rhombohedral phases. No significant change in the rhombohedral angle of neodymium oxide fluoride ($\alpha = 33.03 \pm 0.05°$) was observed in the thermal expansion data below the transition point.

Bevan, *et al.*,[15] have reported for the erbium system a fluorite-related orthorhombic phase. The extra lines observed in the erbium X-ray diffraction photographs could be explained by this phase.

The rhombohedral–cubic transitions are evidently associated with order–disorder of the oxygen and fluorine atoms. As is characteristic for such transitions, the high-temperature form has a larger molecular volume and higher symmetry, and the down-temperature transition is somewhat sluggish. The disordering process must involve migration of the anions through the interstitial holes. Anion migration has been observed[17] *via* the interstices in CaF_2 and $YF_3 \cdot CaF_2$ solids. This migration is expected to become more difficult as the metal ion size decreases since the unit cell shrinks. On this basis one might predict that the transition temperature would increase with decreasing metal ion size. The observed transition temperatures increase from 494° for LaOF to 592° for ErOF. The temperature observed for GdOF, 606°, is the most obvious deviation from a gradual increase in transition temperature. The transition temperature has only a slight composition dependence (Table III), not enough to account for its unexplainable anomalous value.

Attempts to observe a tetragonal–cubic transition by high-temperature X-ray diffraction and differential thermal analysis were unsuccessful. No transition was observed below 1000°, but hydrolysis apparent above 800° confused the observations. The absence of a transition at these temperatures is surprising in light of the mobility of the anions in fluorite structures. However, it was noted that the molecular volume of the tetragonal phases was larger than that of the corresponding cubic and rhombohedral phases, and a transition with a volume decrease would be somewhat unusual.

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Lattice Constants of Actinide Tetrafluorides Including Berkelium[1]

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The lattice constants of ThF_4, PaF_4, UF_4, NpF_4, PuF_4, AmF_4, and CmF_4 were redetermined using modern experimental and computational methods. Lattice parameters for the isostructural BkF_4 were obtained in a similar manner. Trends and volume changes in these tetrafluorides and other series of tetravalent actinide fluoride complexes are discussed.

Introduction

Following our preparation of BkF_4 earlier this year,[2] the lattice constants and volume of this compound were compared with other actinide tetrafluorides or fluoride complexes involving a tetravalent actinide. Penneman has pointed out the significance of the "volume/fluoride" ratio in fluoride compounds[3] and noted certain discontinuities when he plotted the actinide tetrafluoride data with those for $LiMF_5$[4] and $Na_7M_6F_{31}$.[5] The volumes of the highly charged tetravalent actinide may be neglected along with the volume of the lithium ion for such calculations. The values for the sodium compound have been corrected for the volume of the sodium ion (7 Å^3). This information is shown in Figure 1. It can be seen that our berkelium data do not fit the curve for MF_4. Furthermore, that curve is much steeper than those of the complex fluorides. In fact, an extrapolation of that curve apparently will cross those of $LiMF_5$ and $Na_7M_6F_{31}$. While not impossible, such behavior did not appear in harmony with recent studies from this laboratory on systems of these types of compound.

From independent considerations of the molar refractivity of ThF_4, Penneman[6] also suspected that the lattice constants of the thorium compound were too large. If this were true, and the slope of the curve is less steep, our berkelium value falls into place more neatly.

The published values for the MF_4 compounds date from 1949 through the mid 1950's, and significant advances in manipulative techniques, equipment, and computer data reduction have been made since then.

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

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[3] R. A. Penneman, *Inorg. Chem.*, **6**, 431 (1967).

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[6] R. A. Penneman, submitted for publication.

TABLE I

LATTICE CONSTANTS FOR MF_4 (SPACE GROUP C2/c; $Z = 12$)

MF_4	a_0,Å	b_0,Å	c_0,Å	β,deg	Mol vol, Å^3	Ref
ThF_4	13.1	11.01	8.6	126	83.6	16
	12.90 ± 0.04	10.93 ± 0.03	8.58 ± 0.04	126.4 ± 0.2	81.1	This work
PaF_4	12.86	10.88	8.54	126.21	80.3	13
	12.83 ± 0.03	10.82 ± 0.02	8.45 ± 0.03	126.4 ± 0.1	78.7	This work
UF_4	12.73	10.75	8.43	126.33	77.5	7, 8
	12.73 ± 0.01	10.753 ± 0.007	8.404 ± 0.008	126.33 ± 0.05	77.2	This work
NpF_4	12.70	10.64	8.41	126.17	76.5	16
	12.64 ± 0.02	10.70 ± 0.02	8.36 ± 0.02	126.4 ± 0.1	75.8	This work
PuF_4	12.62	10.57	8.28	126.17	74.3	16
	12.59 ± 0.03	10.69 ± 0.02	8.29 ± 0.04	126.0 ± 0.2	75.2	This work
AmF_4	12.49	10.47	8.20	126.1	72.2	14
	12.56 ± 0.04	10.58 ± 0.03	8.25 ± 0.04	125.9 ± 0.2	74.0	This work
CmF_4	12.45	10.45	8.16	126.5	71.1	15
	12.51 ± 0.05	10.61 ± 0.03	8.20 ± 0.05	125.8 ± 0.2	73.6	This work
BkF_4	12.47 ± 0.06	10.58 ± 0.04	8.17 ± 0.05	125.9 ± 0.2	72.8	2

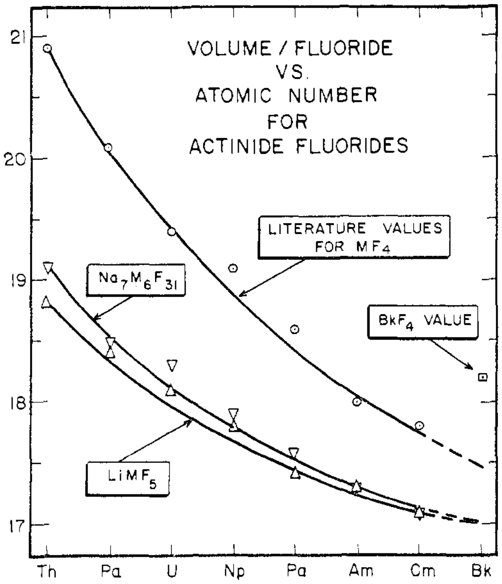

Figure 1.—Volume/fluoride ratio (Å^3) *vs.* atomic number for tetravalent actinide fluorides.

Perhaps most important, there are now available larger quantities of longer lived isotopes than were used in the early work. Therefore, we decided to reexamine the entire series of MF_4 compounds using a consistent pattern of data collection and evaulation.

Single-crystal data and atom positions are available only for UF_4.[7,8] Using these values we generated a theoretical powder pattern for UF_4 using the ANIFAC[9] program. Our observed powder diffraction data for UF_4 fitted this listing nicely and a subsequent calculation of the lattice constants of UF_4, using our powder data with the PØWLES[10] program, showed good agreement with the single-crystal results. We felt that this agreement verified our computational approach and provided a firm basis for assignment of lines and indices for other actinide tetrafluorides when radiation effects or small sample size precluded films of top-notch quality.

Experimental Section

General Information.—Analytical Reagent grade chemicals were used. All actinide stock solutions contained ≤1% total cationic impurity unless otherwise specifically noted below.

Conventional 114.6-mm Debye–Scherrer cameras were used with Ilford "G" film and a Norelco X-ray unit. External, filtered copper radiation was generally employed except in three experiments (Pa, Am, Cm) in which an internal 0.0003-in. nickel shield was mounted inside the camera between the sample and film.[11] This shield was very effective in reducing film fogging due to nuclear radiation from the material being photographed. All photographs were taken using the line-focus port of the Norelco unit. Line intensities were estimated visually.

Manipulations of the intensely radioactive materials were carried out in an inert-atmosphere glove box which was equipped with a nickel-fluorination apparatus. Powder samples of all of the tetrafluorides (except BkF_4) were transferred within the inert-atmosphere box into commercial 0.2-mm X-ray capillaries. One drop of Fluorolube oil (Hooker Chemical Co.) was added to the large top of the capillary to protect the tetrafluoride from moisture or oxygen. The capillaries were then sealed off in air. Details of the preparation of individual actinide tetrafluorides are given below.

ThF_4.—Thorium tetrafluoride was prepared by decomposition of $(NH_4)_4ThF_8$[12] by heating at 350° under vacuum for 5 hr. The material was then equilibrated for 70 hr in a mixture of 1 atm of HF and $^1/_3$ atm of F_2 gas. Thorium tetrafluoride is white.

PaF_4.—Although PaF_4 had been reported quite recently,[13] it was felt that more reliable constants would be obtained using the inner nickel foil shield for the camera and treating the data in terms of the index assignments from the UF_4 comparisons. A new sample of brick red PaF_4 was photographed.

UF_4.—Uranium tetrafluoride of 99.9% purity was used for the comparison standard of our powder techniques *vs.* single-crystal results as discussed in the Introduction. Uranium tetrafluoride is blue-green.

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TABLE II

OBSERVED *vs.* CALCULATED *d* SPACINGS AND INTENSITIES FOR ThF_4 AND PuF_4

ThF_4				PuF_4			
hkl	d_{obsd}	d_{calcd}	I_{estd}	*hkl*	d_{obsd}	d_{calcd}	I_{estd}
$021, 02\bar{1}$	4.283	4.281	7	$021, 02\bar{1}, 111$	4.152	4.190	7
$20\bar{2}, 111$		4.249		$20\bar{2}$		4.150	
$31\bar{1}$	4.015	3.967	4	$31\bar{1}$	3.893	3.892	6
220	3.795	3.763	10	220	3.678	3.691	10
$31\bar{2}$	3.627	3.597	6	$31\bar{2}$	3.515	3.515	6
$13\bar{1}$	3.365	3.353	6	$13\bar{1}$	3.269	3.265	6
112	2.752	2.728	5	$42\bar{1}, 13\bar{2}$	2.669	2.681	5
$13\bar{2}$		2.717		112		2.650	
$42\bar{1}$		2.712					
$60\bar{2}$	2.125	2.128	4	$60\bar{2}$	2.089	2.091	5
$53\bar{3}$	2.030	2.002	5	$53\bar{3}$	1.957	1.955	5
$35\bar{1}$	1.959	1.946	4	$35\bar{1}$	1.899	1.898	4
$15\bar{2}$	1.933	1.926	3	$15\bar{2}$	1.875	1.879	4
$44\bar{3}$	1.918	1.910	5	$44\bar{3}$	1.859	1.864	6
$62\bar{1}$	1.863	1.856	2	$62\bar{1}$	1.821	1.827	3
402	1.659	1.653	3	402	1.628	1.635	4
550	1.515	1.505	5	550	1.482	1.476	2
370	1.430	1.424	3	370	1.378	1.370	2

NpF_4.—Neptunium tetrafluoride was precipitated from solution using aqueous HF and hydrazine hydrochloride as a holding reductant. The tetrafluoride precipitate was washed with dilute HF, methyl alcohol, and acetone and dried in air. The salt was equilibrated with1 atm of HF and $^1/_3$ atm of F_2 gas for 16 hr at 300°. If the temperature is raised to 350–380° under the same conditions, much of the neptunium is lost owing to formation of NpF_6 gas. Neptunium tetrafluoride is green.

PuF_4.—A sample of dusty pink plutonium tetrafluoride of 99.94% purity was furnished for X-ray examination.

AmF_4.—Americium tetrafluoride was first synthesized in 1954 by Asprey.[14] That preparation was carried out using ^{241}Am which has a 56-keV γ ray in its decay scheme. Nuclear radiation of this energy darkens X-ray film with corresponding difficulty in precise reading and measurement of the diffraction lines. A new preparation of AmF_4 was made using longer lived ^{243}Am which is now available in high purity. Americium trifluoride was precipitated from solution with aqueous HF. The pink precipitate was washed with dilute HF, methyl alcohol, and acetone and dried in air. The trifluoride was equilibrated with 1 atm of F_2 gas for 16 hr at 400° to form the rosé tetrafluoride.

CmF_4.—Curium tetrafluoride was first reported in 1957 by Asprey, *et al.*[15] A new preparation was made for the current work using $^{244}CmF_3$. This compound was made in a manner analogous to that used for the americium. Fluorination of curium trifluoride was carried out at 1 atm of F_2 gas at 400° for 70 hr. An X-ray sample of the pale yellow-green material was photographed in the camera with the inner shield.

BkF_4.—The specialized techniques and apparatus for the preparation and handling of 1-μg quantities of BkF_4 have been described.[2]

Results

Films from all of these compounds showed that they were isostructural. The single-crystal studies on UF_4 established the symmetry as monoclinic, space group C2/c.[7,8] Table I lists the lattice constants[2,7,8,13–16] computed from a least-squares refinement of the film data using the PØWLES program. Table II gives a partial listing of observed *vs.* calculated *d* spacings for two typical members of this series, ThF_4 and PuF_4.

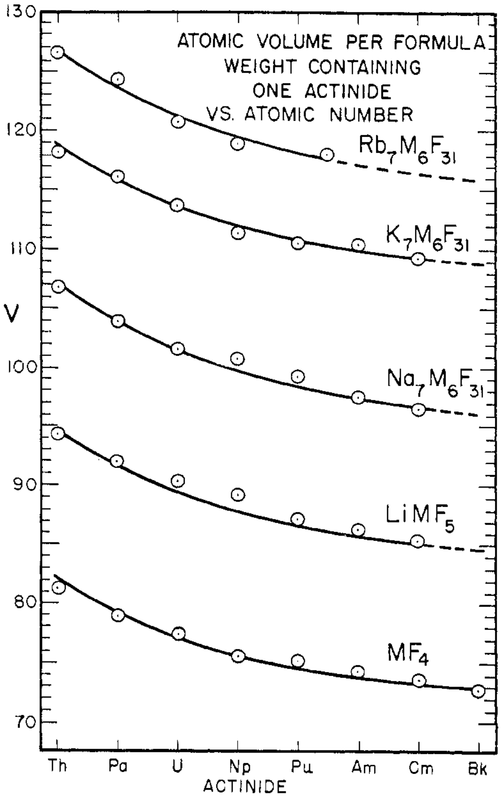

Figure 2.—Volume/formula weight (containing 1 mol of actinide) ratio *vs.* atomic number for tetravalent actinide fluorides.

Discussion

Our new lattice constants of the actinide tetrafluorides differ sufficiently from those in the literature that a considerably flatter curve now results. A more elaborate display of the data is achieved by plotting

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volume/formula weight (containing 1 mol of actinide) *vs.* atomic number for all series of tetravalent complex fluorides including $K_7M_6F_{31}$[17] and $Rb_7M_6F_{31}$.[17] This is shown in Figure 2. (If the volume/fluoride ratio is considered for all of these series, there is considerable crowding and overlap.) The similar shapes of all of the curves is obvious.

The convergence toward a limiting value for volumes in a series of isostructural compounds has been discussed by Bartlett.[18] The new lattice constants for the actinide tetrafluorides yield volumes which are decreasing quite slowly with atomic number. If other tetrafluorides, both simple and complexed, of the transberkelium actinides maintain their same coordination and symmetry, we predict little further decrease in over-all size.

Acknowledgment.—Joseph A. Leary and Arthur N. Morgan of the Los Alamos Scientific Laboratory supplied a sample of very pure PuF_4. Their assistance is gratefully acknowledged.

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On the Rare Earth Dioxymonocarbonates and Their Decomposition

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The polymorphic forms of $Ln_2O_2CO_3$ have been prepared and further characterized by high-temperature X-ray diffraction, tensimetric, and infrared methods. The X-ray study reveals a regular variation with atomic number for cell parameters and decomposition temperatures. The intermediate $Ln_2O_3 \cdot yCO_2$ reported by others is shown to be a mixture of $Ln_2O_2CO_3$ (II) + Ln_2O_3. The crystal structures for the polymorphic forms (type I, tetragonal; type IA, monoclinic; type II, hexagonal) are further elucidated by thermal expansion measurements and by the infrared data. In particular, the orientation of carbonate groups in the three structures is correlated to the resulting vibrational modes in the region 600–1800 cm^{-1}.

Introduction

The lanthanide oxalates and carbonates and their decompositions have been the subject of many investigations. The proposed intermediates are many but are not well characterized. Discrepencies observed in this laboratory indicated a need for the systematic study of the most stable of the intermediate products formed during oxalate decompositions.

Several recent thermogravimetric analysis studies of the decomposition of rare earth oxalates and carbonates indicate the formation of a stable monocarbonate.[1–4] Ropp and Gritz[1] reported the formation of a monocarbonite for the heavier members while Head and Holley[2,3] suggested that the decomposition of the hydrated tricarbonate may be described as

$$Ln_2(CO_3)_3 \cdot xH_2O \longrightarrow Ln_2(CO_3)_3 \longrightarrow Ln_2O_2CO_3 \longrightarrow Ln_2O_3 \cdot yCO_2 \longrightarrow Ln_2O_3$$

where x varies from compound to compound and the composition $Ln_2O_3 \cdot yCO_2$ ($y < 1$) is not always observed. Sastry, *et al.*,[4] showed that three different types of rare earth carbonates can be prepared: $Ln_2(CO_3)_3 \cdot 8H_2O$, $Ln_2O_3 \cdot 2CO_2 \cdot 2H_2O$, and $Ln_2O_3 \cdot 2.5CO_2 \cdot 3.5H_2O$. In the case of neodymium carbonate decomposition, an additional intermediate compound corresponding to the stoichiometry $Nd_2O_3 \cdot 0.3CO_2$ was found just prior to the formation of the oxide. Glasner and Steinberg,[5] in studying the decomposition of the light rare earth oxalates, found the sequence of intermediates

$$Ln_2(C_2O_4)_3 \longrightarrow Ln_2(C_2O_4)(CO_3)_2 \longrightarrow Ln_2(CO_3)_3 \longrightarrow Ln_2O_{0.6} \cdot (CO_3)_{2.4} \longrightarrow Ln_2O(CO_3)_2$$

Work in this laboratory by Sawyer, *et al.*,[6] has revealed the existence of three polymorphic crystalline forms of $Ln_2O_2CO_3$. All are layer-type structures built up of slabs of $(Ln_2O_2^{2+})_n$ polymers and CO_3^{2-} groups. Type I has the square $(Ln_2O_2^{2+})_n$ layers found in LnOCl and related compounds, while type II has the hexagonal $(Ln_2O_2^{2+})_n$ layers found in the A-form sesquioxides. Sawyer, *et al.*, found evidence for the existence of type I for La, Pr, Nd, Sm, Eu, and Gd. The pattern for $La_2O_2CO_3$ (I) is very similar to that of tetragonal $Bi_2O_2CO_3$ and can be indexed on the basis of this structure. After continued heating of $La_2O_2CO_3$ (I) in air at 420–500°, some reflections in the original pattern split, suggesting a monoclinic dis-

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