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are now underway to theoretically interpret the spectrum and derive the applicable spectroscopic parameters. Theoretical intensity calculations will then be possible.

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Thermal expansion coefficients of the anhydrous trichlorides of cerium, plutonium and americium

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INTRODUCTION

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 $P \, 6_3/m - C_{e,s}^3$, 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.

EXPERIMENTAL

Sample preparation. PuCl₃ was prepared from high purity* ²⁸⁹Pu 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.

CeCl₃ and AmCl₃ (⁴⁴¹Am) 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.

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 dia. 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

* By the copper spark method the only impurities detected, expressed in μg per 50 μg of the element studied were, for plutonium: Ca ≤ 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.⁽³⁾ In the case of cerium analysis limits of detection for Al and Ca were 0.1 and 0.05 μg respectively.

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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°C, $\pm 3^{\circ}$ C at 600°C and $\pm 5^{\circ}$ C at 800°C. Lattice parameters for CeO₂ at various temperatures have been reported by BRAUER and GINGERICH.⁽⁴⁾ From their data we calculate

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

We also measured the lattice parameter of CeO₂ as a function of temperature from room temperature to 800°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 hr.

Lattice parameter calculations. To minimize random errors, line positions 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 eccentricity 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. This program provides several correction functions which can be applied to the observed values of $\sin^2\theta$. Among them, we have chosen

$$\left(\frac{1}{\sin\theta}+\frac{1}{\theta}\right)\times\sin^2 2\theta.$$

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° (80° for CeCl_a) 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 (\sim 0.02 per cent). In general the relative error in c is larger than in a owing to a smaller number of diffracting planes having high 1 Miller indices. We estimate the uncertainty in the absolute value of the lattice parameters to be about \pm 0.004 Å.

RESULTS

Table 1 summarizes the lattice parameters of the trichlorides as a function of temperature. Room temperature data for CeCl₃ and PuCl₃ agree reasonably well with literature results. Our value for the c axis of AmCl₃ 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 AmCl₃ reported here and those found recently by ASPREY, KEENAN and KRUSE,⁽⁸⁾ but are not important in the calculation of the expansion coefficients.

Table 2 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 vs. temperature are linear within our accuracy. Table 3 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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	t(°C)	$a(\text{\AA} \pm 0.004)$	$c(\text{\AA} \pm 0.004)$
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 \pm 3	7.505	4.345
	519 \pm 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 \pm 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 \pm 2	7.452	4.250
	516·5 ± 3	7.469	4.256
	607·5 \pm 3	7.483	4.262

TABLE 1.--LATTICE PARAMETERS OF THE TRICHLORIDES

TABLE 2.—COMPARISON OF VARIOUS DATA FOR THE ROOM TEMPERATURE LATTICE PARAMETERS

	<i>a</i> (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 ⁽⁹⁾
	7.445 ± 0.004	4.316 ± 0.004	this work
PuCl ₃	7.395 ± 0.001	4.247 ± 0.001	ZACHARIASEN ⁽¹⁾
-	$7 \cdot 392 \pm 0 \cdot 004$	4.244 ± 0.004	this work
AmCl ₃	7.385 ± 0.01	4.249 ± 0.01	ZACHARIASEN ⁽¹⁾
	7.390 ± 0.003	4.234 ± 0.002	ASPREY, KEENAN and KRUSE
	7.384 ± 0.004	4.225 ± 0.004	this work

Table 3.—Coefficients of thermal expansion (20°C) in $^{\circ}C^{-1}$

	α _a	a.
CeCl ₃ PuCl ₃ AmCl ₃	$\begin{array}{c} (2.13 \pm 0.1) \times 10^{-5} \\ (2.40 \pm 0.1) \times 10^{-5} \\ (2.40 \pm 0.1) \times 10^{-5} \\ (2.40 \pm 0.1) \times 10^{-5} \end{array}$	$\begin{array}{c} (1.74 \pm 0.1) \times 10^{-5} \\ (1.37 \pm 0.1) \times 10^{-5} \\ (1.38 \pm 0.1) \times 10^{-5} \end{array}$

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Exchange between Fe²⁺ and Fe³⁺ in ice*

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INTRODUCTION

HORNE⁽¹⁾ has reported the interesting result that isotopic exchange occurs between Fe^{2+} and Fe^{3+} in solid aqueous media. He suggests that the reaction mechanism is the same in the liquid and solid phases because a single line in a log k vs. 1/T plot represents the data approximately both for the liquid and solid phases if an order-of-magnitude correction is made in the solid-phase data to allow for the probable concentration of the reactants in the HClO₄-H₂O eutectic (6 M HClO₄) which solidifies at -58° C.

We also have studied the $Fe^{2+} - Fe^{3+}$ exchange reaction in solid aqueous media and confirm that exchange does indeed occur, but we have not been able to reproduce HORNE's rate measurements and, therefore, cannot support his suggestion concerning the mechanism. We had difficulty in obtaining reproducible data, as did HORNE, and in addition we encountered unidentified catalytic effects. However, when these were minimized our measured rate constants were considerably larger than HORNE's. The discrepancy may, of course, be due entirely to catalytic effects which affected HORNE's measurements less than ours, but until this complex kinetic system is more thoroughly studied, we believe that caution should be exercised in drawing conclusions about the reaction mechanism.

EXPERIMENTAL

A rate was determined from a number of separate experiments carried out more or less concurrently. One millilitre each of Fe^{2+} and Fe^{*8+} (tagged with ⁵⁹Fe) solutions, 0.6 M in HClO₄ and at 0°C, were mixed in a glass-stoppered 50-ml Erlenmeyer flask and frozen. Freezing occurred within ~30 sec. After standing at the desired temperature for the desired time, the solid was melted by adding a solution of 2,2'-bipyridyl and by swirling the flask in water at ~30°C. Then sodium acetate and lanthanum carrier solutions were added, and iron (III)-lanthanum (III) hydroxides were precipitated with ammonia.^(2,3) The specific activity of the solution was determined from scintillation-counting and spectrophotometric measurements. Usually about 80 per cent of the iron (II) was recovered, so no large net chemical change occurred, except possibly for the experiments in which the concentration of iron (III) was much less than that of iron (II).

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