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The optical properties of liquid plutonium at 632.8 nm

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Abstract

The optical properties and normal, spectral emissivity of liquid plutonium at 632.8 nm were measured over a temperature range of 2016–2189 K using rotating analyzer ellipsometry. The purity of the liquid was maintained in a containerless environment using electromagnetic levitation and heating. The material investigated contained 1 wt% Ga that was added during the casting process. The measured values of the optical property results are given as a function of temperature by $\epsilon_\lambda = 5.38 \times 10^{-5}T + 0.250$, $n_\lambda = -1.29 \times 10^{-4}T + 3.82$, and $k_\lambda = -7.04 \times 10^{-4}T + 5.77$ over the investigated temperature range.

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1. Introduction

The optical properties, index of refraction, n_λ, and extinction coefficient, k_λ, of liquid metals are of interest, in part, because of their application to non-contact, radiometric temperature measurements of non-blackbodies [1]. Because liquid metals are specularly reflecting and opaque in the visible spectrum, the normal, spectral reflectivity, R_λ, and emissivity, ϵ_λ, are related by Kirchhoff's law, $R_\lambda + \epsilon_\lambda = 1$. The normal, spectral reflectivity may be calculated from the optical properties, n_λ and k_λ, using the Fresnel relations, which are well known in optics. 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

$$\frac{1}{T} = \frac{1}{T_B} + \frac{\lambda}{C_2}\ln[\varepsilon_\lambda], \tag{1}$$

where C_2 is the second radiation constant and Wien's law is assumed applicable. In general, the emissivity is a function of the temperature, wavelength, and sample purity.

Liquid metals such as the lanthanides and actinides are difficult to study at high temperatures because of their extreme chemical reactivity. To maintain the purity of samples, measurements have either been made on very short time scales or using containerless techniques. Mulford and Sheldon [2] reported high temperature, thermophysical properties of liquid uranium using an isobaric, rapid heating method known as the isobaric expansion technique (IEX) [3]. Their brightness temperatures were subsequently corrected to true thermodynamic temperatures using the emissivity obtained from rotating analyzer ellipsometry (RAE) on electromagnetically levitated uranium [4,5].

Similar studies of plutonium and other actinides are more difficult due to their greater radiotoxicity. Mulford and Sheldon [6,7] extended the IEX method to transuranium elements, but had to estimate a value for the spectral emissivity to obtain thermodynamic temperatures. Boivineau [8] reported thermophysical properties of plutonium up to 4000 K using the IEX method, but

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did not attempt to obtain temperatures from available multi-spectral, optical pyrometry. Instead, temperatures were estimated from the measured enthalpy and the assumed constant heat capacity of the liquid. Temperatures were estimated, in part, because the low melting arrest of plutonium could not be observed pyrometrically and used as calibration point, but also because emissivity data above the melting point were non-existent. It should be noted that multi-wavelength pyrometry cannot be used to obtain both the emissivity and temperature without questionable assumptions concerning the wavelength dependence of the emissivity [9,10].

For reactive liquid metals at very high temperatures, only non-contact temperature measurements are possible. The successful application of radiometric methods requires that the emissivity be known at the effective wavelength of the pyrometer. Although the total, hemispherical emissivity of alpha plutonium has been measured [11] at 362 K using a novel radiometric method and the known specific power of ^{239}Pu, until now, the optical properties and spectral emissivity of liquid plutonium have not been reported. We have taken the optical properties of the 1 wt% Ga alloy used in this study to be characteristic of pure plutonium, but additional measurements are needed to verify this assumption.

2. Experimental procedure

In preparation for experiments on plutonium, a study was recently completed on the optical properties of liquid cerium [12]. Cerium was chosen because its chemical reactivity is similar to plutonium, particularly with respect to its oxidation and oxide vaporization behavior. The cerium results demonstrated the sensitivity of the optical properties to dissolved oxygen in experiments where metered amounts of oxygen were allowed to dissolve in the levitated liquid. The cerium work also demonstrated that reactive liquid metals could be studied without measurable oxidation using the same apparatus that was used for the plutonium experiments. Although thermodynamic arguments were made in the case of cerium that indicated oxygen, and to a lesser extent nitrogen, could be vaporized at very high temperature, no such calculations were possible for plutonium [13]. To limit oxidation of the plutonium, all sample manipulations were performed in inert atmosphere glove boxes, which reduced the oxygen content to less than 50 ppm. Levitation and melting of the plutonium were performed in helium in a secondary chamber within the glove box. The helium was passed through a zirconium chip furnace, which reduced the oxygen content to sub-ppm levels.

The purification and preparation of the delta stabilized plutonium used in this work has been described in detail elsewhere [14]. Briefly, the double electrorefined metal was further purified by floating molten zone refining followed by an in situ distillation, alloying and casting step. Zone refining reduced the total impurity content of the electrorefined metal from 590 ± 88 to 174 ± 26 ppm where impurity levels are given as weight fractions. Uranium accounted for 110 ppm of the measured 174 ppm in the zone refined plutonium. The distillation step was performed using a Crystallox™ levitation crucible and reduced the ^{241}Am content to 1.50 ± 0.30 ppm in the as-cast specimen. ^{235}U grows into plutonium at 30 ppm per year and ^{241}Am typically increases by about 120 ppm per year, depending on the initial ^{241}Pu concentration. Approximately three years had elapsed between the purification and the ellipsometry measurements. During the casting process, sufficient gallium was added to make a 1 wt% alloy. The final cast rod was machined to a diameter of 0.635 cm. Samples for ellipsometry were cut from this 1 wt% gallium rod using a tubing cutter.

The details of the RAE instrumentation and technique have been described previously [12]. Using this method, monochromatic, linearly polarized light is reflected from an electromagnetically levitated specimen at a known angle of incidence, 72.84°, and the polarization state of the reflected light is determined from intensity ratio measurements at three different azimuths of a Glan-Thompson analyzing prism. In general, the reflected light will be elliptically polarized and the optical properties may be determined from the change in polarization state upon reflection.

Fromm and Jehn [15] have described the factors affecting electromagnetic forces and power absorption in levitation melting. Plutonium liquid was difficult to levitate because of its high density and resistivity and very small surface tension. Nominal values for the density, resistivity and surface tension near the melting point are 16.6 g/cm^3, 100 μΩcm, and 0.550 N/m, respectively. For sufficiently high frequencies, the electrical resistivity does not affect the levitation force. However, it was not practical to change the frequency of the RF generator, 270 kHz, and this resulted in somewhat less than the optimal force. The current density in the sample is a complicated function of position [16], but the current and force are concentrated at the surface in a thin shell, ≈1 mm, due to the skin effect and near the equator. Because of the low surface tension and high density, samples tended to drip out of the coil. Weisberg [17] found it impossible to levitate lead because of its small ratio of surface tension to density, but this ratio for plutonium is even smaller, about 0.77 that of lead.

Several preliminary experiments were required to find a successful coil design and operating conditions for the levitation of liquid plutonium. The best coil was wound with 0.318 cm outer diameter copper tubing on a 0.685 cm diameter mandrel. The coil consisted of four lower turns and two upper turns wound in the reverse sense. The coil loop required to change the sense of the windings for the upper turns was positioned approximately parallel to the

RF coil leads such that the field due to the reverse loop and leads tended to cancel. The gap between the lower and upper turns of the coil was 0.356 cm. Successful levitation was obtained only when the Pillar Industries, 50 kW, generator was operated at full power output. The preferred sample mass was in the range 1.2–1.5 g, although samples up to 2.3 g were also briefly levitated.

The maximum temperature of the measurements was limited by the vapor pressure of plutonium, 102 Pa at 2200 K [18]. Samples were levitated in helium at reduced pressure, 1.3×10^4 Pa, to achieve the highest temperature initially and to volatilize impurities. To obtain the temperature dependence of the optical properties, the helium pressure was slowly increased to provide additional convective cooling. The minimum temperature achievable using convective cooling was approximately 2000 K. It was not possible to reduce the temperature by decreasing the RF power and still levitate the sample in the coil gap. In fact, small reductions in the RF power resulted in a higher temperature because of better coupling with the field as the sample position moved further into the coil. Eventually, plutonium condensate shorted the windings of the coil, ending the experiment. Optical property measurements on levitated liquid platinum were performed before each plutonium experiment to align the optics and maximize the reflected intensities, and to validate the operation of the apparatus by comparison of the platinum optical property results with previously reported values [19].

3. Results

3.1. Platinum

At temperatures in the range from 2458 to 2505 K, the average values of optical property results obtained for liquid platinum are $\epsilon_\lambda = 0.366 \pm 0.002$, $n_\lambda = 3.07 \pm 0.02$ and $k_\lambda = 4.13 \pm 0.02$. The uncertainties are sample standard deviations of 17 data points. Krishnan et al. [19] obtained $\epsilon_\lambda = 0.38 \pm 0.01$, $n_\lambda = 3.15 \pm 0.15$, and $k_\lambda = 4.00 \pm 0.15$ at a temperature approximately 230 K below the average value for the current results. The influence of temperature on the optical properties is small enough that the two sets of results agree within the precision of the measurements.

3.2. Plutonium

The levitated liquid had a uniform brightness as viewed through the optical pyrometer. It did not show any bright regions that are often observed when samples are contaminated with oxygen.

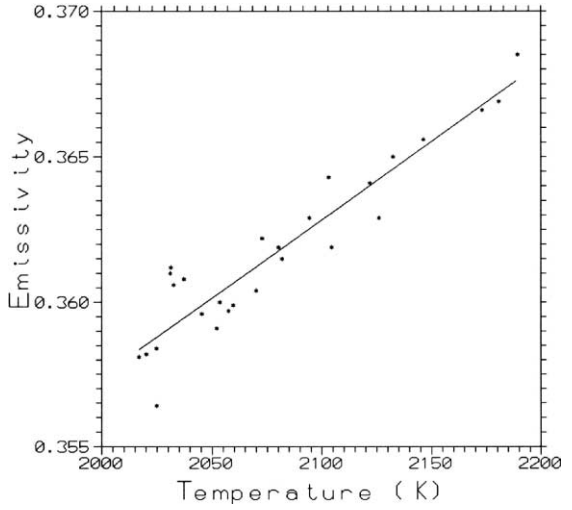

Fig. 1. The normal, spectral emissivity of liquid plutonium as a function of temperature at 632 nm.

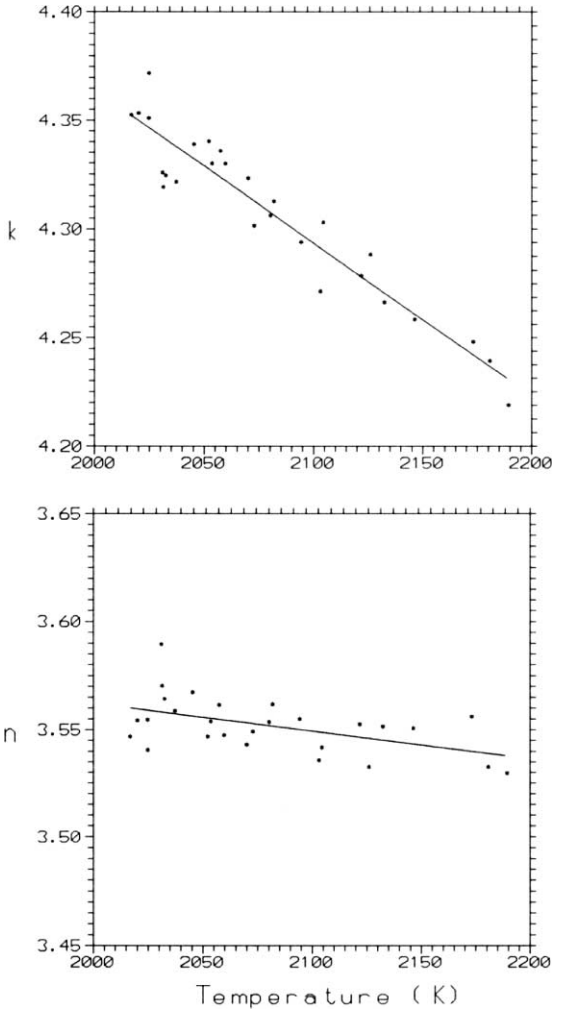

Fig. 2. The optical constants, n and k, of liquid plutonium as a function of temperature at 632.8 nm.

Normal, spectral emissivity and optical property data for liquid plutonium at 632.8 nm are shown in Figs. 1 and 2, respectively, as a function of temperature. The straight lines drawn through the data in Figs. 1 and 2 represent least squares fits, which are given in Eqs. (2)–(4) for $\epsilon_\lambda(T)$, $n_\lambda(T)$, and $k_\lambda(T)$, respectively

$$\epsilon_\lambda(T) = 5.38 \times 10^{-5} T + 0.250, \tag{2}$$

$$n_\lambda(T) = -1.29 \times 10^{-4} T + 3.82, \tag{3}$$

$$k_\lambda(T) = -7.04 \times 10^{-4} T + 5.77. \tag{4}$$

4. Discussion

The random and systematic errors associated with the levitation/RAE method have been discussed previously [12,20,21]. The estimated accuracy in the optical constants is 1.5%, which propagates into an accuracy in the emissivity of about 1.5% of the emissivity values.

A small and systematic error in the plutonium temperatures arises in our use of spectral emissivity values measured at a wavelength of 632.8 nm to correct apparent temperatures obtained with a pyrometer whose effective wavelength is 650 nm. The typical variation of emissivity with wavelength for metals (cf. Ref. [10]) suggests that, at 2100 K, the true temperatures could be 0–2 K greater than the derived values. This possible error is within the precision of the apparent temperature measurements.

Fig. 3 compares the emissivity data for liquid plutonium with published results for liquid uranium [5]. Each set of results is shown as the fitted curve over the temperature range of the plutonium and uranium experiments. A large temperature range was possible in the work on liquid uranium because uranium is less volatile and more easily levitated than plutonium, and by using CO_2 laser beam heating to supplement the electromagnetic heating of levitated liquid uranium.

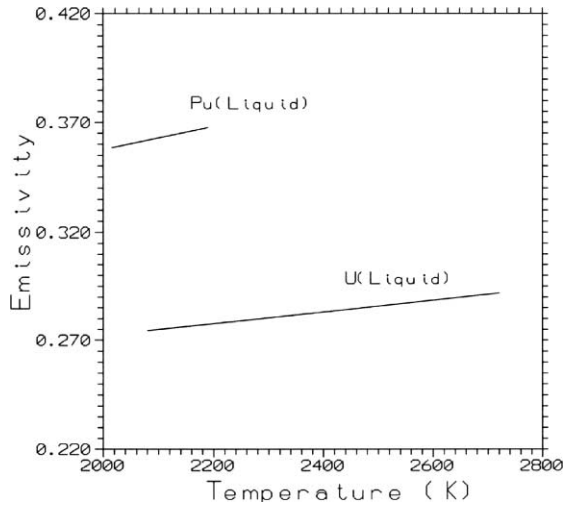

Fig. 3. The normal, spectral emissivity of liquid plutonium (this work) and liquid uranium [5] at 632.8 nm.

The results in Fig. 3 show that the spectral emissivity of one actinide metal would be a poor approximation to that of another actinide, especially where accurate radiometric temperature measurements are required. At 2100 K, the application of uranium emissivity data to correct an apparent temperature measurement on plutonium would yield a temperature error of +55 K. Extrapolation of the plutonium emissivity results suggests that the error would increase to +110 K at 2800 K. Errors resulting from using the actual plutonium emissivity results, extrapolated to higher temperatures, are much smaller. For example, if the temperature coefficient of $\epsilon_\lambda(T)$ for plutonium is assumed accurate to $\pm 50\%$, the emissivity at 2800 K would be 0.401 ± 0.019, contributing an error of only ± 17 K to the temperature measurement.

Additional spectral emissivity measurements would be required to accurately measure the much higher temperatures accessed by pulse heating techniques, such as the experiments reported by Boivineau [8] on liquid plutonium at temperatures up to 4000 K. The short duration of pulse heating experiments precludes the use of the current ellipsometric method because the mechanical rotation of the polarization state analyzer crystal is slow. However, 4-detector photopolarimeter techniques are very fast and have been applied to obtain emissivity measurements at MHz rates in a few pulse heating experiments at temperatures to 5000 K and above [22,23]. A smaller wavelength than the 632.8 nm used in the work is recommended for such measurements. A smaller wavelength will reduce the influence of errors in emissivity and spectral radiant intensity measurements on the derived values of the true specimen temperature.

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