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Introduction

The determination of the chemical properties of macroscopic aggregates of short-lived radio-isotopes presents an interesting experimental challenge because of the continuous release of relatively enormous amounts of energy from radioactive decay. The decay energy of the einsteinium isotope of mass number 253, for example, amounts to 3,500 kilocalories per mole per minute.

We have previously reported (1) successful experiments to determine the absorption spectrum of einsteinium in aqueous solution with ^{253}Es concentrations as high as 3 M.

Here we report the first determinations of the structures of solid compounds of ^{253}Es by x-ray diffraction. In experiments prior to those described herein, we were unable to obtain satisfactory x-ray diffraction patterns from compounds of ^{253}Es at room temperature, even when freshly-prepared samples were inserted into the x-ray beam within three minutes after sample preparation. This result was not unexpected in view of the estimated rate of lattice damage by radiation. It appeared likely, however, that under conditions favorable to rapid annealing and resynthesis of the solids, lattice order could be maintained to a degree sufficient to yield diffraction effects.

Experimental

A. Materials

About 3 μg of einsteinium (consisting almost entirely of the 20.47-day alpha-emitting ^{253}Es) produced in the HFIR at Oak Ridge National Laboratory were made available for the work described here. This material was carefully purified by techniques described previously for berkelium (2) and californium (3), except that somewhat larger ion exchange column diameters were required because of the excessive radiolysis resulting from the higher specific activity of the einsteinium solutions. Because of rapid self-contamination of ^{253}Es by its decay product ^{249}Bk (3.3% per day), repurification was necessary at frequent intervals.

B. Sample Preparation

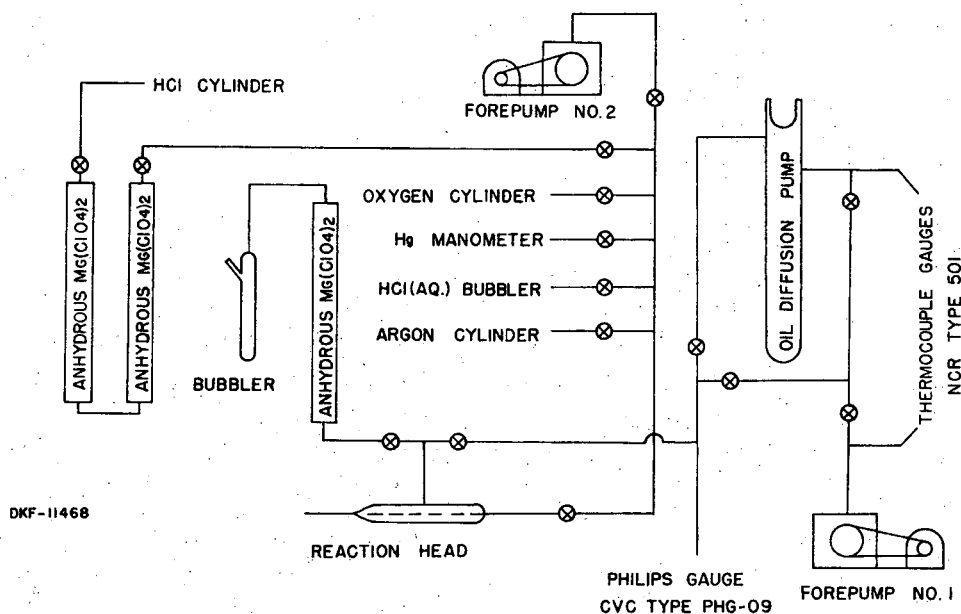
It was known from previous experience that significant concentrations of ^{253}Es could not be attained in Dowex 50 resins possibly because of rapid destruction of ion exchange sites; hence, the single resin bead techniques used for the preparation of compounds of berkelium and californium (2-9) were not applicable in the case of ^{253}Es .

Accordingly, small pieces of highly-purified porous charcoal (0.18 mm cubes) were used in place of the ion exchange resin beads. Material of satisfactory purity (ash = 5 ppm) was obtained by lengthy extraction of commercial coconut charcoal (Fisher lot number 5768) with organic solvents and hot mineral acids.

The einsteinium eluted from the final cation clean-up column in a minimum volume of high-purity 6 M HCl was collected in a leached quartz microcone and evaporated to ~ 1 μl volume. A 0.18 mm cube of charcoal was added

and the solution allowed to evaporate to dryness during continuous centrifugation. The charcoal chip, containing from 250-500 nanograms of ^{253}Es , was transferred to a thinwalled capillary drawn from a quartz standard-taper joint. The capillary was then attached to the sample preparation vacuum line shown in Fig. 1. The charcoal was converted to CO_2 by heating to 600°C in oxygen for 10 minutes, leaving white einsteinium oxide as a solid residue.

FIG. 1.



SAMPLE PREPARATION VACUUM LINE

Einsteinium trichloride was obtained by heating the oxide in anhydrous $\text{HCl}(\text{g})$ for 20 minutes at 500°C . Einsteinium oxychloride was formed by heating the oxide in a mixture of approximately 500 mm $\text{HCl}(\text{g})$ and 10 mm $\text{H}_2\text{O}(\text{g})$ at 500°C for 20 minutes. Following sample preparation, the capillaries were

sealed so as to leave approximately 200 μ l of the appropriate gas (HCl or a mixture of HCl and H₂O) at a total pressure of 700 mm Hg.

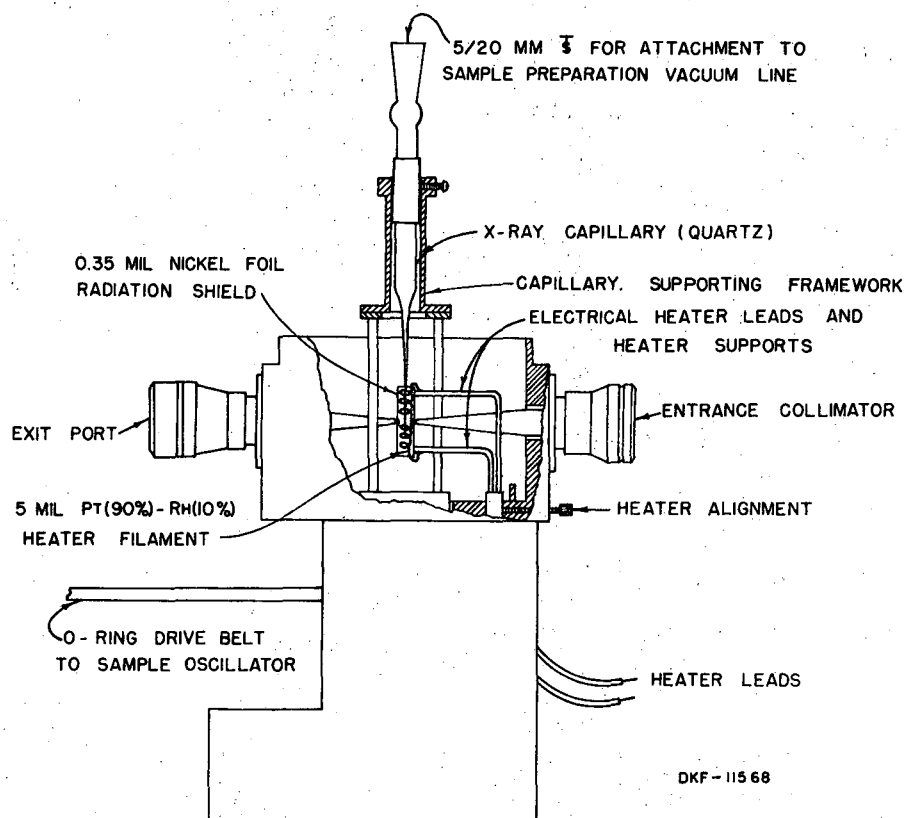
Several independent preparations of both EsCl₃ and EsOCl were performed; all contained berkelium in amounts ranging from 4 atom-% to 21 atom-%.

C. X-ray Diffraction Equipment

The diffraction equipment used has been described previously (6). However, a new anode system permitted operation at beam currents up to 8.5 mA. A 57.3 mm diameter Philips-Norelco Precision Powder Camera was modified to include a platinum-10% rhodium heating coil and 0.009 mm nickel radiation shield for heating the sample. Further modifications included a frame and extended cover to accommodate long capillaries in a vertical position. The capillary support prevented full rotation of the sample. However, oscillatory motion of \sim 100 degrees was provided. The heating coil and shield support were assembled in such a way as to intercept the diffracted x-rays only at a Bragg angle of nearly 90°. The x-ray camera is shown in Fig. 2.

Temperature calibration was established to within $\pm 10^\circ$ C by correlating heater coil current with the melting points of standard substances enclosed in x-ray capillaries. To protect the x-ray film (Ilford G Industrial type) from light from the heating coil as well as fluorescent light from the sample, the film was wrapped in 0.009 mm nickel foil which further served to filter Cu K _{β} radiation. Exposure times ranged from 50 to 110 minutes at a 45 kV accelerating potential and 8.5 mA beam current. Increased exposure beyond 110 minutes was of no value because of film darkening by radiation arising from the decay of ²⁵³Es.

FIG. 2



MODIFIED X-RAY CAMERA

Results and Discussion

Diffraction lines were obtained only when the samples were heated to an ambient temperature of about 400 to 425° C; in the case of EsCl_3 no diffraction lines were obtained at 450° C. It is reasonable to suppose that at this higher temperature the EsCl_3 was in a molten state. The melting point appears low when compared to the melting point of ~575° C observed for CfCl_3 (3,7), but it is likely that the temperature of the sample was substantially

above that of its surroundings due to its intense radioactivity.

Although some decrease in line sharpness as compared to room temperature films was to be expected, the broadening was not obvious and line positions could be measured as accurately as on films obtained at room temperature of other actinide compounds. Nineteen diffraction lines were obtained for EsCl_3 at observed two-theta values ranging from 14 to 67 degrees; thirteen lines were obtained for EsOCl in the range from 13 to 78 degrees. The methods of evaluating x-ray diffraction data have been described previously (2,3,6).

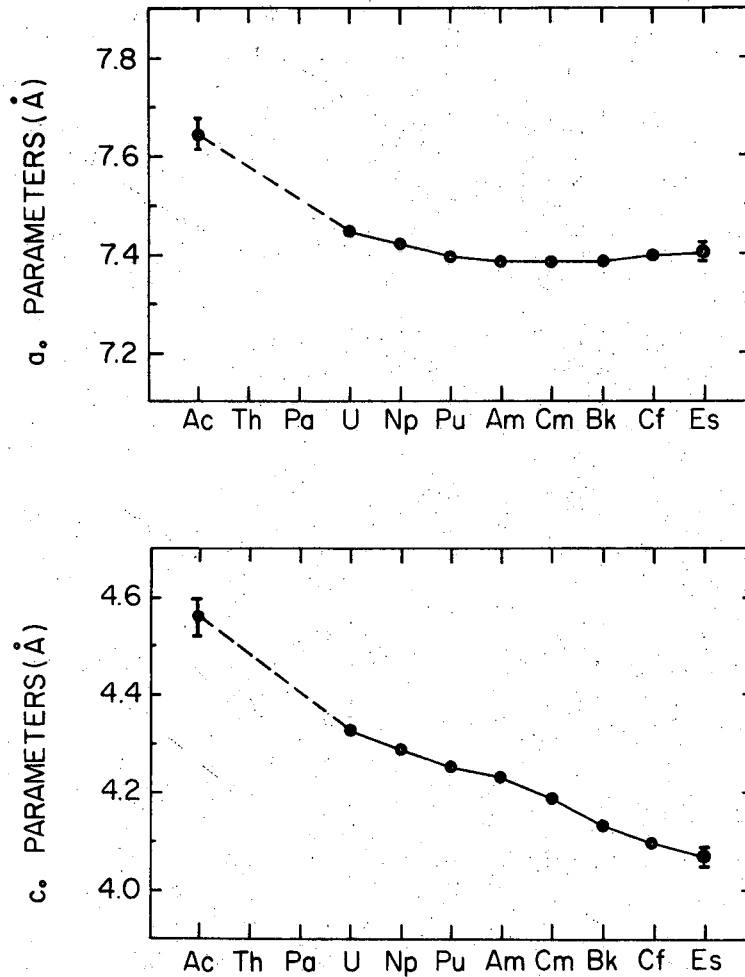
Einsteinium oxychloride exhibits the tetragonal PbFCl -type structure at $\sim 430^\circ \text{C}$ with $a = 3.97 \pm 0.01 \text{ \AA}$ and $c = 6.75 \pm 0.02 \text{ \AA}$.

At about 425°C , EsCl_3 was found to exhibit the hexagonal UCl_3 -type structure with $a = 7.47 \pm 0.01 \text{ \AA}$ and $c = 4.10 \pm 0.02 \text{ \AA}$. The error limits represent the 95% confidence interval for variations in lattice parameters between different preparations.

The high-temperature lattice parameters for EsCl_3 were corrected to 20°C using the thermal expansion data for AmCl_3 and PuCl_3 reported by Fuger (10). These room temperature values were corrected for known ^{249}Bk content in accordance with Vegard's law. The corrected lattice parameters are $a = 7.40 \pm 0.02 \text{ \AA}$ and $c = 4.07 \pm 0.02 \text{ \AA}$, the large estimated error limits reflecting principally the uncertainty in sample temperature due to self-heating by nuclear decay.

The EsCl_3 results agree reasonably well with trends in the a and c lattice parameters for the other UCl_3 -type actinide trichlorides when extrapolated to $Z = 99$ (Fig. 3).

FIG. 3



LATTICE PARAMETERS OF THE UCl_3 -TYPE
HEXAGONAL ACTINIDE TRICHLORIDES

XBL 6812-6367

The ionic radius of Es^{3+} based on the room temperature lattice parameters of $EsCl_3$ is 0.97 Å. This radius was computed from the weighted averages of nearest-neighbor anion-cation distances, correcting from 9-fold to 6-fold coordination (11), and assuming the ionic radius of the chloride

ion to be 1.81 Å (12). The molecular volume of EsCl_3 is 96.7 Å³.

Thus, while the ionic radius, molecular volume, and c parameter continue to decrease in comparison to the lighter actinides, the a parameter appears to increase. Green (3) observed a similar, but less pronounced, effect in CfCl_3 and attributed the expansion of the a parameter to repulsive interactions between the crowded apical and equatorial chloride ions.

The prediction of a change to the PuBr_3 structure type at EsCl_3 made by Peterson and Cunningham (13) is not borne out by our results. It is possible, however, that this structure type might be assumed by EsCl_3 at room temperature.

Techniques of the type described here may be of considerable use in future investigations of the inorganic chemistry of the actinide elements beyond einsteinium.

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Footnote

*The experimental work reported here is taken from a thesis to be submitted by D. K. Fujita to the Graduate Division of the University of California in partial fulfillment of the requirements of Doctor of Philosophy.

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