

$\text{Sr}_3\text{U}_{11}\text{O}_{36}$: Crystal Structure and Thermal Stability

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The crystal structure of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ has been determined by X-ray, electron, and neutron diffraction. The structure is related to $\alpha\text{-U}_3\text{O}_8$, with uranium in both octahedral and pentagonal bipyramidal coordination. The enthalpy of formation has been determined and is discussed in relation to the other strontium uranium oxides. © 1991 Academic Press, Inc.

1. Introduction

In the system Sr-U-O several hexavalent compounds have been identified: $\text{SrU}_4\text{O}_{13}$, $\text{Sr}_2\text{U}_3\text{O}_{11}$, SrUO_4 , Sr_2UO_5 , and Sr_3UO_6 (1); the structures of the last three compounds have been determined (2, 3). Although the structure and physicochemical properties of the first mentioned compound $\text{SrU}_4\text{O}_{13}$ appear to be closely related to U_3O_8 , up to this time only the dimensions of its orthorhombic subcell could be determined (1). A renewed study showed its composition to be slightly different, corresponding with the formula $\text{Sr}_3\text{U}_{11}\text{O}_{36}$. A structure determination of this phase is described in the present paper.

2. Experimental

The title compound was prepared by heating a stoichiometric mixture of SrO and

U_3O_8 in a gold boat in oxygen at 1000°C for 20 hr. After repeated grindings and heatings a phase-pure compound was obtained; no indication of the presence of U_3O_8 was found by X-ray diffraction. A chemical analysis of the final product yielded the following results: Sr $7.59 \pm 0.02\%$ (calcd. 7.605), U (total) $75.76 \pm 0.04\%$ (calcd. 75.74%), U(IV) $0.34 \pm 0.01\%$.

The enthalpy of formation of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ was derived from its enthalpy of solution which was measured calorimetrically in 5 M HCl, according to the procedure described before (4).

The X-ray powder diffraction patterns were recorded with a focusing Guinier camera (Table I) using $\text{CuK}\alpha_1$ radiation, and $\alpha\text{-SiO}_2$ as an internal standard. The presence of the repetition of a similar structural motive is evident from the intensity distribution of a small set of strong reflections and a large set of weak reflections. The former set is

TABLE I
X-RAY DIAGRAM OF Sr₃U₁₁O₃₆ ($a = 28.508(3)$, $b = 8.3806(9)$, $c = 6.7333(9)$ Å; $Pmmn$)

$d(\text{exp})$	h	k	l	$d(\text{calc})$	I	$d(\text{exp})$	h	k	l	$d(\text{calc})$	I	$d(\text{exp})$	h	k	l	$d(\text{calc})$	I
8.058	1	1	0	8.044	25	2.304	7	3	0	2.305	<5	1.8314	14	2	0	1.8321	30
6.573	1	0	1	6.553	8	2.296	6	2	2	2.298	5	1.7959	7	4	1	1.7963	50
6.303	3	1	0	6.288	<5	2.245	0	0	3	2.244	<5	1.7790	7	2	3	1.7798	50
6.095	2	0	1	6.088	<5	2.237	1	0	3	2.237	<5		0	4	2	1.7794	
5.264	0	1	1	5.250	20	2.224	9	1	2	2.225	<5	1.7652	14	2	1	1.7678	<5
4.750	6	0	0	4.753	10	2.216	2	0	3	2.217	<5		2	4	2	1.7657	
4.594	3	1	1	4.595	5	2.1672	0	1	3	2.1679	<5	1.7423	14	0	2	1.7427	25
4.199	0	2	0	4.192	90	2.1443	1	3	2	2.1443	<5	1.7297	8	2	3	1.7299	<5
3.878	6	0	1	3.883	<5		2	1	3	2.1433		1.7204	3	3	3	1.7210	5
3.663	7	1	0	3.664	10	2.1124	3	1	3	2.1137	5	1.6996	4	3	3	1.6995	<5
3.489	7	0	1	3.485	100	2.0964	0	4	0	2.0961	40	1.6828	0	0	4	1.6832	20
3.371	0	0	2	3.366	60		11	2	1	2.0937			13	2	2	1.6832	
3.147	6	2	0	3.144	8	2.0845	13	0	1	2.0856	5	1.6245	15	1	2	1.6240	5
3.108	1	1	2	3.105	8	2.0732	4	1	3	2.0741	<5	1.6087	14	2	2	1.6092	25
3.054	2	1	2	3.052	<5	2.0592	4	3	2	2.0587	<5		4	1	4	1.6077	
3.015	5	2	1	3.019	<5	2.0365	14	0	0	2.0368	30	1.5609	0	2	4	1.5620	20
2.950	8	1	1	2.949	10	1.9971	0	4	1	2.0014	<5		1	2	4	1.5597	
2.865	4	1	2	2.861	8		9	3	1	2.0012		1.4329	7	4	3	1.4339	30
2.849	10	0	0	2.851	8	1.9656	7	0	3	1.9657	30	1.3962	0	6	0	1.3974	20
	6	2	1	2.849		1.9507	14	0	1	1.9496	<5						
2.781	1	3	0	2.782	<5	1.9168	6	4	0	1.9179	<5						
2.747	6	0	2	2.747	5	1.8998	8	0	3	1.8992	5						
2.682	7	2	1	2.680	80	1.8667	13	2	1	1.8673	8						
2.627	0	2	2	2.625	50	1.8533	15	1	0	1.8540	8						
2.582	2	2	2	2.582	8		8	1	3	1.8522							
	0	3	1	2.581													
2.491	3	3	1	2.491	<5												
2.479	7	1	2	2.479	<5												
2.326	11	1	1	2.324	5												

given by $h(=7p)kl$, $p+l=2n$, and $k=2n$. This motive is also seen in the electron diffraction patterns, Fig. 1a & b.

3. Composition and Stability

Cordfunke and Loopstra (*l*) prepared a compound with a Sr/U ratio ≈ 0.25 , but some U₃O₈ appears always to be present in samples with this composition. A pseudo-subcell with $a' = 6.734$, $b' = 4.193$, and $c' = 4.065$ Å, $\beta = 90^\circ 16'$, was found. Although this subcell is closely related to α -U₃O₈, indexing of the whole pattern was not possible.

A careful study of samples with Sr/U ratios varying from 0.25 to 0.33 by X-ray and electron diffraction showed that at the composition Sr/U = 0.273 a phase-pure product was obtained. Since almost all uranium is present in the hexavalent state, the composition of this phase is Sr₃U₁₁O₃₆.

The enthalpy of solution of the compound was measured calorimetrically in a 5.0 M HCl solution. By combining the enthalpy of solution, $-(794.9 \pm 1.2)$ kJ · mole⁻¹, with the enthalpy of solution of SrCl₂, $-(34.19 \pm 0.49)$ kJ · mole⁻¹, and the enthalpy of formation of SrCl₂(s) (5), the enthalpy of formation of Sr₃U₁₁O₃₆ was calcu-

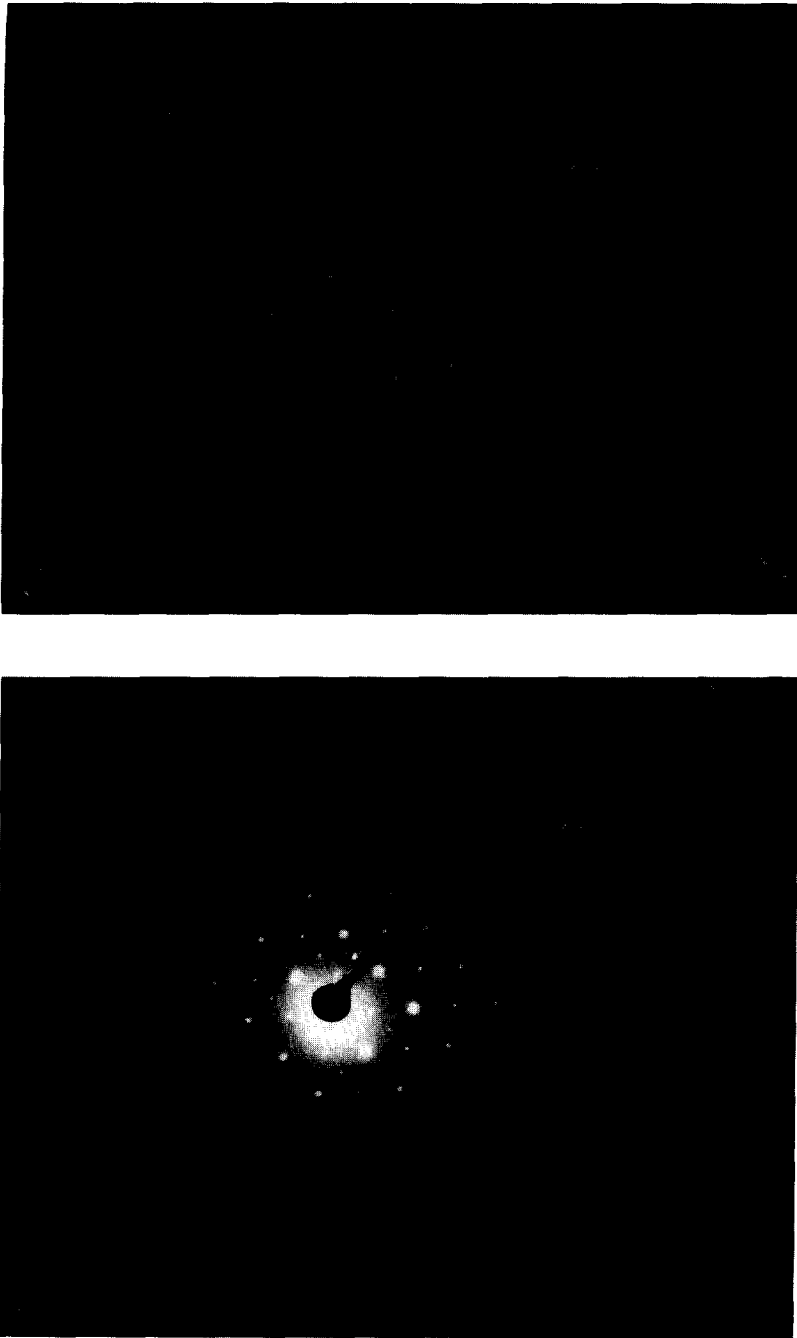


FIG. 1. (a) Electron diffraction pattern of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ taken with incident beam along [010], (b) Electron diffraction pattern of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ taken with incident beam along [100].

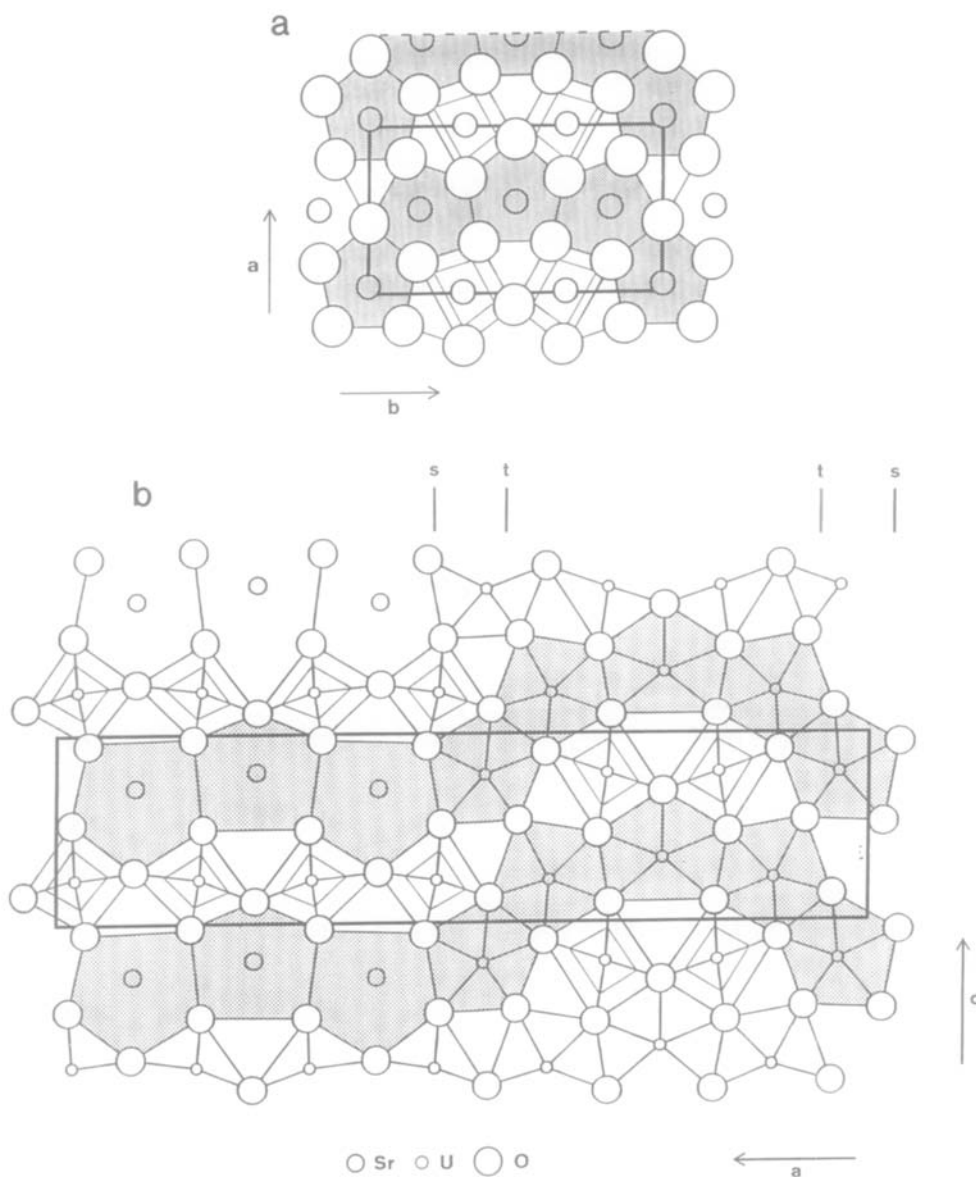


FIG. 2. (a) Section of $\alpha\text{-U}_3\text{O}_8$ at $z = 0$, after Ref. (8). (b) Section of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ at $y = \frac{1}{4}$.

lated to be $-(15,905.6 \pm 22.5) \text{ kJ} \cdot \text{mole}^{-1}$. When heated in air above 1130°C $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ decomposes into $\text{Sr}_2\text{U}_3\text{O}_{11}$ and U_3O_8 (1).

4. Structure Determination

The true unit cell of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ was determined by means of electron diffraction, us-

ing a Siemens Elmiscop 102 fitted with a double tilt and lift cartridge. All patterns could be interpreted with an orthorhombic unit cell with $a = 7c'$, $b = 2b'$, $c = a'$. Systematic absences indicate the space group $Pmmn$ (59). The unit cell under investigation contains 28 metal atoms leading to

TABLE II
FRACTIONAL COORDINATES OF $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ AT 298 K

Atom	Site	x	y	z
Sr1	2b	0.75	0.25	0.793(4)
Sr2	4f	0.5997(8)	0.25	0.707(3)
U1	2a	0.25	0.25	0.334(3)
U2	4f	0.3868(5)	0.25	0.224(3)
U3	4f	0.6805(6)	0.25	0.228(2)
U4	4f	0.3180(6)	0.25	0.785(2)
U5	4f	0.4676(5)	0.25	0.780(2)
U6	4f	0.5265(5)	0.25	0.228(2)
O1	4e	0.25	0.464(3)	0.311(3)
O2	8g	0.3839(4)	0.476(2)	0.263(3)
O3	8g	0.5344(5)	0.515(2)	0.214(2)
O4	8g	0.6810(5)	0.523(2)	0.226(3)
O5	4f	0.3144(8)	0.25	0.099(3)
O6	4f	0.4609(8)	0.25	0.132(3)
O7	4f	0.5987(7)	0.25	0.270(3)
O8	2b	0.75	0.25	0.111(4)
O9	2a	0.25	0.25	0.685(4)
O10	4f	0.3929(8)	0.25	0.898(3)
O11	4f	0.5409(9)	0.25	0.932(3)
O12	4f	0.6709(7)	0.25	0.963(3)
O13	4f	0.3287(9)	0.25	0.467(3)
O14	4f	0.4264(9)	0.25	0.538(4)
O15	4f	0.5220(7)	0.25	0.520(3)
O16	4f	0.6846(8)	0.25	0.492(3)

Note. $R_p = 3.87\%$; $R_{wp} = 5.09\%$.

the probable formula $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ with a Sr/U ratio of 0.273, assuming a formal valency of 6 for uranium.

Since no single crystals were available, Rietveld's method (6) for refinement of neutron powder diffraction data on the powder diffractometer at the Petten high flux reactor was used. A wavelength of 2.570(1) Å from the (111) plane of a copper monochromator was used with 30' collimation. The angular range $5^\circ < 2\theta < 154^\circ$ in steps of 0.1° was used. The collected data from 20 g of the compound were corrected for absorption (7), $\mu R = 0.098$. Preferred orientation was assumed to be absent.

The trial model was constructed from the structure elements of $\alpha\text{-U}_3\text{O}_8$ (8) ($a = 6.716(1)$, $b = 11.960(2)$, $c = 4.1469(5)$ Å, $C2mm$) and modified by the requirements of

the space group and by reducing the oxygen-to-metal ratio from 2.667 for U_3O_8 to 2.571 by combining the folded structure of $\alpha\text{-U}_3\text{O}_8$ with a linear part of this structure (Fig. 2). The distribution of Sr and U was derived from the X-ray and electron diffraction intensities of the $h00$ and $h02$ reflections, assuming the metal atoms form (close-) packed layers. In the refining of the neutron diffraction data the program DBW3.2S, version 8802, was used (9).

The final refinement was made using 423

TABLE III
ATOMIC DISTANCES AT 298 K OF $\text{Sr}_3\text{U}_{11}\text{O}_{36}$

Pentagonal bipyramids			Octahedrons		
Sr1			U3		
O1	2.49(2)	2 ×	O4	2.28(2)	2 ×
O8	2.14(3)		O7	2.35(3)	
O12	2.53(2)	2 ×	O8	2.13(2)	
O16	2.75(3)	2 ×	O12	1.80(3)	
			O16	1.78(3)	
Sr2			U4		
O2	2.35(2)	2 ×	O4	1.91(2)	2 ×
O7	2.94(3)		O5	2.12(3)	
O11	2.26(3)		O9	2.05(2)	
O12	2.67(3)		O10	2.26(3)	
O15	2.54(3)		O10	2.16(3)	
O16	2.82(3)				
U1			U6		
O1	1.80(2)	2 ×	O3	2.23(2)	2 ×
O5	2.42(3)	2 ×	O6	1.98(3)	
O9	2.36(4)		O7	2.08(3)	
O13	2.42(3)	2 ×	O11	2.03(3)	
			O15	1.97(3)	
U2					
O2	1.91(2)	2 ×			
O5	2.23(3)				
O6	2.20(3)				
O10	2.20(2)				
O13	2.33(3)				
O14	2.40(3)				
U5					
O3	1.97(2)	2 ×			
O6	2.38(3)				
O10	2.27(3)				
O11	2.33(3)				
O14	2.01(3)				
O15	2.33(3)				

reflections (the 63 variables include a scale factor, six background parameters, three half-width parameters defining the Gaussian peak shape, the counter zero error, an asymmetry parameter, the unit cell dimensions, the atomic position parameters, and an overall thermal parameter). The final coordinates are listed in Table II, the atomic distances in Table III.

5. Discussion

The structure of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ consists of layers with the metal atoms in octahedral (U3, U4, and U6) and pentagonal bipyramidal (Sr1, Sr2, U1, U2, and U5) coordination. The layers are connected by vertex sharing to give a three-dimensional structure as in $\alpha\text{-U}_3\text{O}_8$ (8). The structural relation with $\alpha\text{-U}_3\text{O}_8$ (Fig. 2a) is evident from the intersection of the unit cell at $y = \frac{1}{4}$ given in Fig. 2b, showing a layer of $\text{Sr}_3\text{U}_{11}\text{O}_{36}$.

The layer is a combination of the $\alpha\text{-U}_3\text{O}_8$ chain indicated by s—s in Fig. 2b together with the smaller linear motive of $\alpha\text{-U}_3\text{O}_8$ indicated by t—t. In this way a folded chain of eight edge-sharing pentagonal bipyramids connected by six octahedrons is formed. The folded chain gives a unit cell with seven polyhedra in [100]. The folding introduces a mirror plane; the other mirror plane is in the middle of the linear motive.

The strontium atoms replace the uranium atoms in the linear motive of $\alpha\text{-U}_3\text{O}_8$. Neighboring layers are related via inversion centra (at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in Fig. 2b), resulting in alternation of Sr1 and Sr2 with U1 and U2, respectively, in [010]. Moreover, U3 and U5 alternate with U4 and U6, respectively. The same structure is found in the compounds $M_3\text{U}_{11}\text{O}_{36}$, with $M = \text{Pb}, \text{Ca}, \text{and Cd}$ (10).

The $\text{SrO-}\text{UO}_3$ system is interesting in that it has no less than five uranates with uranium in the hexavalent state. Of these, $\text{Sr}_3\text{U}_{11}\text{O}_{36}$ and $\text{Sr}_2\text{U}_3\text{O}_{11}$ have structures which are closely related to U_3O_8 or $\alpha\text{-SrUO}_4$ (1), in which sixfold and sevenfold coordination of

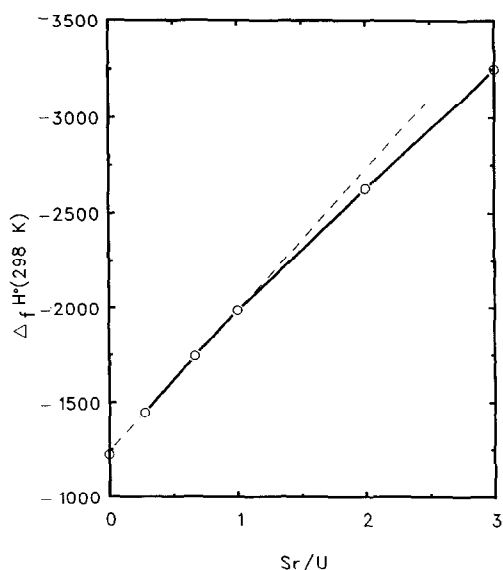


FIG. 3. The enthalpies of formation of strontium uranates as a function of the SrO/UO_3 ratio.

uranium by oxygen is found in the (pseudo-) hexagonal layers. In $\beta\text{-SrUO}_4$, Sr_2UO_5 , and Sr_3UO_6 a different coordination is found (3), uranium being 6-coordinated in (pseudo-) tetragonal layers. The difference in coordination is reflected in the enthalpies of formation of these uranates (11, 12), as is shown in Fig. 3.

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References

1. E. H. P. CORDFUNKE AND B. O. LOOPSTRA, *J. Inorg. Nucl. Chem.* **29**, 51 (1967).
2. W. H. ZACHARIASEN, *Acta Crystallogr.* **1**, 281 (1948).
3. B. O. LOOPSTRA AND H. M. RIETVELD, *Acta Crystallogr. B* **25**, 787 (1969).
4. E. H. P. CORDFUNKE, W. OUWELTJES, AND G. PRINS, *J. Chem. Thermodyn.* **7**, 1137 (1975).

5. E. H. P. CORDFUNKE, R. J. M. KONINGS, AND W. OUWELTJES, *J. Chem. Thermodyn.*, in press.
6. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
7. K. WEBER, *Acta Crystallogr.* **23**, 720 (1967).
8. B. O. LOOPSTRA, *Acta Crystallogr. B* **26**, 656 (1970).
9. WILES, SAKTHIVEL, AND YOUNG, School of Physics, Georgia Institute of Technology, Atlanta.
10. D. J. W. IJDO, to be published.
11. "Thermochemical Data for Reactor Materials and Fission Products" (E. H. P. Cordfunke and R. J. M. Konings, Eds.), North Holland, Amsterdam (1990).
12. E. H. P. CORDFUNKE AND W. OUWELTJES, *J. Chem. Thermodyn.*, in press.