermodynamic arguments, that oxygen, and to a lesser extent nitrogen, can be removed by vaporization at high temperature.

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Fig. 1. Schematic diagram showing the relative orientations of the laser, sample, and rotating analyzer ellipsometer. The components are the sample (1), levitation chamber (2), polarizer (3), video camera (4), mirrors set for 72.84° incidence angle (5), laser (6), beam attenuator (7), chopper (8), ellipsometer (9), pyrometer (10), glovebox (11), RF feedthrough and coil (12).

Fig. 2. The normal, spectral emissivity of liquid cerium as a function of temperature at 632.8 nm. Samples are Goodfellow 1 (□), Goodfellow 2 (*), and ESPI (+).

Fig. 3. The optical constants, n and k, of liquid cerium as a function of temperature at 632.9 nm. Samples are Goodfellow 1 (□), Goodfellow 2 (*), and ESPI (+).

Fig. 4. Temperature and emissivity history for the ESPI sample.

Fig. 5. The effect of dissolved oxygen on the emissivity of liquid cerium at 1772 K.

Fig. 6. Optical property, nk, versus temperature.

Fig. 7 Plot of nk versus temperature illustrating sample cleaning at >2100 K

Fig. 8. Calculated pressure-composition diagram for Ce-O at 2200K.

Fig. 9. Calculated pressure-composition diagram for Ce-N at 2200K.

6

9

7

8

11

4

2

12

1

10

5

3

5

Emissivity

Temperature (K)

Time (sec)

4

Pure Ce

Start of oxidation

Oxygen saturated

nk

Temperature (K)

6