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Crystal Structure Studies of the SystemsNaF-UF<sub>4</sub>, NaF-ThF<sub>4</sub> and NaF-LaF<sub>3</sub>

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ABSTRACT**CLASSIFICATION CANCELLED**

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Declassification Officer By P. M. B.

In the NaF-UF<sub>4</sub> system the following intermediate phases have been found: NaUF<sub>5</sub>,  $\gamma$ -Na<sub>2</sub>UF<sub>6</sub>,  $\beta$ -Na<sub>2</sub>UF<sub>6</sub>,  $\gamma$ -Na<sub>2</sub>UF<sub>6</sub> and Na<sub>3</sub>UF<sub>7</sub>.

NaLaF<sub>4</sub> is the only intermediate phase observed in the system NaF-LaF<sub>3</sub>.

In the course of an incomplete study of the system NaF-ThF<sub>4</sub> the phases NaTh<sub>2</sub>F<sub>9</sub>,  $\beta$ -Na<sub>2</sub>ThF<sub>6</sub>,  $\gamma$ -Na<sub>2</sub>ThF<sub>6</sub> and Na<sub>4</sub>ThF<sub>8</sub> have been observed.

Crystal structure data are given for all of the phases.

INTRODUCTION

This paper gives the results of crystal structure investigations of the phase systems NaF-UF<sub>4</sub> and NaF-LaF<sub>3</sub>. Some results of an incomplete study of the system NaF-ThF<sub>4</sub> are also given.

All chemical preparations were made by the writer by melting together the component fluorides in a platinum crucible in the open air. In order to minimize hydrolysis and sublimation the heating was done so rapidly that complete melting occurred within one minute. The melts were either quenched or left by themselves to cool.

The phase composition of the various samples and the chemical formulas of the individual phases were determined through interpretation of the x-ray diffraction patterns. Thermal analysis data were not taken.

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### 1. The System NaF-UF<sub>6</sub>

The probable existence of NaUF<sub>5</sub> is reported in the pre-war literature.\*

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\*Gmelins Handbuch der Anorganischen Chemie

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During the war professor C. A. Kraus\*

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\*C. A. Kraus, Report [A] M-291

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made a study of the phase diagram NaF-UF<sub>6</sub> using the method of thermal analysis. The existence of the compound NaUF<sub>5</sub> was confirmed. However, none of the four additional phases found by the present writer was observed.

Table 1 shows the chemical composition and the phase composition of the various melts which were examined. Several meltings were carried out for each chemical composition. Since the rate of cooling was not controlled, the phase composition at a given chemical composition sometimes varied from one preparation to the next. This was particularly true of samples with 33% UF<sub>6</sub>.

There are five intermediate phases in the NaF-UF<sub>6</sub> system. These are: NaUF<sub>5</sub>,  $\alpha$ -Na<sub>2</sub>UF<sub>6</sub>,  $\beta$ -Na<sub>2</sub>UF<sub>6</sub>,  $\gamma$ -Na<sub>2</sub>UF<sub>6</sub> and Na<sub>3</sub>UF<sub>7</sub>. Two of these phases, namely  $\beta$ -Na<sub>2</sub>UF<sub>6</sub> and Na<sub>3</sub>UF<sub>7</sub>, do not have sharply defined chemical formulas. This conclusion was reached from the detailed interpretation of their x-ray diffraction patterns and the conclusion is confirmed by the wide homogeneity ranges observed for these two phases.

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In the following the crystal structure of the individual phases will be briefly discussed. Detailed accounts of the crystal structure determinations may later appear elsewhere.

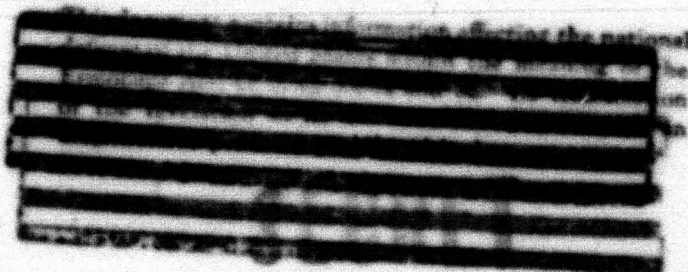
TABLE 1. Phases in the System NaF-UF<sub>4</sub>

Atom % UF <sub>4</sub>	Phases Present
67	UF <sub>4</sub> + NaUF <sub>5</sub>
50	NaUF <sub>5</sub>
40	a. $\alpha$ -Na <sub>2</sub> UF <sub>6</sub> b. $\alpha$ -Na <sub>2</sub> UF <sub>6</sub> + trace NaUF <sub>5</sub>
36	$\alpha$ -Na <sub>2</sub> UF <sub>6</sub>
33	a. $\alpha$ -Na <sub>2</sub> UF <sub>6</sub> + $\beta$ -Na <sub>2</sub> UF <sub>6</sub> b. $\beta$ -Na <sub>2</sub> UF <sub>6</sub> c. $\beta$ -Na <sub>2</sub> UF <sub>6</sub> + $\gamma$ -Na <sub>2</sub> UF <sub>6</sub>
31	$\gamma$ -Na <sub>2</sub> UF <sub>6</sub>
29	Na <sub>3</sub> UF <sub>7</sub>
27	Na <sub>3</sub> UF <sub>7</sub>
25	Na <sub>3</sub> UF <sub>7</sub>
20	Na <sub>3</sub> UF <sub>7</sub> + NaF

NaUF<sub>5</sub>  
NaUF<sub>5</sub> is rhombohedral. The lattice dimensions are:

$$a = 9.08 \pm 0.01 \text{ \AA}, \quad \alpha = 107^\circ 56'.$$

The unit cell contains six molecules NaUF<sub>5</sub> and the calculated density is  $\rho = 5.81$ .



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The space group is  $R\bar{3} (C_{3i}^2)$ . One set of six sodium atoms, one set of six uranium atoms and five sets of six fluorine atoms are in positions  $\frac{1}{2} (xyz)(y\bar{x}z)(x\bar{y}z)$ . The parameters for the sodium and uranium atoms are:

	$x$	$y$	$z$
Na	$6/13$	$2/13$	$5/13$
U	$3/13$	$1/13$	$9/13$

The sodium and uranium atoms are arranged in a face-centered pseudo-cubic lattice in which every thirteenth site is vacant. This pseudo-cell is a rhombohedron with a volume  $4/13$  that of the true cell and it has dimensions  $a = 5.72\text{\AA}$  and  $\alpha = 90^\circ 51'$ .

The structure of  $\text{NaUF}_5$  is closely related to that of fluorite.

The compounds  $\text{KUF}_5$ ,  $\text{KThF}_5$ ,  $\text{KCeF}_5$  are isomorphous.

#### $\alpha\text{-Na}_2\text{UF}_6$

The chemical formula of this phase should be written as:



The parameter  $x$  ranges from 1.33 (corresponding to  $\text{Na}_2\text{UF}_6$ ) to about 1.60.

The phase is cubic face-centered with a lattice constant which varies somewhat with the parameter  $x$ . The values of this lattice constant and the calculated density are:

$x$	$a$	$\rho$
1.33	$5.565 \pm 0.005\text{\AA}$	5.08
1.45	$5.578 \pm 0.005$	5.35
1.60	$5.602 \pm 0.001$	5.66

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In the cell are four sodium plus uranium atoms and 8.0 - 8.8 fluorine atoms. The uranium and sodium atoms are distributed at random over the sites  $(000)(\frac{1}{2}\frac{1}{2}0)(\frac{1}{2}0\frac{1}{2})(0\frac{1}{2}\frac{1}{2})$ . Eight fluorine atoms are at  $\pm (\frac{1}{2}\frac{1}{2}\frac{1}{2})(\frac{1}{2} \frac{3}{4} \frac{3}{4})(\frac{3}{4} \frac{1}{2} \frac{3}{4})(\frac{3}{4} \frac{3}{4} \frac{1}{2})$ . The additional fluorine atoms are distributed at random over the sites  $(00\frac{1}{2})(\frac{1}{2}00)(0\frac{1}{2}0)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ .

For  $x = 1.33$  the structure is that of fluorite. For larger values of  $x$  the structure is analogous to that of mixed crystals  $\text{CaF}_2\text{-ThF}_3$ ,  $\text{SrF}_2\text{-LaF}_3$ .

For  $x = 1.33$  the metal to fluorine distance is 2.42A.

$\text{K}_2\text{UF}_6$ ,  $\text{K}_2\text{ThF}_6$  and  $\text{KLaF}_4$  have isomorphous forms.

#### $\beta\text{-Na}_2\text{UF}_6$

When melts of composition  $\text{Na}_2\text{UF}_6$  are quenched, the resulting samples consist of  $\beta\text{-Na}_2\text{UF}_6$  and  $\gamma\text{-Na}_2\text{UF}_6$ , occasionally with small amounts of  $\alpha\text{-Na}_2\text{UF}_6$ . Samples with as much as 60% of  $\beta\text{-Na}_2\text{UF}_6$  have been made.

$\beta\text{-Na}_2\text{UF}_6$  is hexagonal with one molecule per unit cell. The lattice dimensions and the calculated density are:

$$a_1 = 5.94 \pm 0.01\text{A}, \quad a_3 = 3.74 \pm 0.01\text{A}, \quad \rho = 5.74.$$

The probable structure is based upon the space group  $\text{C6h}2\text{m} (\text{D}_{3h}^3)$ .

The atomic positions are:

- 1 U in (000)
- 2 Na in  $\pm (\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$
- 3 F<sub>I</sub> in  $(x_1 00)(0x_1 0)(x_1 x_1 0)$
- 3 F<sub>II</sub> in  $(x_2 0\frac{1}{2})(0x_2 \frac{1}{2})(x_2 x_2 \frac{1}{2})$

with  $x_1 = -0.42$  and  $x_2 = 0.225$ .

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AA uranium atom is linked to three  $F_I$  atoms at 2.49A and to six  $F_{II}$  atoms at 2.30A. A sodium atom is bonded to six  $F_I$  atoms at 2.56A and to three  $F_{II}$  atoms at 2.30A.

There is some intermixture of uranium and sodium atoms.

The double fluorides  $K_2UF_6$ ,  $Na_2ThF_6$ ,  $K_2ThF_6$ ,  $NaLaF_4$  and  $KLaF_4$  all have forms isomorphous with  $\beta$ - $Na_2UF_6$ .

#### $\beta$ - $Na_2UF_6$

This phase is obtained in pure form if melts of composition  $Na_2UF_6$  are cooled slowly.

The diffraction patterns can be interpreted in accordance with orthorhombic symmetry with periods.

$$a_1 = 5.56 \pm 0.02A, a_2 = 4.01 \pm 0.01A, a_3 = 11.64 \pm 0.04A.$$

The unit cell contains two molecules giving a calculated density of  $\rho = 5.06$ .

The two uranium atoms are in a body-centered arrangement: (000) ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ).

No isomorphous compound is known.

#### $Na_3UF_7$

The chemical formula of this phase is to be written as



with the parameter  $x$  in the range  $0 \leq x \leq 0.30$ .

The phase is tetragonal body-centered, the lattice periods varying with the parameter  $x$ . For  $x = 0$  and  $x = 0.29$  the lattice constants and

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the calculated density are:

x	$a_1$	$a_3$	$\rho$
0	$5.448 \pm 0.007\text{\AA}$	$10.896 \pm 0.014\text{\AA}$	4.49
0.29	$5.503 \pm 0.005$	$11.006 \pm 0.010$	4.85

The space group is  $I4/mmm (D_{4h}^{17})$ . The atomic positions are:

$(000)(\frac{1}{2}\frac{1}{2}\frac{1}{2}) +$

$2U$  in  $(000)$   
 $(6-x) Na+xU$  in  $(00\frac{1}{2})$  and  $(0\frac{1}{2}\frac{1}{2})(\frac{1}{2}0\frac{1}{2})$   
 $(14+3x)F$  in  $\frac{1}{2}(uuv)(\bar{u}\bar{u}v)(u\bar{u}v)(\bar{u}uv)$   
 with  $u = \frac{1}{4}$  and  $v = 1/8$ .

Each metal atom is linked to an average of 7.0 - 7.4 fluorine atoms with  $Na-F = U-F = 2.36 - 2.38\text{\AA}$ .

The unit cell and structure of  $Na_3UF_7$  correspond to two fluorite unit cells put one on top of the other with uranium atoms occupying one fourth and sodium atoms occupying three fourths of the metal sites and with two of the sixteen fluorine atoms removed at random.

## 2. The System NaF-LaF<sub>3</sub>

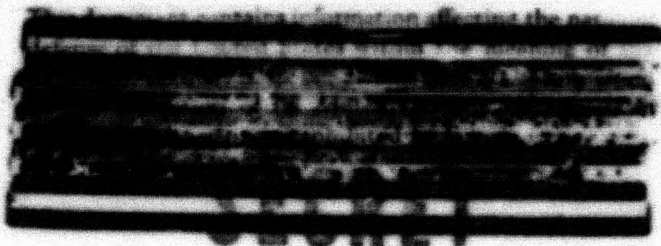
In the system  $NaF-LaF_3$  there is only one intermediate phase and this is the compound  $NaLaF_4$ .

$NaLaF_4$

$NaLaF_4$  is hexagonal. The lattice dimensions are:

$$a_1 = 6.167 \pm 0.001\text{\AA}, \quad a_3 = 3.819 \pm 0.002\text{\AA}.$$

The structure is disordered with  $3/2$  molecules per unit cell. The calculated density is  $\rho = 4.68$ .



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The structure is that of  $\beta$ - $\text{Na}_2\text{UF}_6$  described in the preceding section. The atomic positions are:

1 La	in	(000)
0.5La + 1.5 Na	in	$\pm(1/3 \ 2/3 \ 1/2)$
$\text{F}_I$	in	$(x_1 00)(0x_1 0)(\bar{x}_1 \bar{x}_1 0)$
$\text{F}_{II}$	in	$(x_2 0 \frac{1}{2})(0x_2 \frac{1}{2})(\bar{x}_2 \bar{x}_2 \frac{1}{2})$

with  $x_1 = -0.42$ ,  $x_2 = 0.25$

The average metal to fluorine distance is 2.53A.

There are isomorphous forms of  $\text{KLaF}_4$ ,  $\text{Na}_2\text{UF}_6$ ,  $\text{K}_2\text{UF}_6$ ,  $\text{Na}_2\text{ThF}_6$  and  $\text{K}_2\text{ThF}_6$ .

### 3. The System NaF-ThF<sub>4</sub>

The writer has not completed a systematic study of the system NaF-ThF<sub>4</sub>. There are, however, some results which can be given.

#### NaTh<sub>2</sub>F<sub>9</sub>

NaTh<sub>2</sub>F<sub>9</sub> is cubic body-centered with four molecules per unit cell and a lattice constant

$$a = 8.705 \pm 0.001\text{A}.$$

The calculated density is  $\rho = 6.58$ .

The space group is  $\overline{\text{Ic}}3\text{m} (\text{T}_d^3)$  and the atomic positions are:  
 $(000)(\frac{1}{2}\frac{1}{2}\frac{1}{2})+$

4Na	in	$(\frac{1}{2}00)(0\frac{1}{2}0)(00\frac{1}{2})$
8Th	in	$(xxx)(\bar{x}\bar{x}\bar{x})(\bar{x}x\bar{x})(x\bar{x}x)$

$$\text{with } x = 0.187 \pm 0.004.$$

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$12F_I$  in  $\pm(x00)(0x0)(00x)$

with  $x = 0.235$ .

$24F_{II}$  in  $(xxx)(xx\bar{x})(\bar{x}xx)(\bar{x}xx)(\bar{x}xx)(\bar{x}xx)$   
 $(\bar{x}xx)(\bar{x}xx)(\bar{x}xx)(\bar{x}xx)(\bar{x}xx)(\bar{x}xx)$

with  $x = 0.19$ ,  $\bar{x} = 0.46$ .

There are nine fluorine atoms about each thorium atom and six fluorine atoms about each sodium atom. The interatomic distances are

$Th-F = 2.40\text{\AA}$ ,  $Na-F = 2.34\text{\AA}$ .

The structure is essentially that of  $U_2F_9$  with sodium atoms fitting into holes of the latter structure.

No phase intermediate in composition between  $ThF_4$  and  $NaTh_2F_9$  has been found. There are no data for the range 35-65 mole percent  $ThF_4$  in the system  $NaF-ThF_4$ . However, three intermediate phases have been observed in the range 0-33 mole percent  $ThF_4$ .

#### $\beta-Na_2ThF_6$

$\beta-Na_2ThF_6$  is occasionally observed when melts of composition  $Na_2ThF_6$  are quenched.  $\beta-Na_2ThF_6$  is hexagonal and isomorphous with  $\beta-Na_2UF_6$  described above.

The hexagonal unit cell containing one molecule has dimensions

$$a_1 = 5.99 \pm 0.02\text{\AA}, \quad a_3 = 3.81 \pm 0.01\text{\AA}.$$

The calculated density is  $\rho = 5.46$ .

The space group and atomic positions are the same as given for  $\beta-Na_2UF_6$  in the preceding section.

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$\gamma$ - $\text{Na}_2\text{ThF}_6$

Melts of composition  $\text{Na}_2\text{ThF}_6$  normally yield the  $\gamma$ -form.

$\gamma$ - $\text{Na}_2\text{ThF}_6$  is hexagonal with two molecules per unit cell. The lattice dimensions and the calculated density are:

$$a_1 = 6.14 \pm 0.01\text{\AA}, \quad a_2 = 7.36 \pm 0.02\text{\AA}, \quad \rho = 5.37.$$

$\text{Na}_4\text{ThF}_8$

$\text{Na}_4\text{ThF}_8$  is cubic body-centered with twelve molecules per unit cell.

The lattice constant is

$$a = 12.706 \pm 0.002\text{\AA}$$

and the calculated density is  $\rho = 4.59$ .

The positions of the thorium atoms are:  $(000)(\frac{1}{2}\frac{1}{2}\frac{1}{2}) +$

$$12 \text{ Th in } \frac{1}{2}(u00)(0u0)(00u)$$

$$\text{with } u = 0.333.$$

This paper is based upon the report CC-3401, January 1946.

Miss Anne Flettinger took all diffraction patterns. Mr. S. C. Koehler measured some of the patterns.

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