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TEMPERATURE DEPENDENCE OF THE OPTICAL
REFLECTIVITY OF CERIUM METAL

by

A. H. Millhouse and T. E. Leinhardt

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ABSTRACT

The optical reflectivity of polished, vacuum-annealed samples of Johnson-Matthey cerium has been examined at 300° and 80°K. The specimens were mounted in an evacuated optical cryostat. All measurements were made with monochromatic light incident upon the plane surfaces of the samples at an angle of 45°. The source of the radiation was a modified Bausch & Lomb grating monochrometer. Type 1P28 photomultipliers were used as detectors. Results indicate that there is a decrease in the ratio of the reflectivity at 80°K over that at 300°K in the 4000- to 6000- Å region. In one specimen, this amounted to about a 20% change. Below 4000 Å, the ratio increases rapidly as shorter wavelengths are approached.

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I

INTRODUCTION

When cerium specimens are cooled a rapid decrease in resistivity is observed beginning at a temperature between 100°K and 120°K . This decrease has been attributed to a transition from the normal f. c. c. structure (γ cerium, lattice constant $a = 5.14 \text{ \AA}$) to a collapsed f. c. c. form (α cerium, lattice constant $a = 4.84 \text{ \AA}$) resulting from a 4f, 5d electron transition.¹

In addition to γ and α cerium it has been found that a third allotropic form of cerium exists.² This is a hexagonal close-packed phase with $a = 3.68 \text{ \AA}$ and $c = 11.92 \text{ \AA}$ which is called β cerium. The crystal structure of the metal depends on its temperature and past history.^{3, 4} X-ray studies on a sample cut from the same block of cerium as the one used in this experiment and annealed the same way showed the following percents of the three crystallographic phases present:⁵

	T ($^{\circ}\text{K}$)	γ (%)	β (%)	α (%)
(I)	300	90	10	0
(II)	85	80	20	0
(III)	300	80	20	0
(IV)	85	60	30	10

The purpose of this experiment was to ascertain what effect, if any, these transitions would have on the reflectivity of the metal in the visible and near ultraviolet part of the spectrum.

II

REVIEW OF LITERATURE

The published literature on the optical properties of rare earth metals is sparse. Wilburn⁶ has reported on the infrared reflectance of several rare earth elements, but not of cerium.

A comprehensive article on the experimental work done on the optical properties of metals prior to 1957 has been written by L. G. Schulz⁷ and articles on the theory have been written by several authors.^{8, 9, 10}

A review of work done on the rare earths before 1961 is provided by Spedding and Daane.¹¹

III

EXPERIMENTAL APPARATUS

The sample was mounted in a liquid air cryostat containing two quartz windows (1 inch diameter, 1/16 inch thick) mounted 90° apart. A cutaway view of the cryostat and sample mount is shown in figure 1. A copper-constantan thermocouple was connected to the sample in the cryostat to monitor its temperature during the experiment.

A Bausch and Lomb Grating Monochromator (Cat. No. 33-86-40-01) was used as a source of monochromatic light. This instrument has a focal length of 250 millimeters and a ruled grating area of 50 x 50 millimeters. The grating has 600 grooves/mm, and a blaze angle of 5°10'. The reciprocal linear dispersion is 6.6 millimicrons per millimeter in the first order. As received from the factory the monochromator has a hand operated wavelength drum which is mechanically coupled to the grating. Wavelengths can be read from this drum to the nearest millimicron. A motor was added to the monochromator to rotate the drum continuously at a rate of 41.2 degrees/minute (22.8 millimicrons/minute). The monochromator has adjustable entrance and exit slits which were set at approximately 0.1 millimeter during the whole experiment.

Figure 1. Cross sectional view of cryostat showing sample (a), copper constantan thermocouple (b), quartz window (c), sample mount (d), lead washer (e), polyethylene clamps (f), o-rings (g), and wax seal (h).

The light sources used in conjunction with the monochromator were a tungsten filament bulb (G. E. 18 A/T10/1P-6V) and a mercury vapor lamp (G.E. Hanovia serial 38072 Type S H).

Two Amphenol 1P28 photomultiplier tubes were used as radiation detectors. The output of these tubes was recorded on a Varian Model G - 10 Graphic Recorder and a Varian Model G - 14 Graphic Recorder.

The cryostat was evacuated by means of an oil diffusion pumping system to prevent oxidation of the sample. This system was not equipped with a cold trap. Previous measurements, both with and without a cold trap, showed that use of a cold trap produced no significant change in the data.

An optical lever arrangement with a mirror mounted in the same position as the sample, shown in figure 1, indicated that the rotation of the sample about the axis of the sample holder, due to cycling between 300°K and 80°K , was less than 0.001 radian.

EXPERIMENTAL PROCEDURE

The cerium sample was cut from a 100 gram block of the metal obtained from Johnson, Matthey & Company Limited, and labelled by them as batch number M163. The specimen dimensions were approximately 2.60 cm x 1.70 cm x 0.20 cm with a mass of 5.39 grams.

Before each run the specimen was pre-polished using silicon carbide paper, number 320-A, with glycerine as a lubricant until a smooth average surface was obtained. The surface was then cleaned using acetone and methyl alcohol. After cleaning the surface the specimen was annealed in a vacuum (<10 micron of Hg) at a temperature of approximately 700°F for at least 3 hours. During annealing the specimen was contained in a tantalum boat to prevent contact between the sample and the hot pyrex annealing tube. After annealing, the specimen was polished lightly as before to remove the thin film of oxide on its surface due to the annealing process. The sample was then mounted in the liquid air cryostat as shown in figure 1.

A simplified diagram of the experimental setup is shown in figure 2.

After the sample was mounted in the cryostat it was positioned to receive the incident radiation at an incidence

Figure 2. Simplified diagram of experimental setup.

angle of 45° . The sample chamber was then sealed and connected to the oil diffusion pumping system.

A beam splitter was used to divide the beam into two parts one of which was monitored directly by a photomultiplier tube (detector #1), the other part was monitored by a second photomultiplier tube (detector #2) after being reflected from the sample. A quartz beam splitter was used with the mercury vapor lamp and a glass beam splitter with the tungsten filament bulb.

The output of detector #1 was recorded on the G-10 recorder and that of detector #2 on the G-14 recorder. A switch was used so that the thermocouple output could also be recorded on the G-14 recorder. Both recorders were used on the 10 millivolt full scale setting (2 millivolts per inch).

After the specimen was mounted and the cryostat evacuated, the apparatus assembly was sealed to eliminate background radiation. The wavelength drum was positioned in the wavelength range to be used until maximum deflection on the recorders was obtained. The iris between the beam splitter and detector #1 was then adjusted until the deflections on the recorders were about the same. The wavelength drum was then connected to the motor drive and turned continuously through the wavelength range of interest while records of the output of detectors #1 and #2 were made.

A quantity proportional to the reflectivity at temperature $T(^{\circ}\text{K})$, denoted by R_T , was obtained by dividing the output of detector #2 (R_2) by the output of detector #1 (R_1) at a particular wavelength, i. e., $R_T = R_2/R_1$

In order to ensure that the proportionality constant between R_T and the reflectivity was independent of wavelength the two paths taken by the monochromatic light, shown in figure 2, were made optically identical by the introduction of two quartz windows between the beam splitter and detector #1. Also, runs were made which showed that R_T did not change appreciably when detectors #1 and #2 were interchanged.

V

DATA

The data obtained is shown in figures 1 to 8, inclusive. Each curve in the graphs of R_T is an average of six sets of data and the maximum spread of the data is shown by the error bar in each figure. The time required to obtain the data for determining R_T at each temperature was approximately one hour. The time required to cool the specimen from 300°K to 80°K was approximately 30 minutes, and approximately three hours was required for the temperature of the specimen to increase from 80°K to 300°K . All data was taken immediately after the specimen reached the temperature involved.

Run #1

The results of run #1 are shown in figure 3. This data was taken using the previously described cerium sample, labelled sample J. M. 1-0, and the tungsten filament source.

Figure 3 (a) shows R_T for a complete cycle of temperature from 300°K to 80°K and back to 300°K . The order in which the data was taken is shown in the upper right hand corner of this figure.

Figure 3 (b) shows the ratio $R_{80^\circ\text{K}}/R_{300^\circ\text{K}}$ for the bottom two curves ($\square$ / $\circ$) of figure 3 (a). This figure shows that the reflectivity of the sample decreases when it is cooled to 80°K , the decrease varying from about 10% at 0.6 microns to about 25% at 0.4 microns.

Run #2

The results of this run are shown in figures 4 and 5. The data was taken using sample J. M. 1-0 and the mercury vapor lamp.

Figure 5 shows the ratio $R_{80^{\circ}\text{K}}/R_{300^{\circ}\text{K}}$ for cycle 1 (figure 4, $\square / \circ$) and cycle 2 (figure 4, $\nabla / \triangle$). The curve for cycle 1 shows the same decrease as shown in figure 3 with a marked rise as short wavelengths are approached. The ratio $R_{80^{\circ}\text{K}}/R_{300^{\circ}\text{K}}$ shows a quite different behavior for cycle 2. This is attributed to the change in the fractions of the three crystallographic phases present.

Run #3

The results of run #3 are shown in figures 6 and 7. In this run sample J. M. 1-0 and the mercury vapor lamp were used.

Immediately after cooling the specimen to 80°K , R_T was measured ($\square$, figure 6). The specimen was kept at a temperature of 80°K for 3 hours and R_T remeasured ($\triangle$, figure 6). As shown in figure 6 an isothermal change in R_T , at 80°K , was observed and is attributed to an isothermal change in crystal structure. This type of change has been observed by others.⁵

Run #4

The results of run #4 are shown in figure 8. This run was made using an unannealed aluminum sample whose dimensions and surface preparation were the same as sample J. M. 1-0.

Within the spread of the data there was little change in the reflectivity of the aluminum sample when it was cooled.

Other experimental results¹² show a much flatter dependence of reflectivity on wavelength than was observed here. This is probably due to the different preparation of the surface. However, the change in reflectivity due to cooling is in agreement with other experimental results.⁷

Figure 3. Results of run #1.

Figure 4. Results of run #2.

Figure 5. Results of run #2 (continued).

Figure 6. Results of run #3.

Figure 7. Results of run #3 (continued).

(a)

(b)

Figure 8. Results of run #4.

VI

DISCUSSION OF RESULTS

The experimental results presented in figures 3 to 7, inclusive, show a decrease in the reflectivity of the annealed cerium sample when it is cooled from 300°K to 80°K. This decrease varies from about 10 percent at 0.60 microns to between 25 and 50 percent at 0.33 microns, and below 0.33 microns begins to rise again. The reflectivity changes markedly with continued cycling and in one case an isothermal change was found.

The photoelectric work function of cerium is 2.84 electron volts.¹³ Since this energy was in the range of interest in this experiment a measurement of the photoelectric current was made. A probe was introduced into the cryostat at about one centimeter from the face of the polished cerium sample. The sample chamber was then evacuated and the sample illuminated with monochromatic light (mercury vapor bulb) of about the same intensity as that used in the reflectivity measurements. The probe was connected in series with a 300 volt battery which in turn was connected in series with a 39 kohm resistor. The other end of the resistor was then connected to the cerium sample. The voltage drop across the resistor was measured on the G-14 recorder using the 10 millivolt full scale setting. Although a current of 10^{-7} ampere could have been detected by this circuit, no noticeable

current was observed when the wavelength of the incident monochromatic light was varied from 0.3 to 0.5 microns.

The basic theory of the optical properties of metals is the Drude free electron theory.^{8, 9, 10} The mechanism of absorption assumed in this theory is that of conduction electrons, and the success of this theory depends on how strong this mechanism is for the particular metal and wavelength interval of interest.

Other mechanisms that contribute to absorption and cause deviations from the Drude theory are reviewed in an article by Roberts,¹⁴ one of which is the absorption due to internal photoelectric effects or band transitions. These other mechanisms of absorption tend to be strongest toward the ultraviolet and their effects often trail off into the near infrared.⁷

Clark¹⁵ has made calculations using the Drude theory and experimentally determined valencies and conductivity for cerium. These calculations show a slight increase of the reflectivity, in the visible part of the spectrum, when cerium is cooled from 300°K to 80°K. The observed decrease must be a combination of several mechanisms of absorption. However, since the detailed band structure of cerium is not known, no quantitative description of the absorption process can be given.

VII

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