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THE CRYSTAL STRUCTURE OF ACTINIUM METAL AND ACTINIUM HYDRIDE

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ABSTRACT

The crystal structures of actinium metal and actinium hydride were determined by analyses of X-ray diffraction patterns. Both structures were found to be face-centered cubic with the following lattice constants:

	a_o
Ac	5.311 ± 0.010 Å
AcH_2	5.670 ± 0.006 Å.

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1. Introduction

Fried, Hageman, and Zachariasen[1] have prepared and identified nine compounds of actinium. The compounds were prepared by methods which have been used in the preparation of similar lanthanum compounds and were identified by analyses of X-ray diffraction patterns. The crystal structures of actinium and lanthanum compounds were found to be very similar.

The half-life of Ac^{227} is approximately 22 years and the betas and gammas emitted by actinium samples (derived mostly from the daughters of actinium) cause darkening of X-ray films and make diffraction patterns rather difficult to obtain. Fried, Hageman, and Zachariasen minimized this difficulty by using very small samples (about 10 μg) and by using actinium which had been freshly separated from its daughters.

Klemm and Bommer[2] have prepared samples of lanthanum metal (in capillary tubing) by using liquid potassium for the reduction of anhydrous $LaCl_3$. The samples contained KCl, which was used as an internal standard for the X-ray camera, and proved very satisfactory for X-ray diffraction experiments.

This paper describes the adaptation of the method of Klemm and Bommer for the preparation of microgram quantities of actinium metal and an analysis of X-ray diffraction patterns obtained from such samples.

2. Experimental Procedure

2.1 The Purification of Actinium

The only daughters of Ac^{227} which exhibit half-lives longer than about 36 min are 18.9 day Th^{228} and 11.2 day Ra^{223}. Therefore, the removal of these two daughters effectively purifies Ac^{227} from all daughter contamination except for 21 min Fa^{223} which is formed from about 1.2% of the primary actinium disintegrations.

Actinium was separated from thorium and radium in the following manner.

a. A solution containing about 2 mg of actinium in 20 ml of 0.1 M HCl was extracted with an equal volume of a solution containing 2% TTA (thenoyltrifluoroacetone) in benzene. During this extraction, the Th^{227} entered the organic solution while the Ac^{227} and Ra^{223} remained in the HCl solution.

b. The HCl solution was then passed through a column of Dowex-50 resin. The column was approximately 1 cm in diameter and 10 cm long. The resin column was then eluted with 100 ml of 4 M HNO_3 at a rate of approximately 1/2 ml per minute. The elution removed the Ra^{223} and the first traces of Ac^{227} from the resin column.

c. The resin column was next eluted with 150 ml of 6 M HNO_3 at a rate of 1/2 ml per minute. This eluate contained the major portion of the Ac^{227}. Actually, the resin-column

procedure is adequate for a relatively efficient separation of actinium, thorium, and radium, since the thorium remained on the resin column after the HNO_3 elutions. However, the Ra^{223} formed by decay of Th^{227} during the 6 M HNO_3 elution is swept from the column and collected in the actinium fraction. The extraction procedure (step a) was introduced so that the Ra^{223} contamination of the final actinium fraction would be as low as practicable.

d. The Ac^{227} was relatively free from radioactive contamination at this stage of the purification procedure. However, the 6 M HNO_3 contained dissolved resin, or resin products, and it was necessary to remove this material since it interfered in subsequent attempts to prepare actinium metal. The balance of the purification procedure was designed to eliminate the resin impurity.

e. The actinium fraction was evaporated to dryness. The residue was dissolved in dilute nitric acid and actinium oxalate was precipitated by the addition of saturated oxalic acid. The precipitate was collected by centrifugation and then washed with oxalic acid solution. Most of the dissolved resin, or resin products, remained in solution.

f. The actinium oxalate was dissolved in 1 ml of 8 M HNO_3 and transferred (by pipette) to a platinum crucible. The centrifuge tube then was washed with 1 ml of 8 M HNO_3 which was also transferred to the platinum crucible.

g. The solution in the crucible was evaporated to dryness and the crucible then ignited (in air) at a temperature of 1000°C for a period of 1 hour. The ignition destroyed traces of resin carried by the actinium oxalate precipitate and converted the actinium oxalate to actinium oxide.

h. The Ac_2O_3 was dissolved in 2 ml of 6 M HCl to form a solution containing about 1 μg of Ac per microliter of solution. The solution was centrifuged to remove any insoluble material.

2.2 The Preparation of Powder Samples of Actinium and Lanthanum Metal

All procedures, except the separation of actinium from its daughters, were developed and tested with the use of lanthanum as a "stand-in" for actinium.

2.2.1 The Formation of Anhydrous $AcCl_3$. Anhydrous $AcCl_3$ was formed directly in the capillary of the apparatus shown in Fig. 1. This capillary later served as the sample holder during the X-ray exposure and was about 0.1 mm in diameter with a wall thickness of approximately 0.01 mm.

Anhydrous $AcCl_3$ (or $LaCl_3$) was prepared by the reaction of the hydroxide with excess NH_4Cl.[3] A description of the procedure follows.

a. Ten microliters of 6 M HCl containing about 1 μg of Ac (or La) per milliliter was pipetted into the apparatus shown in Fig. 1 and delivered into the depression labeled A (Fig. 1).

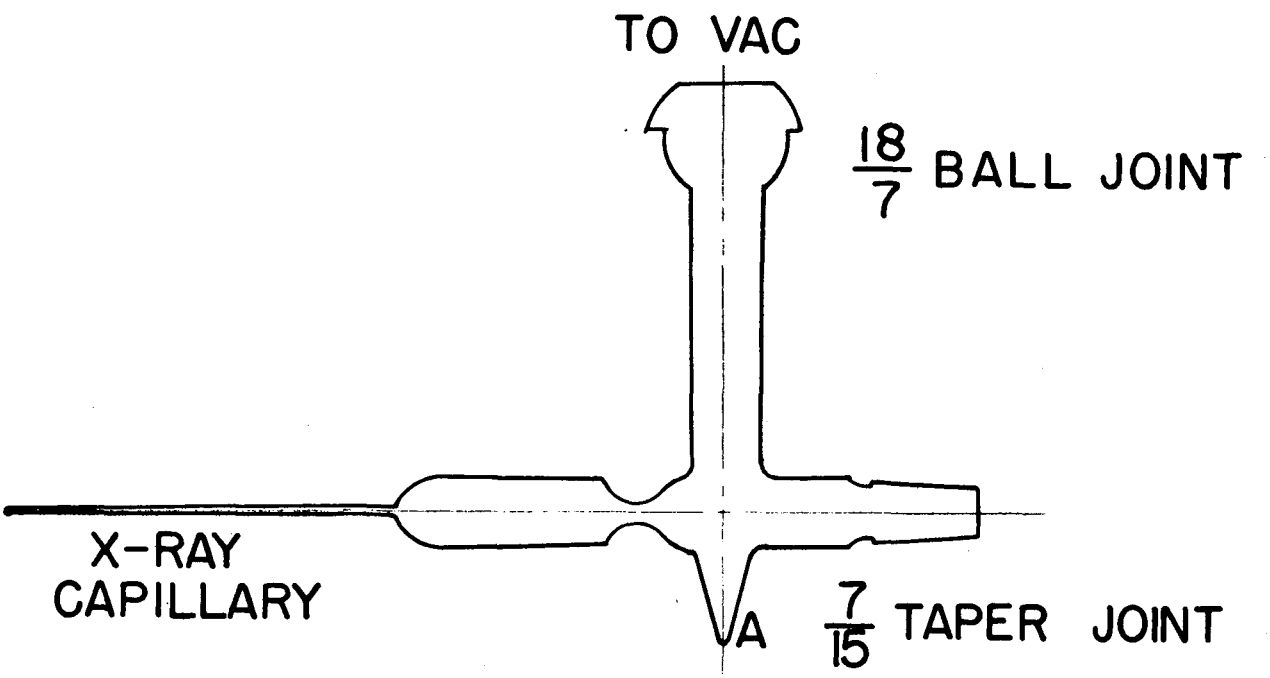

Fig. 1. Sample preparation apparatus.

To this was added 10 μl of conc. NH_4OH. The solutions were mixed by a combination of swirling and tapping the glass apparatus. The solution was then evaporated and the salt dried under vacuum.

b. The dried salt (about 3 mg of NH_4Cl and 0.012 mg of $Ac(OH)_3$) was ground to a powder by means of a thin tantalum rod (0.03" diameter). The powdered salt was transferred to the capillary by a combination of tapping and shaking while the glass apparatus was held in a vertical position, i.e., with the capillary pointed down.

c. The apparatus was attached to a vacuum system by means of the 18/7 ball joint with the capillary pointed downward. The 7/15 taper joint was capped and the system was evacuated. A tube furnace was placed around the capillary and as high on the apparatus as practicable. The furnace was turned on and the capillary was heated to a temperature of 250°C. This temperature was maintained for at least 20 min. During this time the $Ac(OH)_3$ was converted to anhydrous $AcCl_3$ and the excess NH_4Cl was distilled into the upper portion of the glass apparatus.

2.2.2 The Reduction of $AcCl_3$. Finely divided actinium (or lanthanum) metal was formed in the capillary through the reduction of $AcCl_3$ (or $LaCl_3$) by potassium vapor. A description of the procedure follows.

a. The glass apparatus was cooled and filled with helium to a pressure greater than atmospheric pressure. The 7/15 taper cap was removed and, with helium flowing from the apparatus, approximately 0.1 gm of potassium metal, which had been outgassed by melting in vacuum, was dropped into the apparatus. The 7/15 cap was then replaced and the apparatus was evacuated.

b. The potassium was melted with a torch and "herded" through the constriction and into the tube to which the capillary was attached. The apparatus was then sealed (and separated) at the constriction.

c. The tube containing the potassium and the attached capillary was placed inside a furnace and heated to a temperature of 350°C for a period of 10 min. During this time the $AcCl_3$ was reduced to actinium metal by potassium vapor which diffused into the capillary. Liquid potassium did not enter the capillary.

d. At this point in the procedure, a mixture of KCl and actinium metal was contained in the lower 1/8" to 1/4" of the capillary tubing. The capillary was then sealed off (by means of a torch) at a point approximately 1" from the bottom.

2.3 X-Ray Diffraction Studies

An X-ray diffraction pattern was obtained as soon as practicable after the preparation of the powder sample of actinium metal (Section 2.2.2, step d). The gamma-ray background

from actinium samples increases with time, although about 48 hours are required for the original background (from Fa^{223}) to double in intensity.

2.3.1 Apparatus. All exposures were taken on Eastman, No-Screen X-ray film in a North American Phillips 114.59 mm diameter powder camera. Copper radiation from a General Electric CA-6 X-ray diffraction tube was used in a General Electric XRD-1 unit. The films were measured, without magnification, by means of a pointer attached to a slide and vernier. The measurement of any one sharp line has a possible error of $\pm$ 0.1 mm.

2.3.2 Exposure Procedure. Since actinium decays primarily by the emission of low energy beta particles, it was decided to use unfiltered radiation on the sample and place a nickel foil (0.0004" thick) next to the film, between the film and the sample. The foil filtered out, or absorbed, the K_β radiation from the copper as well as absorbing the weak beta particles emitted by the sample. This exposure technique was tested with a 10 μg sample of lanthanum metal in the La-KCl mixture. A satisfactory diffraction pattern was obtained with a 3 hour exposure time. This exposure time was adopted for subsequent experiments with lanthanum and with actinium.

3. Experimental Results

From an analysis of the X-ray diffraction pattern obtained with a La-KCl sample, it was found that lines from two face-centered cubic (f.c.c.) structures were present in addition to the KCl diffraction lines. The lattice constant a_o for one of these structures was found to be 5.304 Å, a value in very close agreement with the a_o value reported by Klemm and Bommer[2] for the beta form of lanthanum metal. An a_o value of 5.669 Å was found for the second f.c.c. structure. This value is in very close agreement with the lattice constant reported by R. N. Mulford[4] for LaH_2. The experimental data, as well as calculated results, are presented in Table 1. The observed diffraction angles (θ) are identified with corresponding lattice indices for KCl, β La, and LaH_2. Potassium chloride was used as an internal standard for the X-ray camera. The β La and LaH_2 diffraction angles were corrected to this standard. Relative intensities were computed for the f.c.c. or beta form of lanthanum metal. These values are presented in Table 1.

TABLE 1

DIFFRACTION ANGLES AND LINE INTENSITIES FOR La-LaH_2-KCl SAMPLE

Indices			θ(degrees)		$Sin^2\theta$		Relative intensities*	
KCl	β La	LaH_2	Obs.	Corr.	Obs.	Calc.**	Obs.	Calc.
		111	13.65	13.65	0.05544	0.05538	M	
100			14.18				VS	
	111		14.58	14.58	0.06340	0.06327	S	1.00
		200	15.75	15.75	0.07368	0.07384	MW	
	200		16.93	16.93	0.08480	0.08436	MS	0.50
110			20.28				S	
		220	22.64	22.63	0.1481	0.1477	MW	
	220		24.25	24.30	0.1693	0.1687	M	0.32
111			25.05				M	
		311	26.75	26.80	0.2033	0.2031	W	
	311		28.78	28.79	0.2319	0.2320	MS	0.42
200			29.33				W	
	222		30.23	30.24	0.2536	0.2531	W	0.12
		400	32.83	32.84	0.2947	0.2954	W	
210			33.15				M	
211			36.80				MW	
	331		39.20	39.26	0.4005	0.4007	MW	0.17
	420		40.40	40.50	0.4218	0.4218	MW	0.15
300			47.18				W	
	333		48.90	49.00	0.5696	0.5694	MW	0.15
310			50.65				VW	

*Intensity designations: VS = very strong, S = strong, M = medium, MS = moderately strong, MW = moderately weak, W = weak, and VW = very weak.

**$Sin^2\theta$ calculated with a_o = 5.304 Å for β La and a_o = 5.669 Å for LaH_2.

The X-ray diffraction pattern obtained with an Ac-KCl sample was very similar to the La-LaH_2-KCl diffraction pattern. In addition to the KCl lines, the Ac-KCl pattern exhibited lines for two different f.c.c. structures with a_o values of 5.311 Å and 5.670 Å. Because of the strong similarity between the Ac-KCl and La-KCl patterns and the fact that identical methods were used in the preparation of samples, it is believed that the two f.c.c. structures found in the actinium sample may be attributed to actinium metal (with a_o = 5.311 Å) and to actinium hydride (AcH_2, with a_o = 5.670 Å). The measured diffraction angles and observed line intensities for the Ac-AcH_2-KCl diffraction pattern are presented in Table 2. Relative line intensities were calculated for a f.c.c. form of actinium metal and are included in the table.

TABLE 2

DIFFRACTION ANGLES AND LINE INTENSITIES FOR Ac-AcH_2-KCl SAMPLE

Indices			θ (degrees)		$Sin^2\theta$		Relative intensities	
KCl	Ac	AcH_2	Obs.	Corr.	Obs.	Calc.*	Obs.	Calc.
		111	13.58	13.58	0.05514	0.05536	M	
100			14.18				VS	
	111		14.58	14.58	0.06337	0.06310	MW	1.00
		200	15.78	15.78	0.07396	0.07382	MW	
	200		16.83	16.83	0.08383	0.08413	W	0.51
110			20.28				S	
		220	22.60	22.58	0.1474	0.1476	MW	
	220		24.18	24.23	0.1684	0.1683	VW	0.39
111			25.05				MW	
		311	26.73	26.78	0.2030	0.2030	MW	
	311		28.68	28.73	0.2311	0.2314	VW	0.48
210			33.10				M	
		331	36.33	36.26	0.3498	0.3506	F	
211			36.93				F	
		420	37.43	37.36	0.3682	0.3691	F	
221			47.33				F	
		531	53.60	53.55	0.6470	0.6459	F	

*$Sin^2\theta$ calculated with a_o = 5.311 Å for actinium metal and a_o = 5.670 Å for AcH_2.

Although the analysis of the La-LaH_2-KCl diffraction pattern appeared to be quite certain, an experiment was performed to confirm the presence of β La and LaH_2 in the sample prepared by the reduction of $LaCl_3$ with potassium vapor. A portion of the La-LaH_2-KCl sample was heated in hydrogen (H_2 pressure of 400 mm of Hg) for 30 min at a temperature of 350°C. An X-ray diffraction pattern was obtained with this sample. It was found that all diffraction lines corresponding to β La had disappeared, whereas the lines corresponding to the hydride had increased in number and in intensity. Also the unit cell of LaH_2 had expanded slightly. One may conclude, therefore, that metallic lanthanum in the sample reacted with hydrogen to form LaH_2 and that some excess hydrogen probably dissolved in the LaH_2. Results obtained from the X-ray diffraction pattern are presented in Table 3.

TABLE 3

DIFFRACTION ANGLES AND LINE INTENSITIES FOR LaH_x-KCl SAMPLE

Indices		θ (degrees)		$Sin^2\theta$		Relative intensity
KCl	LaH_x	Obs.	Corr.	Obs.	Calc.*	Obs.
	111	13.55	13.53	0.05473	0.05482	S
100		14.20				VS
	200	15.65	15.63	0.07259	0.07309	MS
110		20.25				
	220	22.40	22.43	0.1456	0.1462	MS
111		25.08				M
	311	26.60	26.62	0.2008	0.2010	MS
	222	27.88	27.90	0.2190	0.2193	MW
200		29.30				MW
	400	32.68	32.73	0.2922	0.2924	VW
210		33.15				M
	331	36.03	36.10	0.3473	0.3472	MW
211		36.80				MW
	420	37.10	37.17	0.3650	0.3655	MW
	422	41.35	41.45	0.4382	0.4386	W
220		43.75				VW
	333	44.55	44.65	0.4939	0.4934	W
300		47.20				W
	531	53.13	53.21	0.6400	0.6396	W
	600	54.15	54.23	0.6583	0.6578	W

*$Sin^2\theta$ calculated for a_o = 5.698 Å.

The results obtained in the X-ray diffraction studies are summarized in Table 4. The table includes values of a_o (the lattice constant), r_o (the atomic radius), and d (the density of the crystal).

TABLE 4

Substance	Crystal structure	a_o (angstrom units)	r_o (angstrom units)	d (gm/cc)
β La	f.c.c.	5.304 ± 0.006	1.87	6.18
LaH_2	f.c.c.	5.669 ± 0.006		5.14
LaH_x	f.c.c.	5.698 ± 0.006		
Ac	f.c.c.	5.311 ± 0.010	1.88	10.07
AcH_2	f.c.c.	5.670 ± 0.006		8.35

4. Discussion

4.1 The Source of the Lanthanum and Actinium Hydrides

Although LaH_2 and AcH_2 were detected in metallic samples prepared by the reduction of anhydrous chlorides with potassium vapor, it must be noted that the source of the hydrogen is unknown. However, the samples were very small and LaH_2 and, presumably, AcH_2 are readily formed and are quite stable. Hence, only traces of hydrogen or hydrogen-forming impurities (KH in the relatively large quantity of potassium, for example) in the reaction system would be adequate to form the quantities of LaH_2 and AcH_2 which were found.

4.2 Attempts to Prepare Alpha Lanthanum

Lanthanum exists in two crystal forms. The low-temperature form (α La) has a hexagonal close-packed structure, and the high-temperature form (β La) has a f.c.c. structure. Since actinium and lanthanum are very similar, one would expect actinium to exist in corresponding alpha and beta forms. Thus, one might conclude that the observed f.c.c. structure of actinium metal is β Ac, or the high-temperature form.

Zintl and Neumayer[5] have demonstrated that α La is converted to β La upon heating to a temperature of 350°C for a period of several days. Trombe and Foex[6] measured the coefficient of linear expansion of lanthanum and detected a hysteresis between 150°C and 375°C. They attributed this hysteresis to the coexistence of two forms of lanthanum. From these observations, one may conclude that α La is stable below a temperature of 150°C, that the α La to β La and, presumably, the β La to α La conversions occur between 150°C and 350°C, and that β La is stable at temperatures above 350°C to 375°C.

Attempts were made to develop a method for the conversion of β La to α La which could be adopted for the analogous conversion of β Ac to α Ac. Since only a relatively small quantity of actinium was available and since the gamma-ray background of actinium samples increases rather rapidly, any such method should be relatively rapid and be adaptable to the small, mixed Ac-KCl samples. The experiments were based on the observations of Zintl and Neumayer and of Trombe and Foex and are summarized briefly below:

a. A low-temperature reduction was effected by treating an excess of $LaCl_3$ with liquid potassium metal at a temperature of 95°C. Lanthanum metal was produced in the beta form and no evidence was found for the presence of α La.

b. A mixed sample of β La and KCl was slowly cooled from 380°C to 150°C over a period of 8 hours. The lanthanum metal remained in the beta form.

c. A mixed sample of β La and KCl was held at a temperature of 140°C. Intermittently, the sample was cooled and an X-ray diffraction pattern obtained. No change in the diffraction pattern could be detected after a total heating time of 28 days.

Since the efforts to effect the β La to α La conversion were unsuccessful, no attempts were made to prepare a low-temperature form of actinium.

A recent paper by Zeigler, Young and Floyd[7] describes a more complete study of the interconversion of α La and β La. These workers found that the $\alpha \rightarrow \beta$ conversion could be effected by heating α La to temperatures between 254°C and 400°C. However, the reverse process ($\beta \rightarrow \alpha$ conversion) could be effected only by rather severe deformation of β La. Such deformation resulted from filing metallic lanthanum. These results confirm the more limited observations made in this laboratory.

5. Summary

Actinium metal and actinium hydride have been prepared and their crystal structures determined from an analysis of X-ray diffraction patterns Both structures were found to be face-centered cubic, with a_o = 5.311 ± 0.010 Å for metallic actinium and a_o = 5.670 ± 0.006 Å for AcH_2.

From analogy with the crystalline forms of lanthanum metal, one might identify the f.c.c. actinium as a high-temperature form of actinium (β Ac). Attempts to develop a method for the preparation of a low-temperature form of actinium (α Ac) were unsuccessful.

The AcH_2 was formed as an impurity in the preparation of metallic actinium, and was identified by the similarity of its diffraction pattern to that of LaH_2 which was formed as an impurity in a similar preparation of metallic lanthanum. The identity of the LaH_2 impurity was confirmed experimentally.

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