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α- and β-Na_2UO_4: Structural and Thermochemical Relationships

E. H. P. Cordfunke

Netherlands Energy Research Foundation ECN, Petten, The Netherlands

and

D. J. W. IJdo

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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The crystal structures of α- and β-Na_2UO_4 have been determined by neutron powder diffraction. In α-Na_2UO_4 edge-shared UO_6 octahedra extend in chains along the c axis. In β-Na_2UO_4 the UO_6 octahedra share corners with each other to form two-dimensional perovskite layers. The octahedra are tilted around both the b and c axes of the unit cell, α- and β-Na_2NpO_4 probably have the same structures. The enthalpy of transition of α-Na_2UO_4 to β-Na_2UO_4 has been determined both by DTA measurements and by calorimetric measurements. The unusually high value obtained can be explained from a structural point of view.

INTRODUCTION

Because sodium is used as a coolant in fast breeder reactors much research has been done on the system Na–U–O. The compounds $Na_2U_2O_7$, Na_2UO_4 (α and β), Na_4UO_5, $NaUO_3$, and Na_4UO_5 (α and β) are all well known. Cordfunke *et al.* (1) published the thermodynamic properties of Na_2UO_4, $Na_2U_2O_7$, and $NaUO_3$. However, only the crystal structures of β-Na_4UO_5 (2) and $NaUO_3$ (3) are known in any detail.

A review of the structural information on Na_2UO_4 covering the years up to 1974 is given by Keller (4). The experimental evidence for the structures given therein is quite meager, and not in agreement with the powder diffraction diagrams given by Cordfunke and Loopstra (5). The lattice parameters of α- and β-Na_2UO_4 (5) and of some related compounds are given in Table 1. Recently, Gasperin (6) reported the crystal structure of β-Na_2UO_4 with space group *Fmmm*, as obtained from single crystal X-ray diffraction. In agreement with the literature (4) the structure is related to the K_2NiF_4 type (7); however, the Na–O distances are unreliable. Gasperin concluded that Na and O are delocalized and the structure contains domains with space group $P2_1/b$. The structure determination of β-Na_2UO_4 is important for the understanding of the tilting of BO_6 octahedra in the oxides A_2BO_4, related to the K_2NiF_4 structure type containing a small A ion as in Pr_2NiO_4 (8), and $La_{1-x}Ba_xCuO_4$ (9) which are (super) conductors.

EXPERIMENTAL

α-Na_2UO_4 was prepared by carefully mixing stoichiometric amounts of Na_2CO_3 and U_3O_8 and heating the mixture to 1193 K in a golden crucible until the reaction was complete as described before (5). β-Na_2UO_4 was prepared from the α-compound by heating at 1220 K in a closed platinum capsule in order to avoid decomposition to $Na_2U_2O_7$.

The enthalpy of formation of β-Na_2UO_4 at 298.15 K was obtained from its enthalpy of solution in 1.5 mole dm^{-3} H_2SO_4. The details of the calorimetric measurements have been described elsewhere (1). The sample used was phase-pure, and the U content was determined titrimetrically with dichromate and found to be 68.50 ± 0.06% (calculated as 68.40%).

The X-ray diffraction patterns were made on single-coated film with a focusing Guinier camera (FR 552, Enraf-Nonius, Delft, The Netherlands) using Cu$K\alpha_1$ radiation (λ = 1.5405981(3) Å) with α-SiO_2 (hexagonal, a = 4.9133(2) Å, c = 5.4053(4) Å) as an internal standard.

The neutron diffraction measurements were taken on the powder diffractometer at the HFR in Petten. Neutrons with λ = 2.57176(3) Å were obtained using the beam reflected from the *hkl* (111) planes of a single crystal of copper, reducing the λ/n contamination to less than 0.1% by means of a pyrolitic graphite filter. Soller slits with a horizontal divergence of 30′ were placed between the reactor and the monochromator and in front of the four ^{3}He counters. The sample holder (i.d. = 1.43 cm) consisted of a V tube closed with Cu plugs fitted with O-

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TABLE 1
Lattice Parameters (Å) of Related Compounds from the Literature

Compound	*a*	*b*	*c*	Reference
Sr_2PbO_4	6.159(1)	10.078(2)	3.502(1)	(14)
α-Na_2UO_4	5.734(1)	9.769(1)	3.498(1)	(5)[a]
α-Na_2NpO_4	5.705(5)	9.685(5)	3.455(5)	(20)[a]
La_2CoO_4	5.490	5.488	12.548	(15)
β-Na_2UO_4	5.807(1)	5.979(1)	11.724(2)	(5)
β-Na_2UO_4	5.802(2)	5.969(2)	11.699(3)	(6)
β-Na_2NpO_4	5.785(5)	5.936(5)	11.65(5)	(20)

[a] *a* and *b* axes interchanged.

rings. The diffraction pattern was taken at 300 K and analyzed by means of Rietveld's profile refinement technique (10). Absorption correction was applied according to Weber (11), $\mu R = 0.066$. For the coherent scattering lengths we used the values for O 5.805, Na 3.63, and U 8.417 fm (12). For the refinement of the neutron diffraction data the program DBW 3.2S, version 8802 was used (13). The variables include a scale factor, five background parameters, three half-width parameters defining the Gaussian-like peak shape, the counter zero, an asymmetry parameter, the unit cell dimensions, atomic position parameters, and thermal parameters. A scale factor for the small contribution of the V sample holder was also refined.

STRUCTURE DETERMINATION

Data collection conditions and refinement details including least-squares refined lattice parameters using X-ray Guinier powder data are summarized in Table 2. The lattice parameters of α-Na_2UO_4 (Table 1) suggest a close relationship to the structure of Sr_2PbO_4 (14), so this structure could be used on the trial model. The X-ray powder diffraction data of β-Na_2UO_4 from Cordfunke and Loopstra (5) ruled out the space group *Fmmm* (6), and are almost consistent with the space group *Abma* as found for La_2CoO_4 (15). With the subgroup *Pbca* a successful model could be derived where the UO_6 octahedra are tilted around [110] as in La_2CoO_4 as well as around [001] of the K_2NiF_4 archetype. This model is in full agreement with the X-ray diffraction data (5).

Atomic parameters are listed in Table 3. Selected bond distances and angles are listed in Table 4. The agreement between the observed and calculated profile is shown for α- and β-Na_2UO_4 in Fig. 1.

THE ENTHALPY OF THE PHASE TRANSITION

The enthalpy of formation of a phase-pure sample of β-Na_2UO_4 has been determined calorimetrically at 298.15

TABLE 2
Data Collection Condition and Refinement Details for α- and β-Na_2UO_4

Parameters	Compound			
	α-Na_2UO_4		β-Na_2UO_4	
Space group	*Pbam*		*Pbca*	
	Neutron	X-ray Guinier	Neutron	X-ray Guinier
Diffraction λ (Å)	2.57176(3)	1.540598	2.57176(3)	1.540598
Cell parameters				
a (Å)	9.7623(3)	9.7582(3)	5.8079(3)	5.8053(2)
b (Å)	5.7287(2)	5.7273(3)	5.9753(3)	5.9732(2)
c (Å)	3.4956(1)	3.4949(1)	11.7179(6)	11.7118(4)
V (Å)^3	195.496(11)	195.32(1)	406.650(34)	406.12(1)
Z	2		4	
D_x(Mg · m^{-3})	5.912		5.684	
2Θ range (°)	5–155	17–66	5–153	17–66
Step size (°)	0.1		0.1	
R_p	2.14		1.92	
R_{wp}	2.81		2.54	
R_E	2.00		1.67	
S	1.41		1.52	
D-WD	1.31		1.22	
No. of parameters refined	26		31	
Independent reflections	57	28	93	29
SS/FOM		*F*28 = 110(0.005,51)		*F*29 = 80(0.005,72)

TABLE 3
Fractional Atomic Coordinates and Thermal Parameters ($Å^3$) of α- and β-Na_2UO_4 at 295 K

Compound	x	y	z	B
α-Na_2UO_4	Na 0.1818(4)	0.4436(4)	0.5	1.13(2)
	U 0	0	0	0.36(4)
	O1 0.1760(2)	0.1428(3)	0	0.76(5)
	O2 0.0547(2)	0.2111(3)	0.5	0.78(5)
β-Na_2UO_4	Na 0.0026(6)	0.0550(7)	0.3363(4)	1.39(11)
	U 0	0	0	0.30(7)
	O1 0.2947(5)	0.2080(4)	0.0450(2)	0.94(8)
	O2 0.1077(3)	0.0320(5)	0.1534(2)	1.13(8)

K from its enthalpy of solution in 1.5 mol · dm^{-3} H_2SO_4. The thermochemical cycle from which $\Delta_f H°$ (298.15 K) was calculated, is given for α-Na_2UO_4 in Table 5 of the previous publication (1). For the enthalpy of solution in this solvent the value $-(197.42 \pm 0.54)$ kJ · mol^{-1} was obtained, and from this value we obtain for β-Na_2UO_4 $\Delta_f H°$ (298.15 K) = $-(1882.85 \pm 1.13)$ kJ · mol^{-1}. This value is in good agreement with the value $-(1884.6 \pm 3.6)$ kJ · mol^{-1} selected by Grenthe *et al.* (16). However, in view of the uncertainties in the auxiliary values of the various cycles, as already noted by the latter authors, we here prefer to calculate the enthalpy of transition of α → β-Na_2UO_4 as the difference between the enthalpies of formation of α- and β-Na_2UO_4 as determined in the same medium. We thus obtain $\Delta_{tr}H°$ (298.15 K) = $-(1882.85 \pm 1.13) + (1897.27) = +(14.4 \pm 1.5)$ kJ · mol^{-1}.

For the transition temperature the value of about 1193 K has been reported (5) based on high-temperature X-ray diffraction. This temperature has been confirmed in the present study by DTA measurements at various heating rates (1, 2, 5, and 10 K · min^{-1}). It must be noted that this transition is reversible and very slow near the transition temperature. The enthalpy of transition calculated from the DTA experiments is (24.4 ± 0.5) kJ · mol^{-1}. This value is in perfect agreement with the enthalpy of transition obtained from drop-calorimetric enthalpy-increment measurements by Frederickson and O'Hare (17). The results of the measurements of the latter authors have been recalculated. For α-Na_2UO_4 we used their values, and applied the constraints $\{H°(T) - H°(298.15\ K)\} = 0$ at T 298.15 K and $C_p°$ (298.15 K) = 146.65 J · mol^{-1} K^{-1} (18). We thus obtain (298.15) – 1165 K):

$$\{H°(T) - H°\ (298.15\ K)\}/J \cdot mol^{-1} = 162.5688\ (T)$$
$$+ 12.92942 \times 10^{-3}(T)^2 + 21.00428 \times 10^5(T)^{-1} + 56{,}664.1.$$

In the case of β-Na_2UO_4 the sample dropped irreversibly, and consequently, the measured results should be increased with the enthalpy of transition at 298.15 K for which we take the value 14.4 kJ · mol^{-1} from the present study. With this value as the constraint for $\{H°(T) - H°\ (298.15\ K)\}$ at T = 298.15 K we obtain for β-Na_2UO_4 (298.15 – 1273 K):

$$\{H°(T) - H°(298.15\ K)\}/J \cdot mol^{-1} = 70.4254\ (T)$$
$$+ 59.7378 \times 10^{-3}(T)^2 - 102.0570 \times 10^5(T)^{-1} + 22{,}322.$$

From the two enthalpy increment equations we obtain at the transition temperature $\Delta_{tr}H°(1193\ K) = 25.40$ kJ · mol^{-1}.

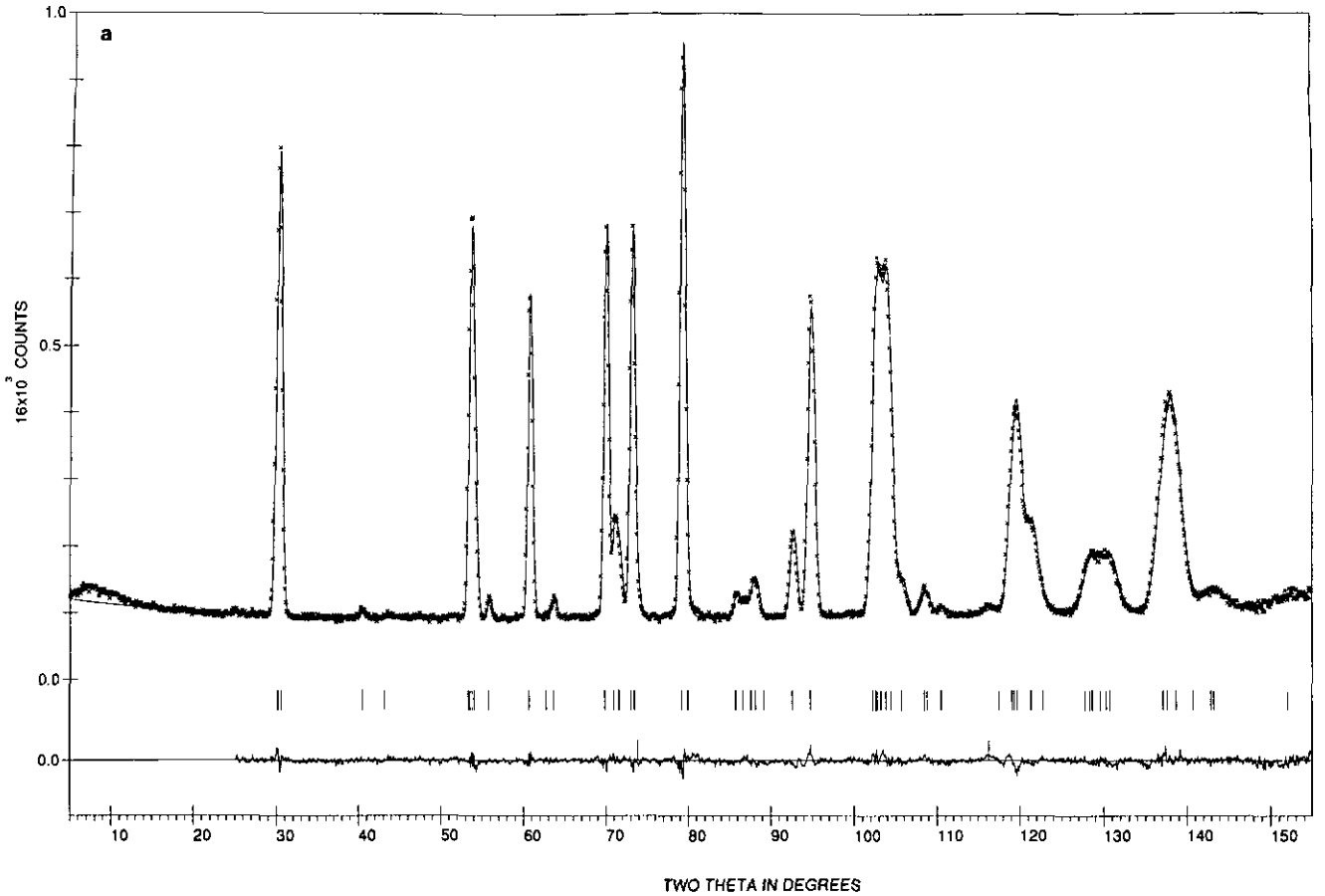
DISCUSSION

In α-Na_2UO_4, edge-shared UO_6 octahedra extend in chains along [001]. The chains are held together by NaO_7 polyhedra (Fig. 2). The U–O1 distances are shorter than the U–O2 distances in agreement with the underbonding of O1 (U + 5 Na) compared with O2 (2U + 3 Na). The same feature is found in the isostructural compounds Sr_2PbO_4 and Ca_2SnO_4 (14), but is less pronounced.

The structure of β-Na_2UO_4 (Fig. 3) can be derived from the K_2NiF_4 structure type by tilting of the UO_6 octahedra. The octahedra share corners with each other to form a two-dimensional perovskite-like array. Between these layers the Na ions are located, Na and unshared O atoms form rock salt layers in the archetype. In the ideal A_2BO_4 (K_2NiF_4 type) the void for A has the same size as an O atom. If the radius of A is too small, the void is reduced in size by tilting of the octahedra. The analysis of the tilt uses two independent rotation angles, ϕ about [110] and ω about [001] of the archetype, interactions between the two being negligibly small. The rotation ϕ lowers the symmetry from *I4/mmm* of the archetype to *Bbmb* (66) or *Abma* (64) depending on the rotations of the second

TABLE 4
Selected Atomic Distances (Å) and Angles (°) in α- and β-Na_2UO_4 at 295 K

α-Na_2UO_4	Na–2O1	2.455(2)	U–2O1	1.903(2)
	Na–2O1	2.507(3)	U–4O2	2.191(1)
	Na–O2	2.335(3)		
	Na–O2	2.666(4)	O1–U–O2	90.99(6)
	Na–O2	2.721(4)	O2–U–O2	105.79(5)
β-Na_2UO_4	Na–O1	2.406(5)	U–2O1	2.178(3)
	Na–O1	2.611(5)	U–2O1	2.180(3)
	Na–O1	2.877(5)	U–2O2	1.913(2)
	Na–O2	2.288(5)		
	Na–O2	2.355(4)	O1–U–O1	91.81(10)
	Na–O2	2.553(5)	O1–U–O2	91.58(9)
			O1–U–O2	91.81(10)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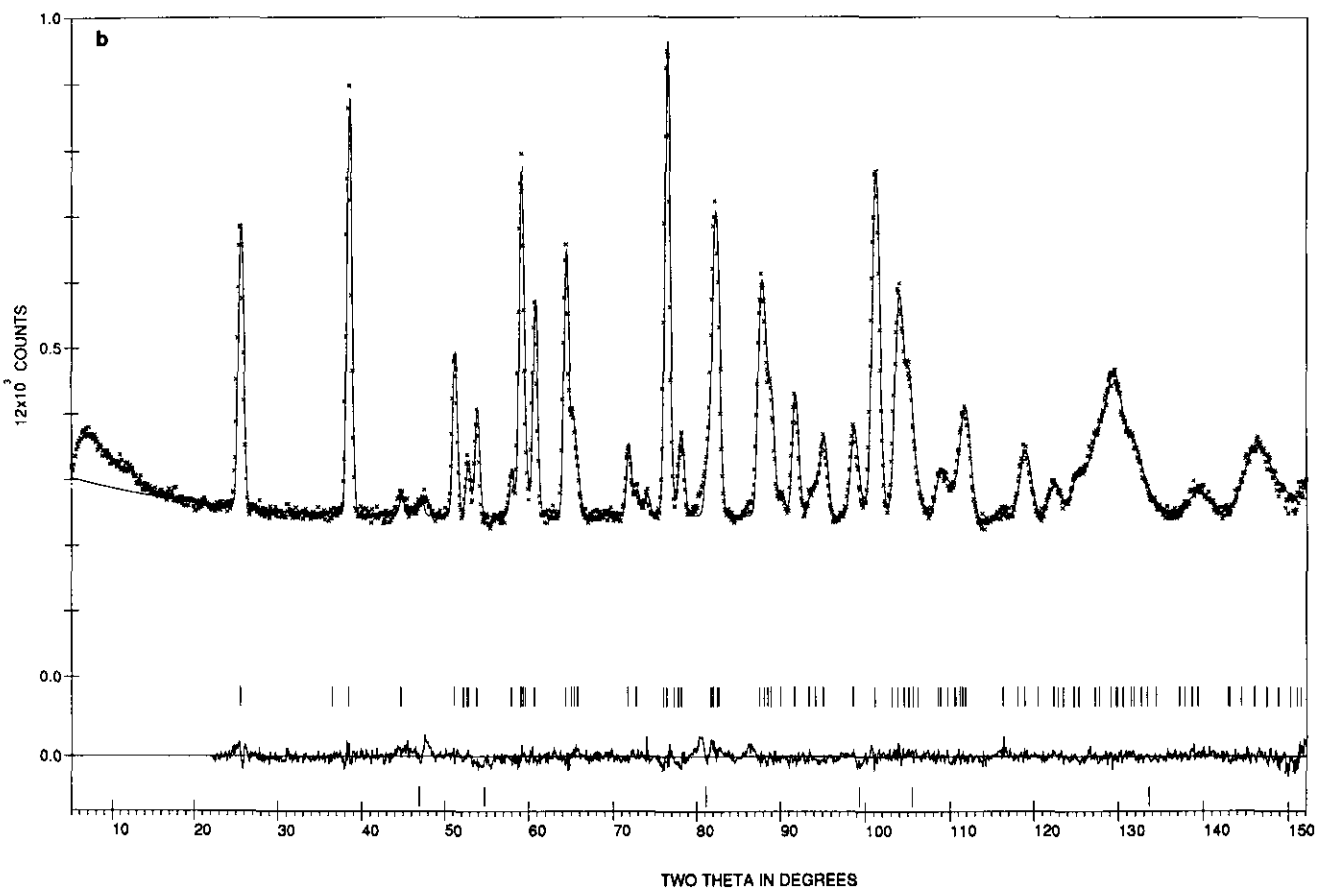
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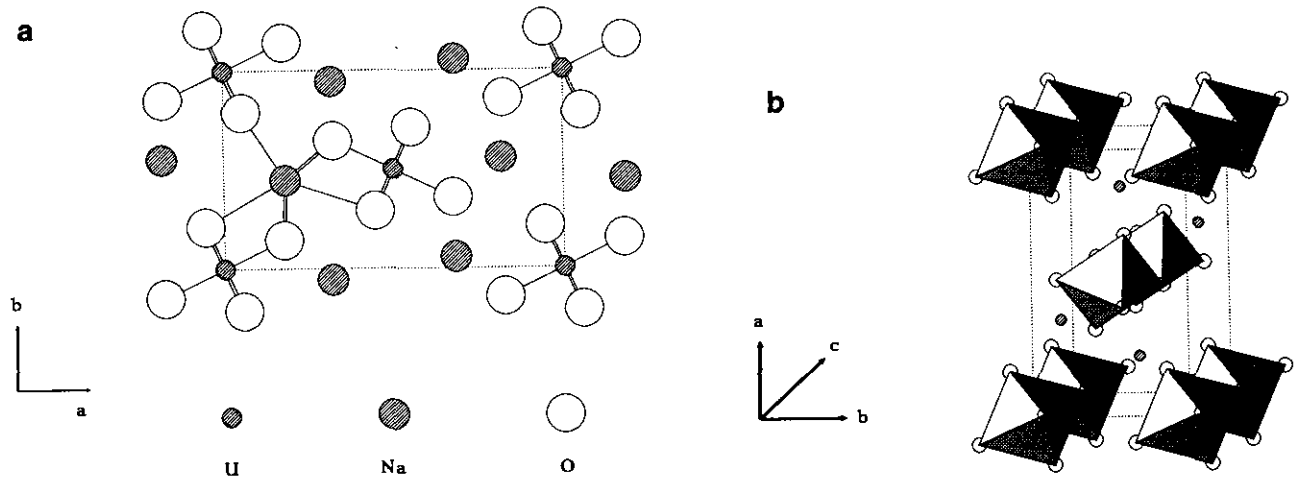

FIG. 2. (a) Projection of α-Na_2UO_4 along the c axis; (b) structure of α-Na_2UO_4.

layer at $z = 1/2$. The unit cell has the lattice parameters $a \approx a'\sqrt{2}\cos\phi$, $b \approx a'\sqrt{2}$, $c \approx c'$, in which a' and c' are the lattice parameters of the tetragonal archetype. The rotation ω again lowers the symmetry. The two possibilities from *Abma* are *Pbca* or *A2/b*11. The rotations reduce the coordination of Na from 9 in the archetype to 6 in the β-Na_2UO_4 structure. From the O1 atomic coordinates the rotation angles can be calculated:

$$\omega = \tfrac{1}{2}[\arctan\{4x(01) - 1\}a/b + \arctan\{1 - 4y(01)\}b/a] = 9.83(2)°$$

$$\phi = \arctan[(2z(01)c\{(1/2a)^2 + [1/2 - 2y(01)b]^2\}^{-1/2}] = 19.6g(2)°.$$

The result is shown in Fig. 3. The layers β-Na_2UO_4 are folded as was already assumed by Hoekstra (19) from infrared spectroscopy. The sample of β-Na_2UO_4 shows a relatively high background in the neutron-diffraction experiment compared to that of α-Na_2UO_4. This is probably due to some nonordered material, formed during the phase transition. A trace of Na_2O could be detected as a

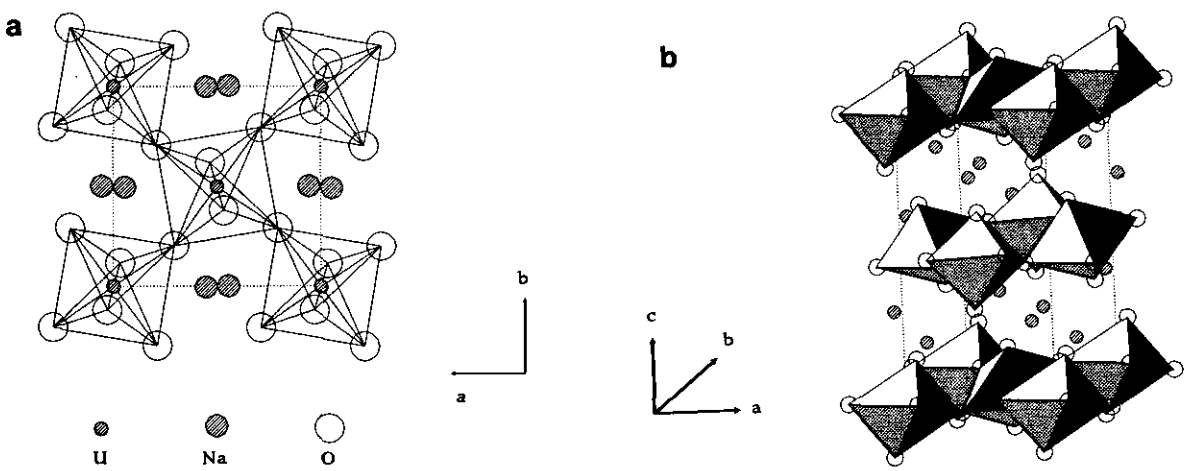

FIG. 3. The 2*d* sheet of octahedra at $z \approx 0$ of β-Na_2UO_4; (b) structure of β-Na_2UO_4.

FIG. 1. Observed (dots) and calculated (full line) neutron diffraction profiles of (a) α-Na_2UO_4 and (b) β-Na_2UO_4. Tick marks below the profiles indicate the positions of the Bragg reflections. Difference (observed − calculated) curve appears at the bottom of the plot.

second phase. The present structure determination of β-Na_2UO_4 uses a subgroup of the space group *Fmmm* accepted by Gasperin (6). Probably Gasperin overlooked a set of weak reflections permitted in space group *Pbca*. The conclusions of Gasperin that Na and O atoms are delocalized is not supported by the current diffraction experiment.

The enthalpy of transition of $\alpha \rightarrow \beta$-Na_2UO_4 has an unusually high value. For instance, in $Na_2U_2O_7$ we measured an enthalpy of transition of only 2.7 $kJ \cdot mol^{-1}$ at 1322 K which is a more common value for a phase transition in uranium compounds. The high value for the enthalpy of transition can be understood from the rigid structure of α-Na_2UO_4 in which coupling of the polyhedra takes place by sharing edges. At the transition temperature, the more open β-Na_2UO_4 structure causes a considerable increase in entropy, and hence a high value for the enthalpy of transition ($\Delta S = \Delta H/T$).

The lattice parameters of α- and β-Na_2NpO_4 (20) are similar to those of Na_2UO_4 (Table 1). Combined with the fact that the radius of Np^{6+} is only slightly smaller than the radius of U^{6+} in six-coordination (0.72 and 0.73 Å, respectively) (21), this leads to the conclusion that Na_2NpO_4 has the same crystal structures as Na_2UO_4.

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