



HAL
open science

Techniques of preparation and crystal chemistry of transuranic chalcogenides and pnictides

D. Damien, R. Haire, J. Peterson

► **To cite this version:**

D. Damien, R. Haire, J. Peterson. Techniques of preparation and crystal chemistry of transuranic chalcogenides and pnictides. *Journal de Physique Colloques*, 1979, 40 (C4), pp.C4-95-C4-100. 10.1051/jphyscol:1979430 . jpa-00218826

HAL Id: jpa-00218826

<https://hal.science/jpa-00218826>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Techniques of preparation and crystal chemistry of transuranic chalcogenides and pnictides (*)

D. A. Damien (**), R. G. Haire and J. R. Peterson (†)

Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37830, U.S.A.

Résumé. — La cristallographie d'un certain nombre de chalcogénures et pnictures d'éléments transuraniens a été étudiée en utilisant les isotopes ^{243}Am , ^{248}Cm , ^{249}Bk et ^{249}Cf . Les composés ont été préparés par réaction directe du métal avec l'élément chalcogène ou pnictogène à température élevée. Les chalcogénures supérieurs ont été dissociés thermiquement pour donner des composés à stœchiométrie plus basse dont les sesquichalcogénures constituent la limite. Seuls les monopnictures de transplutoniens ont été trouvés. Tous les composés ont été étudiés par la technique de diffraction des RX sur poudres.

Dans cet article on a revu les méthodes de préparation des chalcogénures et pnictures à l'échelle du gramme et présenté les méthodes utilisées pour synthétiser les composés transamériciens à une échelle inférieure au milligramme. Les résultats obtenus au cours de cette étude sont comparés aux résultats de la littérature concernant les composés des actinides plus légers et les variations de propriétés le long de la série sont discutées.

Abstract. — The crystal chemistry of a number of transuranic chalcogenides and pnictides has been investigated using ^{243}Am , ^{248}Cm , ^{249}Bk and ^{249}Cf . These compounds were prepared from the corresponding metals by direct reaction with the chalcogen or pnictogen element at elevated temperatures. Higher chalcogenides were thermally dissociated to yield ones of lower stoichiometry, terminating with the sesquichalcogenides; only monopnictides of these transplutonium elements were found. All products were examined by X-ray powder diffraction.

In this paper the methods for preparing the actinide chalcogenides and pnictides on a gram scale are reviewed, and the microtechniques used for submilligram quantities of the transamericium elements are presented. The results obtained during this study are compared to data previously reported for the lighter actinide compounds, and the trends observed across the series are discussed.

1. Introduction. — Chalcogen and pnictogen elements belong to the VIth and Vth columns of the periodic classification, respectively: they are, namely, O, S, Se, Te and N, P, As, Sb (Table I). Among the chalcogen elements, oxygen exhibits a crystal radius which is clearly lower than the crystal radii of the heavier members of the group. As a result, oxides are quite different, both in composition and in structure, from the other chalcogenides, which often form isostructural compounds. Similarly in the pnictogen family, nitrides stay slightly apart. It is interesting to note that the couples sulphur-phosphorus, selenium-arsenic, and tellurium-antimony have very similar crystal radii. Thus,

the substitution of one of these elements for the other allows for the modification of the bonding (chalcogen and pnictogen elements are involved in compounds essentially as 2- and 3- species, respectively) without modifying significantly the interatomic distances.

Table I. — *Crystal radius derived from rare earth monocompounds [1] Å.*

Chalcogen element		Pnictogen element	
O	(1.40) (*)	N	1.549
S	1.844	P	1.920
Se	1.953	As	1.993
Te	2.135	Sb	2.171

(*) Pauling's radius [2].

(*) Research sponsored by the Division of Nuclear Sciences, Offices of Basic Energy Sciences, U.S. Department of Energy under contracts W-7405-eng-26 with Union Carbide Corporation, EY-76-S-05-4447 with the University of Tennessee (Knoxville) and by Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France.

(**) Visiting Postdoctoral Research Associate, Department of Chemistry, University of Tennessee, and Guest Scientist, Oak Ridge National Laboratory, on leave from Centre d'Etudes Nucléaires, B.P. No. 6, 92260 Fontenay aux Roses, France.

(†) Department of Chemistry, University of Tennessee, Knoxville, TN 37916, U.S.A.

Among the compounds formed by these elements, the ones formed with the d transition and 5f metals have been, and are still, intensively investigated because of the variety of their physical properties — semiconducting, conducting, and even supercon-

ducting materials are found [3]. As examples, the molybdenum chalcogenides are known to be superconducting compounds, and recently all the lanthanum pnictides were reported to exhibit superconductivity [4]. During the last decade efforts have also been made in many laboratories to study the 5f element chalcogenides and pnictides, but the radioactivity and also the scarcity of the materials have increased considerably the problems encountered in their preparation and their physical property measurements.

In this paper, we shall review the methods used in the preparation of the various early actinide pnictides and chalcogenides (for uranium, neptunium and plutonium, the syntheses can be performed on a gram scale; for americium and, to a lesser extent, for curium-244, on a multimilligram scale). Then we shall describe the techniques which we have used for the microscale preparations of curium-248, berkelium-249 and californium-249 compounds.

2. Macroscale preparations. — On the several mg to the multigram scale, actinide pnictides and chalcogenides of higher stoichiometry can be prepared starting from the metal hydride or the metal itself. The hydride process leads to a more homogeneous product and faster reactions. Typically, hydride and an excess of chalcogen or pnictogen element (X) are sealed in a quartz tube under high vacuum and heated at moderate temperature (450-700 °C). Chalcogenides of pnictides of lower stoichiometry can be obtained by thermal dissociation of the higher ones, either in a sealed tube where one end of which is kept outside the furnace to allow for the deposition of the non-metal element, or in a vacuum thermobalance, which yields more information about the stoichiometry of the products formed.

Although actinide monpnictides can be obtained by thermal dissociation of a higher pnictide, the monochalcogenides require direct preparation. The following procedure is recommended:

- 1) Heating at moderate temperature (700-800 °C) of a stoichiometric amount of chalcogen element with the metal hydride in a quartz tube sealed under high vacuum.
- 2) Pelletizing of the product formed.
- 3) Heating of the pellets at high temperature (1 200-1 600 °C) in tantalum or tungsten crucibles. This high-temperature heating is performed under high vacuum or in an inert atmosphere.

These macroscale synthesis techniques have been used successfully from thorium through plutonium [5] and to a lesser extent for americium and curium-244 [6, 7]. For the heavier actinides, the scarcity of the elements does not permit the use of macro-amounts of material.

^{248}Cm ($T_{1/2} = 3.4 \times 10^5$ y) is a much more suitable isotope than ^{244}Cm ($T_{1/2} = 18.1$ y), but like ^{249}Bk

($T_{1/2} = 314$ d) and ^{249}Cf ($T_{1/2} = 350.6$ y), it is only available in multimilligram quantities. Thus the synthesis of compounds from these isotopes have to be performed on the submilligram scale using microchemical techniques.

3. Microscale preparations. — **3.1 METALS.** — The starting materials required for the preparation of curium, berkelium and californium chalcogenides and pnictides are the corresponding metals, and thus we shall describe first their preparation. The microscale techniques of metal preparations have been first developed at Berkeley [8] and then at Oak Ridge [9]. ^{248}Cm and ^{249}Bk metals were obtained by reduction of their tetrafluorides with Li metal vapour. (CmF_4 and BkF_4 were obtained by heating the corresponding trifluorides in an atmosphere of ClF_3 or F_2 at ~ 350 °C). The different products were handled in a helium-atmosphere glove box (O_2 , H_2O , N_2 ; all ≤ 10 ppm). The tetrafluoride pieces were placed in a tungsten wire spiral, which was attached to the top of a tantalum crucible containing the lithium metal [10]. The tantalum crucible was put in a tantalum heating coil that was coated with a refractory material [9]. The system was evacuated to 5×10^{-6} mm Hg and then heated to initiate the reduction reaction. Lower temperatures and shorter heating times were used with Bk than Cm, to minimize the loss of Bk metal due to its higher volatility.

The reductions of the fluorides were carried out on the 100- μg to 1-mg scale. The curium metal samples had not melted and appeared as shiny pieces with shapes similar to the initial fluoride pieces. X-ray studies showed that this well-crystallized metal exhibited the dhcp structure. The lattice constants, averaged from 6 independent preparations, are $a_0 = 3.495(4)$ Å and $c_0 = 11.33(3)$ Å (to be compared to the values $a_0 = 3.498$ Å and $c_0 = 11.340$ Å for ^{244}Cm metal [11] and $a_0 = 3.500(3)$ Å and $c_0 = 11.34(1)$ Å for ^{248}Cm [12]).

The curium metal can be melted in an electrically heated tungsten spiral. The current is shut off as soon as melting occurs so that the metal is quenched. These metal samples exhibited either a single fcc phase or mixtures of the fcc and dhcp phases. The lattice constant of the fcc curium phase has been found to vary with the sample preparation [12], suggesting possible vacancies in the structure. The following lattice parameters have been found in this work: 5.060(2) Å, 5.084(2) Å, 5.076(2) Å, 5.068(2) Å. Berkelium metal has a melting point (~ 1000 °C) lower than that of curium, so it was obtained as a melted ingot after the lithium reduction. No structural information could be obtained from this material since it was amorphous. Californium metal has been prepared by reduction of the sesquioxide with lanthanum metal at high temperature in a tantalum apparatus [13], distilling it and then depositing it on a tantalum condenser. Reductions were performed

on the mg scale. Samples of these metals were submitted for mass analysis, and the results are reported in table II for curium-248 (in ppm).

Table II. — ^{248}Cm analysis.

Ta	Mo	Ni	Fe	Cr	V	Cs	K	S
≤ 60	100	10	20	5	20	3	2	30
Si	Al	Na	Mg	Pb	W	Cs	Pr	
10	1	1	11	—	—	—	—	

3.2 COMPOUNDS. — Starting from these actinide metals, pnictides and chalcogenides were prepared on the 20-30 μg scale in quartz capillaries suitable for subsequent X-ray examination. It was preferred to use the pure metals rather than their hydrides in order to retain small pieces rather than powders, which would be very difficult to handle and transfer without loss. Special care was taken to avoid contamination by metallic impurities as well as oxygen, nitrogen and water vapour. This was accomplished by pretreatment of the capillaries and reagents. The capillaries were first leached with hydrochloric acid, then washed with distilled water and alcohol. Following drying, they were heated under high vacuum and kept under vacuum with a stopcock system, which was opened only in the dry-helium atmosphere box used for the transuranic metals. The chalcogen and pnictogen elements were of high purity and had been melted or sublimed and stored under vacuum before use. Typically a capillary was loaded with the appropriate transuranic metal and an excess of non-metal element, sealed under high vacuum (residual pressure $\leq 10^6$ mm Hg) and heated. S, Se, Te and As were reacted with Cm, Bk and Cf metals at 450-500 $^\circ\text{C}$, but the reaction temperature with Sb had to be higher than 550 $^\circ\text{C}$ to get a rapid reaction. Heating times of 15 hours were found to be sufficient to provide complete reaction and to yield good crystallinity. Most of the time the compounds had a gray metallic appearance, except for the tritellurides, which were golden. During heating a small temperature gradient (~ 20 $^\circ\text{C}$) was maintained along the capillary to obtain a compound free of excess chalcogen or pnictogen element. The thinner part of the capillary, which was to be used for X-ray analysis for sample characterization, contained the 5f metal and was placed in the warmer part of the furnace. After heating the product obtained was free of excess pnictogen or chalcogen element, which had gathered at the colder extremity of the capillary.

Dissociations of the higher chalcogenides were performed in a microfurnace consisting of a platinum wire wound on a quartz tube. Only the portion of the capillary containing the product was located inside the furnace, allowing the chalcogen or pnictogen element to deposit in the cooler part of the capillary. The maximum temperatures used were limited by possible reactions of the compounds with

the quartz. Such problems started to appear around 800 $^\circ\text{C}$, however it was still possible to use this dissociation method up to $\sim 1\,000$ $^\circ\text{C}$ for very short periods of time (a few seconds). Following the various heating steps, the samples were submitted for X-ray analysis using standard powder diffraction techniques.

4. Results and discussion. — Previously unknown tritellurides, dichalcogenides and sesquichalcogenides of berkelium and californium have been prepared and characterized by X-ray diffraction. They are presented in table III. All the berkelium and californium chalcogenides appear to be isostructural with the corresponding rare-earth ones [14].

Table III.

(Cf, Bk)Te ₃	(Cf, Bk)Te _{2-x}	ξ Bk ₂ Te ₃	
	(Cf, Bk)Se _{2-x}	η Bk ₂ Se ₃	γ Cf ₂ Se ₃
		γ Bk ₂ Se ₃	
	(Cf, Bk)S _{2-x}	α Bk ₂ S ₃	γ Cf ₂ S ₃
		γ Bk ₂ S ₃	

4.1 TRITELLURIDES. — Like the preceding transuranic elements, berkelium and californium tritellurides exhibit the orthorhombic, NdTe₃-type structure [6], which is observed for all the trivalent rare-earth tritellurides. The lattice parameters for BkTe₃ are: $a_0 = 4.318(2)$ Å, $b_0 = 4.319(2)$ Å, $c_0 = 25.467(6)$ Å. The unit cell is composed of two superposed ditelluride cells, shifted by $a_0/2$, and separated by a Te layer.

4.2 DICHALCOGENIDES. — From their X-ray powder patterns, all the berkelium and californium disulphides, diselenides and ditellurides were found to crystallize in the tetragonal, anti-Fe₂As-type structure, like the corresponding plutonium, americium and curium compounds.

In the case of the ditellurides, the americium-243 compound was considered to be representative of the transuranic ditellurides, and its crystal structure has been refined from single-crystal data [15]. The anti-Fe₂As structure was confirmed, and the stoichiometry was shown to be AmTe_{1.73} (axial ratio $c_0/a_0 = 2.071$). The tellurium vacancies are randomly distributed in the basal plane of the cell. An increase of the tellurium vacancies decreases the a_0 lattice constant without modifying significantly the c_0 axis, so that the c_0/a_0 axial ratio increases. This ratio can therefore be used as an indication of the compound's stoichiometry. It varies from 2.03 to 2.07-2.08 in neptunium and plutonium compounds, corresponding to the stoichiometries (Np or Pu)Te₂ and (Np or Pu)Te_{1.7} respectively [6, 16]. In going from curium to californium the c_0/a_0 ratio is found to remain close to 2.06-2.08, irrespective of the temperatures of the preparations, suggesting that these ditellurides are always prepared as substoi-

chiometric compounds with compositions close to (Cm, Bk, or Cf)Te_{1.7}.

For the disulphides and the diselenides, the variations along the transuranium series are much smaller. The c_0/a_0 axial ratios are 2.02-2.03 for the disulphides from Pu through Cf, and 2.04-2.05 for the corresponding diselenides. This indicates that the compositions of these compounds remain essentially constant and are practically independent of the preparation conditions.

4.3 SESQUICHALCOGENIDES. — Transuranium element sesquichalcogenides crystallize in 4 different structure types: α , γ , η and ξ , where

α is the orthorhombic La₂S₃-type [17, 18] (CN 7 and 8),

γ is the body-centred cubic anti-Th₃P₄-type [19] (CN 8),

η is the orthorhombic U₂S₃-type [20] (CN 7), and

ξ is the orthorhombic Sc₂S₃-type [21] (CN 6).

The actinide sulphides exhibit the α form through Bk and the γ form through Cf. (Although the α form has not been definitively observed with Cf, we cannot exclude the existence of this phase.) Isostructural phases are found in the rare-earth sesquisulphides from lanthanum through dysprosium for the α form and through terbium for the γ one. The η sesquiselenides have been observed for Pu, Am, and Bk in the actinides and from Gd through Dy in the lanthanides. The γ form extends from Np through Cf and from La through Dy, respectively. (The γ form represents here M₂X₃ as well as M₃X₄ or any intermediate composition.)

The η and γ sesquitellurides are formed from Np through Cm and from Np through Am, respectively. Berkelium is the first transuranic element to exhibit the Sc₂S₃-type structure. The same $\eta \rightarrow \xi$ transition occurs in the rare-earth series at Tb, the homolog of Bk, so that in their sesquitellurides Bk and Tb have similar crystal radii.

4.4 MONOPNICTIDES. — Stoichiometries other than monopnictides are seldom formed between transplutonium and pnictogen elements. Using preparation techniques similar to those described earlier, ²⁴⁸Cm, ²⁴⁹Bk and some ²⁴⁹Cf monopnictides have been prepared as single-phase materials. They exhibit the cubic, NaCl-type structure like the other actinide monopnictides. Their lattice parameters, a_0 , are listed in table IV.

Mononitrides. — Nitrides were prepared directly by heating the corresponding metals on a tantalum filament up to 1 300 °C in an atmosphere of nitrogen, which had been purified by passing it over uranium nitride at 600 °C. This apparatus had been previously tested with americium-243. The lattice constant of ²⁴³AmN was found to be 4.990 7(3) Å, which is in good agreement with previously reported data (5.00 Å [22] and 4.995 Å [23]). Stevenson has report-

ed lattice constants for ²⁴⁸CmN (5.027 Å) and BkN (5.010 Å) [12]. Our present values agree very well in the case of curium mononitride, but a noticeable difference occurs in the berkelium nitride parameters.

Table IV.

	N	P	As	Sb	References
²⁴⁸ Cm	5.027				[12]
	5.027	5.743	5.887	6.243	This work
²⁴⁴ Cm	5.041	(5.72)	5.901	6.248	[23]
²⁴⁹ Bk	5.010				[12]
	4.95	5.669	5.833	6.195 6.188	This work
²⁴⁹ Cf	—	—	5.809	6.165	This work

Likely due to less radiation damage, the curium-248 nitride has a lower lattice constant than the same compound containing Cm-244. The former's parameter is also significantly lower than the fcc lattice constant (5.07 Å) of pure curium-248 metal. For monoarsenides and monoantimonides, a definite decrease in a_0 is also observed from Cm through Cf.

4.5 CURIUM-248 MONOCHALCOGENIDES. — Curium monochalcogenides have been prepared on a 80- to 150- μ g scale, starting with stoichiometric amounts of reactants. Considering the small amount of chalcogen that was weighed, the precision of the stoichiometry was not very high, although the microbalance used allowed for a $\pm 1 \mu$ g uncertainty. Curium metal and the chalcogen element were sealed under high vacuum in a quartz capillary which was subsequently heated to carry out the reactions.

Although the ratio of Cm atoms/chalcogen atoms was 1, different phases were obtained depending upon the heating temperature. As an example, in the case of curium and tellurium, at 500 °C, CmTe_{2-x} was found, and at 750 °C, η -Cm₂Te₃ was obtained. Although excess curium metal must be present in these compounds, it was not detected in the X-ray powder patterns. Heating at 750 °C for 20 hours were the conditions adopted in all the preparations of curium monochalcogenides. After this first heating step, the capillaries were opened in the inert atmosphere box and the products transferred into a « V-shaped » tantalum filament, where they were further heated at high temperatures under vacuum. At 1 350 °C, only the γ curium sesquisulphide was formed. It was necessary to heat the samples up to 1 500 °C to get the monosulphide. Curium monoselenide and monotelluride were prepared at more moderate temperatures (1 300° and 1 200 °C, respectively). Their lattice parameters are presented in table V.

Table V.

CmS	5.575 Å
CmSe	5.791 Å
CmTe	6.150 Å

The monochalcogenides were not obtained as single-phase materials. Although the monochalcogenides constituted the major phase, γ sesquisulphide, γ sesquiselenide, and η sesquitelluride lines were also present in the X-ray patterns, along with some oxychalcogenide lines.

It is of interest to compare the lattice constants of curium monosulphide and monoselenide to those of the rare earths and the other transuranium elements (Fig. 1). The curium compounds exhibit lattice

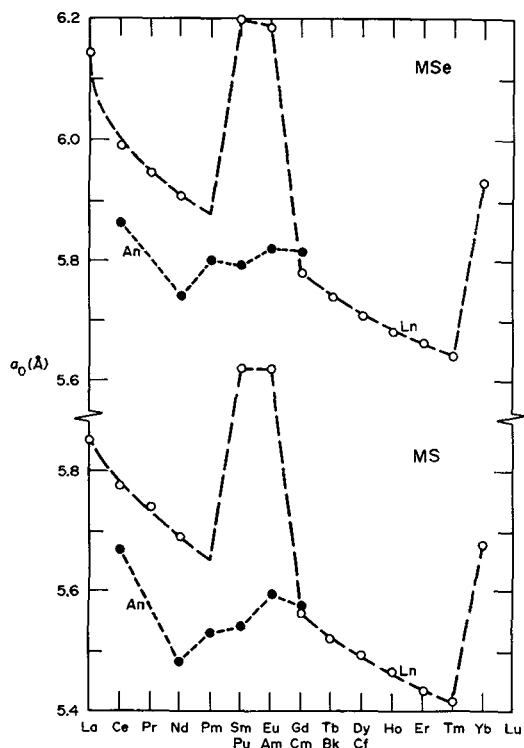


Fig. 1. — Lattice parameters of lanthanide and actinide sulphides and selenides.

parameters which are lower than the corresponding americium ones. On the contrary, curium mononictides (Figs. 2, 3) exhibit the highest lattice parameters in the transuranic series. This difference in behaviour between americium and curium in their monochalcogenides and mononictides can be understood by assuming that americium is partially divalent in the monochalcogenides. The chalcogen elements are ligands which favor low valencies of the cations, as can be seen from examination of the rare-earth monochalcogenides. Of course americium would be far from purely divalent, since for divalent americium monosulphide, for example, a lattice constant of the order of 5.9 \AA would be expected. The possibility of some divalent character for americium in monochalcogenides, proposed here from a comparison with the corresponding curium compounds, had previously been strongly suggested by Johansson on the basis of thermodynamic

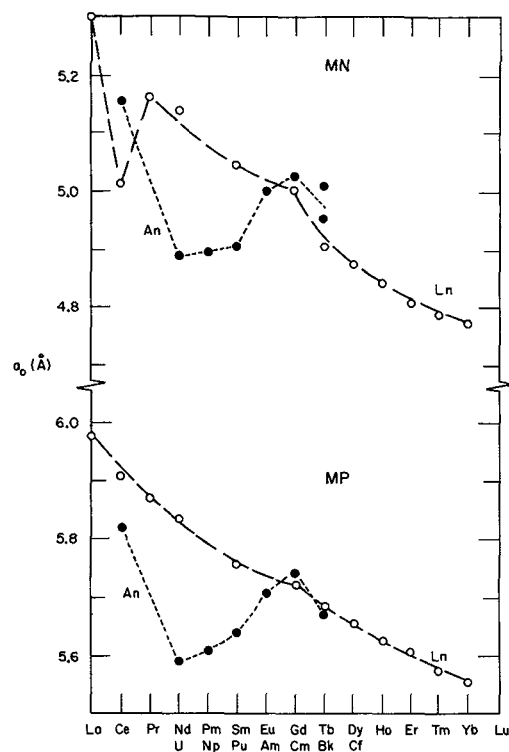


Fig. 2. — Lattice parameters of lanthanide and actinide nitrides and phosphides.

considerations [24]. Another possible explanation is that the 5f electron participation in the bonding is very weak in americium monochalcogenides. In this explanation, the decrease in the lattice constant

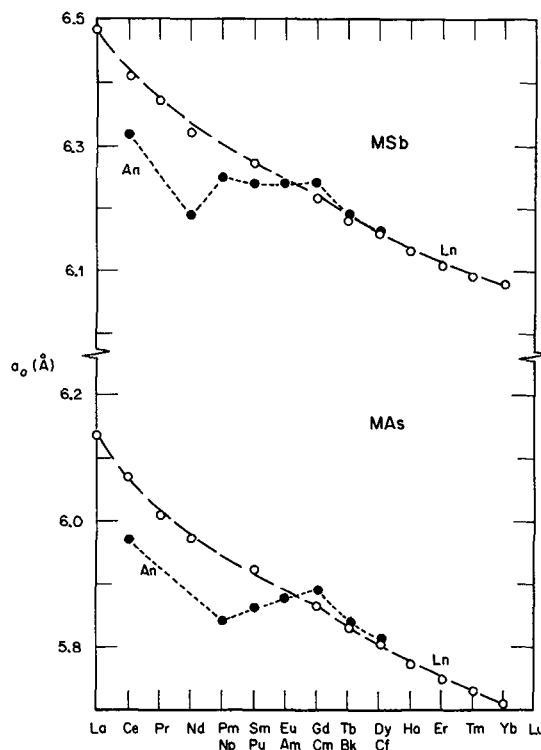


Fig. 3. — Lattice parameters of lanthanide and actinide antimonides and arsenides.

from americium to curium reflects the 5f contraction between two adjacent trivalent actinides. Pnictogen elements have been shown to enhance the actinide 5f electron participation more than the chalcogen elements [7, 23]. Thus, in the mononictides, the maximum in a_0 at curium would mean that the 5f electron participation in americium compounds exists to lower significantly their lattice constants.

In figure 4, the variations of the lattice parameters of the transuranium and rare-earth cubic sesquioxides are presented. For the more ionic compounds (curium through einsteinium) the curve is parallel to the corresponding rare-earth curve, and the lattice constants of the transuranium element sesquioxides are higher than the isoelectronic rare-earth sesquioxides. On the contrary, the lattice constants of berkelium and californium arsenides and antimonides (Fig. 3) are very similar to those of terbium and

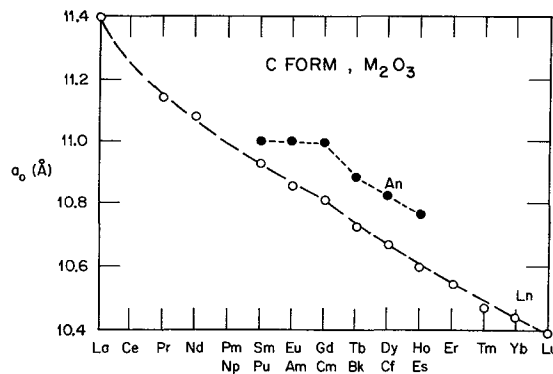


Fig. 4. — Lattice parameters of lanthanide and actinide sesquioxides.

dysprosium, suggesting that the actinide lattice constants are decreased as a result of covalency effects.

References

- [1] ALLBUTT, M. and DELL, R. M., *J. Inorg. Nucl. Chem.* **30** (1968) 705.
- [2] PAULING, L., *The Chemical Bond* (Cornell University Press, Ithaca, New York) 1966, p. 210.
- [3] HULLIGER, F., *Struct. Bonding* **4** (1968) 84.
- [4] HULLIGER, F. and OTT, H. R., *J. Less-Common Met.* **55** (1977) 103.
- [5] MARCON, J. P., CEA Report R-3919 (1969).
- [6] DAMIEN, D., Thesis, Université de Clermont-Ferrand II (1976).
- [7] CHARVILLAT, J. P., Thesis, Université de Clermont-Ferrand II (1977).
- [8] WESTRUM, E. F. and EYRING, L., *J. Am. Chem. Soc.* **73** (1951) 3396; WALLMANN, J. C., CRANE, W. W. T. and CUNNINGHAM, B. B., *J. Am. Chem. Soc.* **73** (1951) 493.
- [9] STEVENSON, J. N. and PETERSON, J. R., *Microchem. J.* **20** (1975) 213.
- [10] NOÉ, M. and PETERSON, J. R., *Transplutonium Elements* (1975), Müller, W. and Lindner, R. Eds. (North-Holland Publishing Co., Amsterdam) 1976, p. 69.
- [11] MÜLLER, W., REUL, J. and SPIRLET, J. C., *Rev. Chim. Minér.* **14** (1977) 212.
- [12] STEVENSON, J. N., Thesis, University of Tennessee (1973).
- [13] HAIRE, R. G. and BAYBARZ, R. D., *J. Inorg. Nucl. Chem.* **36** (1974) 1295.
- [14] FLAHAUT, J., *Inorg. Chem.* **10** (1972), MTP International Rev. of Sci. 190.
- [15] BURNS, J. H., DAMIEN, D. and HAIRE, R. G., to be published in *Acta Cryst.* (1979).
- [16] ALLBUTT, M., JUNKISON, A. R., AERE-R 5541 (1967).
- [17] BESANCON, P. and LARUELLE, P., *C. R. Hebd. Séan. Acad. Sci.* **268 C** (1968) 1090.
- [18] PREWITT, C. T. and SLEIGHT, A. W., *Inorg. Chem.* **7** (1968) 1090.
- [19] ZACHARIASEN, W. H., *Acta Cryst.* **2** (1949) 57.
- [20] ZACHARIASEN, W. H., *Acta Cryst.* **2** (1948) 291.
- [21] DISMUKES, J. P. and WHITE, J. G., *Inorg. Chem.* **9** (1964) 1220.
- [22] AKIMOTO, Y., *J. Inorg. Nucl. Chem.* **29** (1967) 2550.
- [23] CHARVILLAT, J. P., BENEDICT, U., DAMIEN, D., DE NOVION, C.-H., WOJAKOWSKI, A. and MÜLLER, W., *Transplutonium Elements* (1975), Müller, W. and Lindner, R., eds. (North-Holland Publishing Co., Amsterdam) 1976, p. 79.
- [24] JOHANSSON, B., Proceedings 2nd International Conference on the Electronic Structure of the Actinides (1976), Wrocław, p. 49.

DISCUSSION

Dr. SUSKI. — 1. Did you observe any other phase for your substoichiometric americium ditelluride, because this composition $\text{AmTe}_{1.73}$ is close to the stoichiometry of the hexagonal $\text{Th}_7\text{Se}_{12}$ -type phase? 2. Why, you call the delta-phase anti- Th_3P_4 ?

D. A. DAMIEN. — 1. No phase like $\text{Th}_7\text{Se}_{12}$ has been observed in the Am-Te system. 2. Of course, taking into account the small amount of material used in the synthesis, we don't know the stoichiometry of our delta-phase.

Pr. FUGER. — In the Cm metal samples used as starting materials you noted the appearing of a fcc phase. Were you able to eliminate this phase by treatments such as annealing? What proof do you have that this phase is truly Cm metal?

D. A. DAMIEN. — The melting point of this phase corresponds to that of Cm-metal (the nitride one is expected to be much higher).

We have not been able to eliminate the fcc phase by annealing, but, in his thesis, Stevenson has reported this phase change.