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Publication Date

1952-07-01

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Contract No. W-7405-eng-48

THE CRYSTAL STRUCTURES OF NpC AND Pu₂O₃

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July 14, 1952

Berkeley, California

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University of California, Berkeley, California

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ABSTRACT

NpC and Pu₂O₃ have been identified by x-ray diffraction. NpC is face-centered cubic, NaCl structure with

$$\underline{a} = 5.004 \pm 0.005 \text{ \AA}$$

Pu₂O₃ is isomorphous with the hexagonal "A form" for the rare earth sesquioxides with

$$\underline{a} = 3.840 \pm 0.004 \text{ \AA}$$

$$\underline{c} = 5.957 \pm 0.006 \text{ \AA}$$

and has essentially the same atomic parameters as La₂O₃. The lattice dimensions are smaller than predicted for pure Pu₂O₃, implying that the average oxidation number of plutonium is between (III) and (IV).

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The compounds NpC and Pu₂O₃ have been prepared for the first time in this laboratory and have been examined by x-ray powder diffraction methods.

NpC was prepared by Dr. W. A. Jenkins by heating neptunium oxide in a carbon crucible. The diffraction pattern gave two phases, NpC and another phase as yet unidentified. NpC is face-centered cubic, NaCl structure, isostructural with UC⁽¹⁾ and PuC⁽²⁾, with

$$a = 5.004 \pm 0.005 \text{ \AA.}$$

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- (1) R. E. Rundle, N. C. Baenziger, A. S. Wilson and R. A. McDonald, J. Am. Chem. Soc., 70, 99 (1948).
L. M. Litz, A. B. Garrett and F. C. Croxton, ibid, 1718 (1948).
- (2) W. H. Zachariasen, Acta Cryst. 2, 388 (1948).
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The second phase in this pattern does not have a pattern similar to that of UC₂.

Pu₂O₃ was prepared by S. C. Carniglia in an attempt to vaporize plutonium metal in a beryllium oxide crucible. The pattern included the lines of BeO, a second group which is attributed to Pu₂O₃, and some weak lines which are not yet identified. The Pu₂O₃ lines were indexed on a hexagonal lattice with

$$a = 3.840 \pm 0.004 \text{ \AA}$$

$$c = 5.957 \pm 0.006 \text{ \AA}$$

The intensities of these lines cannot be distinguished visually from those of La_2O_3 , which has the so-called "A-form" rare earth sesquioxide structure. The identification of Pu_2O_3 is based on this similarity of intensities and of unit cell dimensions.

With one molecule in the unit cell, the x-ray density of Pu_2O_3 is 11.48 g.cm^{-3} .

According to Pauling,⁽³⁾ the atoms of La_2O_3 are in the following

(3) L. Pauling, Z. Krystallogr. 69, 415 (1928).

special positions of $D_{3d}^3 - C\bar{3}m$:

$$2 \text{ La in } 2(d) \quad 1/3, 2/3, u; 2/3, 1/3, \bar{u}; u = 0.235$$

$$1 \text{ O I in } 1(a) \quad 0,0,0;$$

$$2 \text{ O II in } 2(d) \quad 1/3, 2/3, v; 2/3, 1/3, \bar{v}; v = 0.63$$

The intensities for Pu_2O_3 require that the atomic parameters, at least for the metal atoms, should be nearly the same. With these parameters, plutonium has four oxygen neighbors at 2.36 Å and three at 2.62 Å. These distances correspond to a crystal radius for the plutonium of 0.96 Å on Zachariasen's scale,⁽⁴⁾ if we compare with Ac_2O_3 to eliminate effects

(4) W. H. Zachariasen, Abstract of paper presented at American Crystallographic Association meeting, April, 1950.

due to the structure type. Zachariasen gives 1.00 Å as the crystal radius of plutonium(III). The discrepancy indicates that there is a

deficiency of plutonium in the compound and that it is partly in the (IV) state. The 4 percent difference in radius corresponds to 40 percent plutonium(IV), though this figure is, of course, very approximate.

Previously Zachariasen⁽⁵⁾ had predicted that Pu₂O₃ would have

(5) W. H. Zachariasen, Metallurgical Laboratory Report CK-1367
(June 25, 1944).

lattice constants,

$$\underline{a} = 3.87 \text{ \AA} \text{ (converted from kX)}$$

$$\underline{c} = 6.03 \text{ \AA}$$

with an x-ray density 11.2 g.cm⁻³. The differences between the observed dimensions and these predictions are equivalent to the discrepancy in radii discussed above.

Zachariasen⁽⁶⁾ reported a sample which was identified as containing

(6) W. H. Zachariasen, Metallurgical Laboratory Report CK-1530
(March 30, 1944).

35 percent Pu₂O₃ where Pu₂O₃ was of the body-centered cubic "C form" with

$$\underline{a} = 11.03 \text{ \AA} \text{ (converted from kX),}$$

but believed this to be the "abnormal" form and that the normal form would be the hexagonal form. This lattice dimension also is smaller than expected for pure Pu₂O₃.

We wish to thank Dr. Jenkins and Mr. Carniglia for the preparation of the samples. The x-ray diffraction patterns were taken by Mrs. Helena W. Ruben. This research was performed under the auspices of the U.S. Atomic Energy Commission.