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The crystal structures of Na_3ZrF_7 and Na_3HfF_7.

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Investigations of the binary systems NaF–UF_4, NaF-ZrF_4 (Barton *et al.*, 1958*a*, *b*) and NaF–HfF_4 (Thoma, 1958) undertaken at this laboratory disclosed the presence of compounds of the R_3MX_7 type in all three systems. In the system NaF–UF_4 two forms of Na_3UF_7 are present, an α- and β-form representing high and low temperature polymorphs respectively. The crystal structure of α-Na_3UF_7 determined from X-ray powder diffraction patterns was found to be the same structure previously determined by Zachariasen (1948) from a single crystal pattern. This structure has been reported to be body-centered tetragonal with the unit-cell dimensions

$$a_0 = 5{\cdot}458 \pm 0{\cdot}007,\ c_0 = 10{\cdot}917 \pm 0{\cdot}014\ \text{Å}$$
(Zachariasen, 1948).

This cell contains 2 molecules and has a calculated density of 4·49 g.cm.$^{-3}$.

The X-ray powder films taken of Na_3ZrF_7 and Na_3HfF_7 using a Norelco camera of 114·6 mm. diameter and Cu $K\alpha$ (λ = 1·5418 Å) radiation were next indexed and both found to best fit a body-centered tetragonal unit cell. Only one set of lattice parameters

$$a_0 = 5{\cdot}31 \pm 0{\cdot}02 \quad \text{and} \quad c_0 = 10{\cdot}50 \pm 0{\cdot}02\ \text{Å}$$

are reported because the calculated differences in lattice parameters for Na_3ZrF_7 and Na_3HfF_7 are within the limits of experimental errors. Assuming 2 molecules per unit cell the calculated densities are 3·28 g.cm.$^{-3}$ and 4·26 g.cm.$^{-3}$ for Na_3ZrF_7 and Na_3HfF_7 respectively.

Subsequent studies of the ternary system NaF–UF_4–ZrF_4 (Barton *et al.*, 1958*b*) revealed the existence of a continuous series of solid solution between α-Na_3UF_7 and Na_3ZrF_7 (Fig. 1) (Barton *et al.*, 1958*b*). The above observation of solid solution and a comparison of observed intensities for diffraction planes (Table 1) permitted the conclusion that Na_3ZrF_7 and Na_3HfF_7 are most probably isostructural with α-Na_3UF_7. Thus in accordance with Zachariasen's calculations (1948) for Na_3UF_7 the space group for Na_3ZrF_7 and Na_3HfF_7 is $I4/mmm$–D_{4h}^{17} with

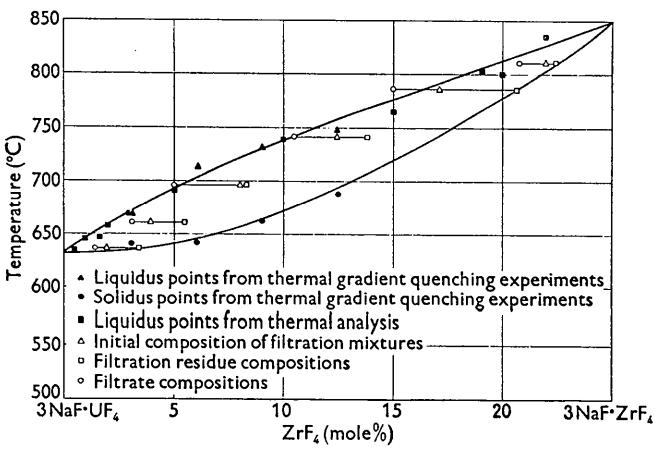

Fig. 1. The system 3 NaF.UF_4–3 NaF.ZrF_4.

Table 1. *Comparison of powder diffraction data for* α-Na_3UF_7, Na_3ZrF_7 *and* Na_3HfF_7

	α-Na_3UF_7		Na_3ZrF_7		Na_3HfF_7	
hkl	I_0	$\sin^2\theta$	I_0	$\sin^2\theta$	I_0	$\sin^2\theta$
002	*m*	0·0199	*m*	0·0213	*m*	0·0214
101	*s*	0·0250	*s*	0·0264	*s*	0·0264
110, 102	*m*	0·0400	*m*	0·0421	*m*	0·0419
112	*vs*	0·0597	*vs*	0·0630	*vs*	0·0630
103	*m*	0·0648	*m*	0·0693	*m*	0·0691
200	*m*	0·0800	*w*	0·0835	*w*	0·0834
004	—	—	*vw*	0·0863	*vw*	0·0862
202	*m*	0·0999	*m*⁻	0·1051	*m*⁻	0·1051
211	*s*	0·1050	*s*⁻	0·1098	*s*⁻	0·1098
114	*m*	0·1201	*m*	0·1276	*m*	0·1273
213	*w*	0·1450	*m*	0·1533	*m*	0·1534
220, 204	*s*	0·1599	*s*	0·1679	*s*	0·1685
222	*w*	0·1800	*w*	0·1886	*w*	0·1884
301	*m*⁻	0·1849	—	—	—	—
310, 302	*m*⁻	0·2001	—	—	—	—
312	*m*	0·2201	*m*	0·2296	*m*	0·2302
303	*w*	0·2248	*w*	0·2365	*w*	0·2362
304	*w*	0·2600	—	—	—	—
321	*w*	0·2650	*m*	0·2767	*m*	0·2771
314	*w*	0·2795	*w*	0·2939	*w*	0·2940

the atoms in the following positions:

2 Zr or Hf	in 2 (*a*)
2 Na_I	in 2 (*b*)
4 Na_{II}	in 4 (*d*)
14 F	in 16(*m*)

The interionic distances for Na–7 F, Zr–7 F, and Hf–7 F were calculated to be 2·28 Å assuming the values of $x = \frac{1}{4}$ and $z = \frac{1}{8}$ to be very close to the true positions for the fluorine atoms in both the Na_3ZrF_7 and Na_3HfF_7 structures.

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