

A Structural Study of the Sodium (V) Uranate, NaUO₃, by Time-of-Flight Powder Neutron Diffraction

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Powder neutron diffraction using the Rietveld profile refinement method modified for time-of-flight data was used to investigate the structure of the distorted perovskite, NaUO₃ (space group *Pbnm*; $a = 5.779(4)$, $b = 5.907(3)$, and $c = 8.283(4)$ Å). The octahedron of oxygen atoms around the pentavalent uranium atom in this compound is slightly distorted with four of six oxygen atoms at 2.152 Å and the other two at 2.145 Å. © 1989 Academic Press, Inc.

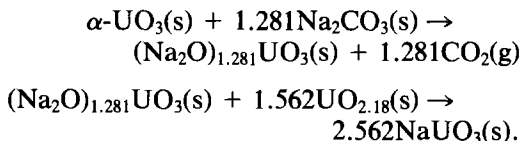
Introduction

NaUO₃ is one of the few compounds thought to contain U(V) in the solid state. Other examples include MUO₃ ($M = \text{Li, K, or Rb}$) (1, 2), Li₃UO₄ (3), and UCl₅ (4). Evidence for the presence of pentavalent U in NaUO₃ is derived from magnetic and ESR measurements (5, 6). The compound has a perovskite-related structure and the optical spectrum is consistent with U(V) in an environment in which there is slight tetragonal distortion (7). An integrated-intensity-based powder X-ray diffraction study of NaUO₃ by Bartram and Fryxell (8) has located the uranium atom positions, but the X-ray intensities are not, however, very sensitive to the oxygen and sodium positional parameters.

In the present work, we report a refinement of the crystal structure of NaUO₃ using Rietveld analysis of time-of-flight powder neutron data. This refined structure is compared with that obtained from integrated neutron intensities published recently by Miyake *et al.* (9).

Sample Preparation and Characterization

NaUO₃ was prepared by a method based on that of Rudörf and Leutner (10), involving the two-stage reaction:



In the first stage, $\alpha\text{-UO}_3$, prepared from uranyl nitrate hexahydrate (11), was inti-

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mately mixed with dried "Analar" Na₂CO₃ and heated in a gold crucible in air at 1023 K for 4 days. The salmon-pink product, a mixture of sodium (VI) uranates, was then mixed and ground with UO_{2.18} analyzed by the reducing-power method described previously (12) and loaded into a nickel tube which had been welded at one end. The mixture was pressed down firmly to ensure that little or no air remained in the tube and the open end crimped and welded. The sealed nickel tube was then heated in an evacuated silica tube at 1073 K for 1 week. The chocolate-brown product which was stable in air, gave sharp X-ray lines characteristic of a well-annealed crystalline sample in close agreement with those of Bartram and Fryxell for NaUO₃ (8). Atomic absorption spectroscopy and reducing-power determinations gave compositions of Na_(0.95±0.05)UO₃ and Na_(0.98±0.04)UO₃, respectively, and further confirmed the nature of the final product.

Collection and Refinement of Neutron Diffraction Data

Powder neutron diffraction data for NaUO₃ were collected at room temperature on the LAD diffractometer at the ISIS Spallation Neutron Source at the Rutherford-Appleton Laboratory, Chilton, Oxon. The sample was loaded into a thin-walled cylindrical vanadium can, sealed with an "O" ring, mounted on a sample stick, and lowered into the LAD sample chamber. This was then evacuated to eliminate any incoherent scattering from the air. Data collection lasted 8 hr and was over the range 2000–17,000 μsec (~0.4–3.5 Å). A similar spectrum was also recorded for the empty vanadium can. Preliminary data display and analysis was performed using the GENIE graphics program on the Rutherford VAX 8600 computer (13). The program enabled data collation, automatic peak fitting, and spectrum manipulation to be performed.

The data from the 150° detector banks were merged to form a unique data set which was then normalized by dividing by the incident spectrum derived from the empty vanadium can measurements. The background of the vanadium spectrum had previously been smoothed by fitting it to an empirical polynomial in time-of-flight and making small corrections for absorption and multiple scattering. Data refinement was performed using crystallographic routines from the Cambridge Crystallography Subroutine Library (CCSL) incorporating a Rietveld-analysis code modified for time-of-flight data (14).

The atomic coordinates for NaUO₃ from Bartram and Fryxell's X-ray study were used as the starting model for the refinement (8). The coherent scattering lengths for Na, U, and O are 0.363×10^{-14} , 0.855×10^{-14} , and 0.580×10^{-14} m, respectively. The least-squares refinement was carried out over the range 2000–14,500 μsec (0.4–3.0 Å) and for the final cycle of refinement, 23 parameters including the scale factor, 5 background parameters, 3 lattice parameters (*a*, *b*, *c*), 2 peak-shape parameters, zero point, atom positions (Na *x*, *y*; O(1) *x*, *y*; O(2) *x*, *y*, *z*), and 4 temperature factors were varied. Inclusion of an extinction correction produced no improvement in the refinement. The refinement proceeded smoothly and the final *R* values are *R*_{pr} = 8.04%, *R*_{wpr} = 9.24%, and *R*_{int} = 4.15%. *R*_{ex} was 2.36%. The agreement between the observed and calculated profiles is shown in Fig. 1.

Discussion of the NaUO₃ Structure

The atomic parameters for NaUO₃ determined in this study are given in Table I and selected atomic distances and bond angles in Table II. The structure can be described as an orthorhombic distortion of the aristotype cubic perovskite ABO₃ (Fig. 2). In the latter, the A atoms are surrounded by 12

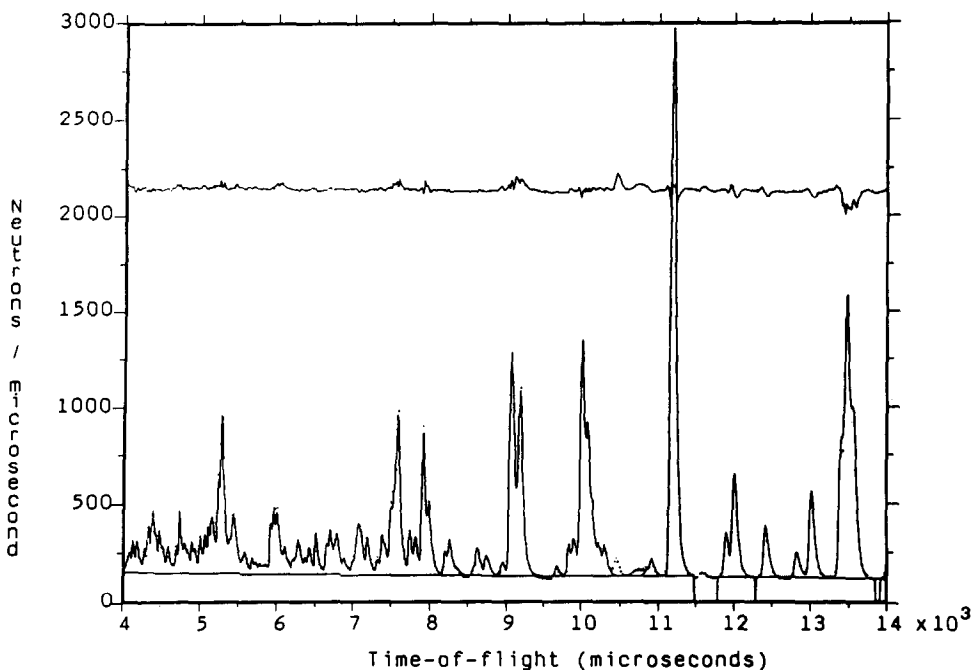


FIG. 1. Final profile fit for NaUO_3 showing observed (points), calculated (lower continuous line), and difference (upper continuous line) plots.

equidistant oxygen atoms and the B atoms by regular oxygen octahedra. Here in NaUO_3 , the $\text{Na}(A)$ and oxygen atoms are displaced from their cubic positions, so that the 12 $\text{Na}-\text{O}$ distances vary over a large range (2.390–3.619 Å). The sodium atoms are thus surrounded by eight nearest-neigh-

bor oxygen atoms. Two of the $\text{Na}-\text{O}$ bond lengths are short (2.390 and 2.411 Å), although $\text{Na}-\text{O}$ bonds of similar lengths have

TABLE I
ATOMIC PARAMETERS FOR NaUO_3 AT ROOM TEMPERATURE

	x/a	y/b	z/c	B (Å ²)	n
Na in 4(c)	-0.0058(9)	0.0287(6)	1/4	1.13(5)	1.0
U in 4(b)	1/2	0	0	0.08(1)	1.0
O(1) in 4(c)	0.0967(4)	0.4692(4)	1/4	0.44(4)	1.0
O(2) in 8(d)	0.6989(3)	0.2997(3)	0.0503(2)	0.58(2)	1.0

Note. Space group: $Pbnm$ (No. 62 of the International Tables in an alternative setting). Unit cell dimensions (refined from neutron data): $a = 5.779(4)$, $b = 5.907(3)$, and $c = 8.283(4)$ Å; $V = 282.8$ Å³. Cell content: 4NaUO_3 .

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN NaUO_3 AT ROOM TEMPERATURE

Around sodium			
Na-O(1)	2.668(4)	O(1)-Na-O(1)	85.7(1)
Na-O(1)	2.390(6)	2 × O(1)-Na-O(2)	64.8(1)
Na-O(1)	3.358(4)	2 × O(1)-Na-O(2)	65.6(1)
Na-O(1)	3.418(6)	2 × O(1)-Na-O(2)	69.7(1)
2 × Na-O(2)	2.865(4)		
2 × Na-O(2)	2.411(4)		
2 × Na-O(2)	2.935(8)		
2 × Na-O(2)	3.619(3)		
Around uranium			
2 × U-O(1)	2.152(1)	O(1)-U-O(1)	180
2 × U-O(2)	2.152(2)	2 × O(1)-U-O(2)	91.3(1)
2 × U-O(2)	2.145(1)	2 × O(1)-U-O(2)	88.7(1)
		2 × O(2)-U-O(2)	180
		2 × O(2)-U-O(2)	91.0(1)
		2 × O(2)-U-O(2)	89.0(1)

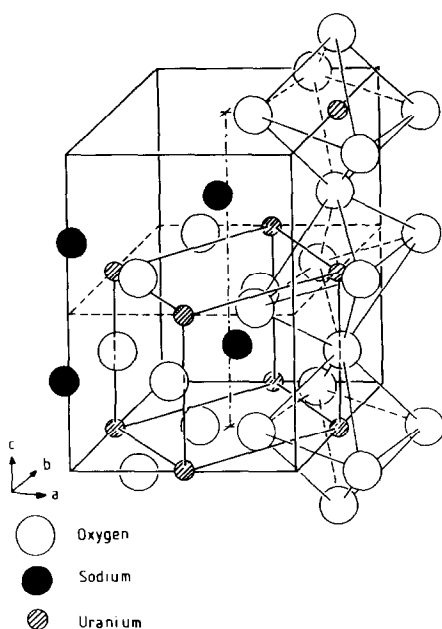


FIG. 2. NaUO₃ and its relation to the idealized perovskite structure.

been found in sodium (VI) uranates such as Na₂UO₄ (15).

The oxygen octahedra around the uranium atoms are very nearly regular. The O–U–O angles are in the range (88.7(1)–91.3(1)°) and there are only slight differences in the U–O distances (2.145(1)–2.152(2) Å). This is consistent with the previous interpretation of the electronic spectrum (7). The uranium–oxygen octahedra themselves are tilted from their regular positions in the cubic perovskite, producing a shortened O–O distance of 3.308(3) Å between adjacent octahedra. The tilting of octahedra, and the distortions of the perovskite structure which result, have been classified by Glazer (16). NaUO₃ is in the (*a*⁻*b*⁺*a*⁻) group with equal tilts about the [100] and [001] axes. Many other perovskites show the same distortion, including GdFeO₃ (17), which is considered to be the prototype of the series, and other rare-earth orthoferrites, as well as sulfides

such as UCrS₃ (18) with U in the *A* sites and BaUS₃ (19) with U in the *B* sites.

There is a decrease in distortion of the perovskite structure down the MUO₃ series (*M* = Li, Na, K, or Rb), reflecting the ability of larger cations to stabilize the regular structure. LiUO₃ (1) adopts a rhombohedral LiNbO₃-type structure consisting of distorted UO₆ octahedra. KUO₃ and RbUO₃, however, both have cubic structures with regular UO₆ octahedra (2).

Comparison with Other Models

The present refinement of the NaUO₃ structure differs in several respects from those of Bartram and Fryxell (8) and Miyake *et al.* (9). The deviation of the oxygen positions from those in an undistorted perovskite structure is considerably larger here than that determined in Bartram's X-ray study (8), although less than that predicted by Miyake *et al.* (9). This is reflected in the metal–oxygen bond lengths. In both the present model and that of Bartram, the oxygen coordination around the uranium is virtually a regular octahedron with U–O bond lengths of 2.15(1) and 2.09(2) Å, respectively. Miyake proposed an irregular octahedron of oxygen atoms around the uranium, with two longer (2.24(2) Å) and four shorter (2.15(1) Å) U–O bonds. The U(V)–O bond length predicted from Shannon ionic radii (20) is 2.11 Å. The mean Na–O bond lengths determined by the present author, by Miyake (9), and by Bartram and Fryxell (8) respectively are 2.69, 2.87, and 2.88 Å. The Na–O bond length from the Shannon ionic radii is 2.53 Å for 8- and 4-coordination around sodium and oxygen, respectively.

In a correctly determined structure, the sum of the bond strengths around a given atom is expected to be within 5% of the formal oxidation state for that atom. The bond strengths are calculated for NaUO₃ for the three models using the expression

TABLE III
BOND STRENGTH-BOND LENGTH CALCULATIONS FOR NaUO₃

Coefficients of bond strength function (Eq. (1)) (21)							
		R (Å)		N			
		Na		4.29			
		U		4.30			
		Present authors		Bartram (8)		Miyake (9)	
		R_{ij} (Å)	s_{ij}	R_{ij} (Å)	s_{ij}	R_{ij} (Å)	s_{ij}
Bond strengths about U							
2 × U-O(1)	2.152	1.65	2.087	1.89	2.158	1.63	
2 × U-O(2)	2.145	1.68	2.084	1.90	2.148	1.67	
2 × U-O(2)	2.152	1.65	2.091	1.87	2.237	1.40	
Σs_{ij}		4.98		5.66		4.70	
Bond strengths about Na							
Na-O(1)	2.668	0.12	2.670	0.12	2.336	0.21	
Na-O(1)	2.390	0.19	2.673	0.12	2.589	0.13	
2 × Na-O(2)	2.866	0.17	2.786	0.20	2.777	0.20	
2 × Na-O(2)	2.411	0.37	3.083	0.13	3.212	0.11	
2 × Na-O(2)	2.935	0.16	2.922	0.16	3.082	0.13	
Σs_{ij}		1.01		0.73		0.78	
Bond strengths about O(1)							
O(1)-Na	2.668	0.12	2.670	0.12	2.336	0.21	
O(1)-Na	2.390	0.19	2.673	0.12	2.589	0.13	
2 × O(1)-U	2.152	1.65	2.087	1.89	2.158	1.63	
Σs_{ij}		1.96		2.13		1.97	
Bond strengths about O(2)							
O(2)-Na	2.935	0.08	2.922	0.08	3.082	0.07	
O(2)-Na	2.411	0.18	3.083	0.07	3.212	0.06	
O(2)-Na	2.145	0.84	2.084	0.95	2.148	0.84	
O(1)-U	2.152	0.83	2.091	0.94	2.237	0.70	
Σs_{ij}		1.93		2.03		1.66	

$$s_{ij} = (R_{ij}/R)^{-N}, \quad (1)$$

where s_{ij} is the strength of a bond between atoms i and j , R_{ij} is the bond length, and R and N are constants (Table III). The values of R and N used in Table III are in fact those determined for the U(VI) ion, rather than the U(V) ion, as few U(V)-containing oxide structures have been determined. It has been shown that the variation of R and N with oxidation state for a particular atom is generally quite small (21).

The present refinement gives values of Σs_{ij} around U and Na, in excellent agreement with the value of five and one expected for U(V) and Na(I), supporting this as the most likely model for the NaUO₃ structure.

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