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# Ernest O. Lawrence Radiation Laboratory

THERMAL EXPANSION COEFFICIENTS OF THE ANHYDROUS TRICHLORIDES OF CERIUM PLUTONIUM AND AMERICIUM

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## ABSTRACT

As shown by Zachariasen[1] anhydrous trichlorides of the lighter lanthanide elements and of the first members of the actinides series exhibit a hexagonal structure, space group $C6_3/m$ - $C_{6h}^2$, with two molecules per unit cell. We report here the thermal expansion coefficients of the trichlorides of cerium, plutonium and americium calculated from powder diffraction patterns, between room temperature and a temperature close to the melting point of the compounds.

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## EXPERIMENTAL

### Sample preparation

$PuCl_3$ was prepared from high purity* $Pu^{239}$ metal in two steps:

a) formation of the hydride by reaction of dry hydrogen on the metal at 400°C;

b) hydrochlorination of the hydride at 500°C.

$CeCl_3$ and $AmCl_3$ ($Am^{241}$) were prepared by hydrochlorination of the oxide at 500°C. The oxides were obtained from high purity* solutions. Preparations were carried out in quartz capillaries connected to a vacuum line. After evacuation ($\leq 10^{-6}$ mm Hg), the samples were sublimed to the tips of the capillaries which were then sealed off. A sharp temperature gradient was required to obtain the sublimate in a narrow band. X ray samples from a few micrograms to a few tens of micrograms were used. None of them showed extraneous diffraction lines.

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*By the copper spark method the only impurities detected, expressed in micrograms per 50 micrograms of the element studied were, for plutonium: Ca $\leq$ 0.01, Mg, 0.01; for americium: Ca, 0.01; Mg, 0.01; for cerium: Mg, 0.02. The limits of detection of various elements by this method are indicated elsewhere.[2] In the case of cerium analysis limits of detection for Al and Ca were 0.1 and 0.05 micrograms respectively.

X ray equipment

The present study has been initiated with a standard Norelco X ray unit type No. 12045 (35 kV-20 mA) and continued with a Jarrell-Ash microfocus X ray unit (45 kV-3.5 mA). Copper K$\alpha$ radiation was used.

The high temperature 9 cm diameter camera has been described by McWhan, Cunningham, and Wallmann.[3] The thermocouple used to measure the sample temperature was calibrated against the melting point of various standard substances which were sealed in quartz capillaries of dimensions similar to those used in the study of the trichlorides. The calibration was checked several times during its period of use. Observation of the melting point was made by means of a microscope through the collimator and catcher holes. Temperature accuracy is believed to be $\pm 2^{\circ}C$ at $350^{\circ}C$, $\pm 2^{\circ}C$ at $600^{\circ}C$ and $\pm 5^{\circ}C$ at $800^{\circ}C$. Lattice parameters for $CeO_2$ at various temperatures have been reported by Braver and Gingerich.[4] From their data we calculate

$$\frac{\text{lattice param at } t' - \text{lattice param at } t}{(t'-t) \times \text{lattice param at } 20^{\circ}C} = 1.17 \times 10^{-6} \text{ in the range } \sim 25\text{-}900^{\circ}C.$$

We also measured the lattice parameter of $CeO_2$ as a function of temperature from room temperature to $800^{\circ}C$, and find the thermal expansion coefficient to be $(1.15 \pm 0.05) \times 10^{-6}$. Recording of the thermocouple output during the exposures insures a check on the temperature stability.

Ilford Industrial G films were used for the X ray measurements. Exposure time ranged between 8 and 15 hours.

Lattice parameter calculations

To minimize random errors line position on the films were read two or three times. After indexing the various reflections, lattice parameters were calculated by the least squares method using a suitable correction function to minimize errors due to excentricity of the sample or divergence and absorption of the X ray beam. We have used a program written by Mueller and Heaton[5] for an IBM 704 computer. The correction function chosen is $\sin^2 2\theta(\frac{1}{\sin\theta} + \frac{1}{\theta})$. Unit weight has been given to each reflection. However when one observed line could be attributed to several planes, fractional weights were given proportionally to their relative intensity. To insure the proper indexing a program written by Smith[6] for calculating the intensity of the various reflections, has been used.

Diffraction lines up to at least $75^\circ$ ($80^\circ$ for $CeCl_3$) were usable even for high temperature results. The least squares fit of the various reflections leads to an error in the calculated value of the lattice parameter which is smaller than the error arising from the uncertainty in the effective camera radius (~0.02%). In general the relative error in c is larger than in a owing to a smaller number of diffracting planes having high l Miller indices. We estimate the uncertainity in the absolute value of the lattice parameters to be about ±0.004 A.

Results

Table I summarizes the lattice parameters of the trichlorides as a function of temperature. Room temperature data for $CeCl_3$ and $PuCl_3$ agree reasonably well with literature results. Our value for the c axis of $AmCl_3$ differs notably from Zachariasen's results[1] but it is in reasonable agreement with recent data of Wallmann and Cunningham.[7] Unresolved differences exist between the lattice parameters for $AmCl_3$ reported here and those found recently by Asprey, Keenan and Kruse,[8] but are not important in the calculation of the expansion coefficients.

Table II summarizes the various room temperature results. Room temperature measurements of the samples after their thermal treatment showed no change in lattice parameters, within the experimental error.

Plots of the lattice parameters versus temperature are linear within our accuracy. Table III shows the thermal expansion coefficients calculated for 20°C. The anisotropy of the expansions is especially large with the actinide compounds. Experiments with other isomorphous halides should be of interest.

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Table I. Lattice parameters of the trichlorides.

| | t°C | a (Å, ± 0.004) | c (Å, ± 0,004) |
|---|---|---|---|
| $CeCl_3$ | 23.5 ± 0.5 | 7.445 | 4.316 |
| | 110 ± 1.5 | 7.456 | 4.322 |
| | 230 ± 2 | 7.473 | 4.330 |
| | 307.5 ± 2 | 7.486 | 4.336 |
| | 424 ± 3 | 7.505 | 4.345 |
| | 519 ± 3 | 7.518 | 4.353 |
| | 723 ± 4 | 7.549 | 4.367 |
| $PuCl_3$ | 23.5 ± 0.5 | 7.392 | 4.244 |
| | 124 ± 1.5 | 7.410 | 4.253 |
| | 240 ± 2 | 7.426 | 4.258 |
| | 376 ± 3 | 7.451 | 4.265 |
| | 485 ± 3 | 7.470 | 4.274 |
| | 590 ± 3 | 7.486 | 4.277 |
| | 700 ± 4 | 7.509 | 4.286 |
| $AmCl_3$ | 23.5 ± 0.5 | 7.384 | 4.225 |
| | 116.5 ± 1.5 | 7.397 | 4.231 |
| | 228 ± 2 | 7.415 | 4.235 |
| | 312 ± 2 | 4.429 | 4.242 |
| | 425 ± 2 | 7.452 | 4.250 |
| | 516.5 ± 3 | 7.469 | 4.256 |
| | 607.5 ± 3 | 7.483 | 4.262 |

Table II. Comparison of various data for the room temperature lattice parameters.

| | a (Å) | c (Å) | Authors |
|---|---|---|---|
| $CeCl_3$ | 7.451 ± 0.004 | 4.313 ± 0.004 | Zachariasen[1] |
| | 7.450 ± 0.004 | 4.315 ± 0.002 | Templeton and Dauben[8] |
| | 7.445 ± 0.004 | 4.316 ± 0.004 | this work |
| $PuCl_3$ | 7.395 ± 0.001 | 4.247 ± 0.001 | Zachariasen[1] |
| | | | Wallmann and Cunningham[7] |
| | 7.392 ± 0.004 | 4.244 ± 0.004 | this work |
| $AmCl_3$ | 7.385 ± 0.01 | 4.249 ± 0.01 | Zachariasen[1] |
| | | | Wallmann and Cunningham[7] |
| | 7,384 ± 0.004 | 4.225 ± 0.004 | this work |

Table III. Coefficients of thermal expansion (20°C) in $^{\circ}C^{-1}$.

| | $\alpha_a$ | $\alpha_c$ |
|---|---|---|
| $CeCl_3$ | $2.13 \pm 0.1 \times 10^{-5}$ | $1.74 \pm 0.1 \times 10^{-5}$ |
| $PuCl_3$ | $2.40 \pm 0.1 \times 10^{-5}$ | $1.37 \pm 0.1 \times 10^{-5}$ |
| $AmCl_3$ | $2.40 \pm 0.1 \quad 10^{-5}$ | $1.38 \pm 0.1 \times 10^{-5}$ |

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