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PREPARATION AND CRYSTAL STRUCTURE OF AMERICIUM METAL

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The crystal structure of americium has been studied using metal produced by two methods. The first method consisted of the reduction of approximately 20 mg quantities of americium trifluoride with barium vapor at 1000°C in an all-tantalum double crucible system. The products were allowed to cool 10 to 16 hours in vacuum, without controlled annealing. Spectrographic analysis of the resulting metal showed two weight percent of impurities which were barium (1.6%), calcium (0.1%), magnesium (0.1%), and aluminum (0.2%). In the second method americium dioxide, prepared by the decomposition of the oxalate in the air at 600°C, was reduced with lanthanum metal at 1200°C. The large difference in the volatility of americium and lanthanum metals enables the product to be separated by distillation. The americium was effused through a 20 mil hole in the crucible cap and collected on a rotatable 10 mil diameter tantalum wire or quartz fiber located ≤ 2 mm above the effusion orifice. Twenty to 100 μgm of americium, typically containing less than 0.5% weight percent of lanthanum were thus collected.

X-ray diffraction patterns were obtained using Cu K α radiation and 90 mm and 114.6 mm diameter cameras. The powder patterns of the microcrystalline metal from the fluoride reductions have been indexed as double hexagonal close-packed with $a = 3.474 \pm 0.005 \text{ \AA}$ and $c = 11.25 \pm 0.02 \text{ \AA}$. The relative intensities calculated from:

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

*This work was performed under the auspices of the U.S. Atomic Energy Commission.

for the space group $P6_3/mmc$ with atomic positions: 2 Am in $(0,0,0)$, $(0,0,1/2)$, and 2 Am in $(2/3,1/3,1/4)$, $(1/3,2/3,3/4)$, are compatible with the visual estimates of the intensities of the powder pattern lines. The intensities and sine squares for all lines for which $I \neq 0$ and $\sin^2 \theta < 0.54$ are listed in Table I. The proposed structure yields a calculated density of $13.61 \pm 0.05 \text{ gm cm}^{-3}$ and a metallic radius of 1.73 \AA .

The powder patterns from the metal produced by the vaporization technique can be interpreted in terms of small amounts of AmO (fcc, $a = 5.05$)¹ and an intimate mixture of the cubic and hexagonal forms of close-packed atoms, resulting from faults in the stacking of the close-packed layers. This type of stacking fault has been treated by Wilson.² The hexagonal reflections with $(h-k)/3 = \text{integral}$ and $l = \text{even}$ superimpose on the cubic reflections and will be sharp. The remaining lines will be broadened because of the stacking faults. The above preparations were predominantly cubic, and the average face centered cubic unit cell constant on the basis of four preparations is $a = 4.894 \pm 0.005 \text{ \AA}$. The calculated density is $13.65 \pm 0.05 \text{ gm/cm}^3$, and the metallic radius is 1.73 \AA . The lines of a typical pattern are listed in Table II.

After one of the vaporized samples, which had been indexed as fcc, was kept at dry ice temperature for a week, the pattern was predominantly hexagonal and agreed with the double hexagonal close-packed structure above. As the large scale reduction yields dhcp structure, and the fcc phase goes to the dhcp phase on cooling, the dhcp phase is probably the α or room temperature form, and the fcc phase becomes stable at a higher temperature.

Graf et al. have reported a dhcp phase of americium with $a = 3.642 \pm 0.005$, $c = 11.76 \pm 0.01 \text{ \AA}$ and metallic radius 1.82 \AA ,³ but in the present work no metal with the larger cell dimensions has been obtained. It should be pointed out, however, that the results of Graf and co-workers were reproduced in many successful reductions using both Am²⁴¹ and Am²⁴³, and that his metal appears to have been as pure as ours. It may be that americium, like cerium, exists in a "collapsed" as well as an expanded phase of the same structure type.

It must also be emphasized that spectrographic analysis is inadequate for the detection of all impurities, and particularly anionic impurities, small amounts of which may have an important effect on the structure.

Magnetic susceptibility measurements and high temperature x-ray studies are now in progress and will be reported in a future publication.

References

1. Y. Akimoto, J. C. Wallmann, B. B. Cunningham, to be published.
2. A. J. C. Wilson, X-Ray Optics, Methuen (London, 1949).
3. P. Graf, B. B. Cunningham, et al., J. Am. Chem. Soc. 78, 2340 (1956).

Table I

DIFFRACTION DATA FOR dhcp AMERICIUM METAL

<u>hkl</u>	<u>sin² θ</u>		<u>intensity</u>	
	<u>calcd.</u>	<u>obs.</u>	<u>calcd.</u>	<u>obs.</u>
10.0	0.0657	0.0663	11	Trace
10.1	0.0704	0.0710	62	M
00.4	0.0752	0.0764	50	S
10.2	0.0845	0.0851	145	VS
10.3	0.1080	0.1079	36	VW
10.4	0.1408	--	8	--
10.5	0.1831	0.1841	16	VVW
11.0	0.1970	0.1973	38	M
10.6	0.2348	0.2353	33	M
20.0	0.2627	--	2	--
20.1	0.2674	--	9	--
11.4	0.2722	0.2727	45	M ⁺
20.2	0.2815	0.2822	24	VW
10.7	0.2953	0.3000	7	M ⁻
00.8	0.3006		7	
20.3	0.3050		7	
20.4	0.3378	--	2	--
10.8	0.3663	--	2	--
20.5	0.3801	--	5	--
20.6	0.4318	0.4327	12	Trace
10.9	0.4462	0.4450	4	Trace
21.0	0.4597	--	1	--
21.1	0.4644	--	7	--
21.2	0.4785	0.4798	21	VW ⁺
20.7	0.4929	0.4972	4	M ⁺
11.8	0.4976		18	
21.3	0.5020	--	7	--
21.4	0.5348	0.5349	2	W
10.10	0.5354		10	

Table II

DIFFRACTION DATA FOR VAPORIZED AMERICIUM

Observed			Calculated						
I	$\sin^2 \theta$	Σh^2	fcc	Hexagonal			AmO		
			$\sin^2 \theta$	I	hk.l	$\sin^2 \theta$	I	Σh^2	$\sin^2 \theta$
S	0.0749	3	0.0746	50	00.2	0.0745	13		
Diffuse									
vw	0.0840				10.1	0.0849	97		
mw	0.1002	4	0.0994	26					
vw	0.1885							8	0.1872
m	0.1995	8	0.1988	19	11.0	0.1988	19		
T	0.2584							11	0.2574
ms	0.2742	11	0.2734	22	11.2	0.2733	23		
mw	0.3003	12	0.2982	6	00.4	0.2981	7		
vw	0.3987	16	0.3676	3					
mw	0.4726	19	0.4722	10					
m	0.4996	20	0.4970	9	11.4	0.4968	9		
mw	0.5967	24	0.5964	8	30.0	0.5963	4		
T	0.6320							27	0.6318
m	0.6719	27	0.6710	3	30.2 00.6	0.6708	8		
							0.6707	3	
w	0.7939	32	0.7952	5	22.0	0.7950	5		
ms	0.8695	35	0.8698	23	22.2 11.6	0.8695	12		
							0.8694	12	
m	0.8948	36	0.8946	13	30.4	0.8943	13		
fcc	A = 0.02485								
hcp	A = 0.06625								
	C = 0.01863								
AmO	A = 0.0234								