

this effect. But the low susceptibilities and the ubiquitous trace of ferro-magnetic impurity combined to make it difficult to examine this region. We can say, however, that certainly no more than 10% of the copper atoms can be considered as atomically dispersed.

It was hoped that the multiple impregnation catalyst would lead to higher, more readily measurable, susceptibilities and to greater dispersion, but such was not the case. It was also hoped that dispersed silver might yield a more readily observable result. The reason for the choice of silver was that the oxidized form is here diamagnetic. But certainly no large fraction of the supported reduced silver became paramagnetic.

Our conclusion from all these negative results is that the tendency for aggregation is so strong that even when the support must be, of necessity, mostly unoccupied surface, still the supported atoms tend to cling together. It will be noted that the larger size of the reduced atoms may lead to greater exchange interaction as compared with the oxidized forms, even though the ion centers do not appreciably move during the oxidation-reduction cycle.

When reduced supported copper is reoxidized the susceptibility goes as high as or higher than in the

original oxidized sample. This shows that no aggregation into crystallites occurs during the oxidation-reduction cycle. In fact the slight increase of susceptibility shown in Fig. 2 may be due to three-dimensional solution of cupric ions in the alumina.

The results on catalytic activity support in a general way this picture of the active surface. The more highly dispersed copper would normally be expected to show greater activity, and such is the case. It is somewhat surprising that no change of activity occurs in the anomalous 11% concentration region. This result must mean that the mere aggregation into definite cupric oxide crystallites has no effect on the activity. There is, of course, the possibility that in the *reduced* form there is no such obvious structural change occurring in this concentration region.

Summary

Susceptibility isotherms are given for copper oxide supported on γ -alumina, for the reduced catalyst, and for related systems. The magnetic data are related to X-ray diffraction studies, and to catalytic activity results on the dehydrogenation of isopropyl alcohol.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY AND DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO]

Double Fluorides of Potassium or Sodium with Uranium, Thorium or Lanthanum

BY W. H. ZACHARIASEN

This paper summarizes the results of studies of the systems KF-UF_4 , KF-ThF_4 , KF-LaF_3 , NaF-UF_4 , NaF-ThF_4 and NaF-LaF_3 . The investigations were carried out within the Manhattan Project during 1945.

The systems were studied by means of the X-ray diffraction method. The systematic survey extends over the entire composition range except for a gap between 35 and 65 mole per cent. ThF_4 in the NaF-ThF_4 system.

1. **The Chemical Preparations.**—All chemical preparations were made by the writer. The systematic studies were carried out by determining the phase compositions of solidified melts by means of X-ray diffraction patterns. Thermal analysis data were not taken, however. In the systems involving potassium fluoride precipitates from solutions were also examined.

The dry method preparations were made by melting together the component fluorides in a platinum crucible. The uranium tetrafluoride was from the Harshaw Chemical Company. Dr. Ralph Livingston had prepared the thorium fluoride by treating $\text{ThF}_4 \cdot x\text{H}_2\text{O}$ with HF. The Los Alamos Laboratory supplied the lanthanum fluoride.

The wet way preparations were obtained in the following ways:

1. Solutions of potassium chloride and uranium tetrachloride, of potassium nitrate and thorium or lanthanum nitrate were precipitated with hydrofluoric acid.

2. Solutions of uranium tetrachloride, of thorium nitrate or of lanthanum nitrate were precipitated with a potassium fluoride solution.

3. Solutions of $\text{K}_2\text{UO}_2\text{F}_6$ or of uranyl nitrate and potassium fluoride were reduced with formic acid and direct sunlight whereby precipitates were formed.

2. **The Identification of the Phases.**—The chemical identity of the various phases was deduced through interpretation of the X-ray diffraction patterns. This unorthodox method of analysis had to be used because the chemical analysts were busy with more important work. Direct chemical analyses of a few single phase preparations were, however, made. These direct analyses were rather unsatisfactory because the alkali content was not determined and because of the customary difficulty in obtaining reliable results for the fluorine percentage.

Because the method is unknown to most chem-

ists it may be useful to discuss in some detail how the chemical formulas of the various phases were determined from the X-ray data.

The method presupposes that the lattice dimensions of the various phases can be deduced from the X-ray diffraction patterns. The observed diffraction intensities can with good approximation be attributed to the heavy atoms since the scattering powers of potassium, sodium and fluorine are small compared to those of uranium, thorium and lanthanum. A small number of degrees of freedom being involved it may accordingly be assumed that intensity considerations have led to a determination of the number and positions of the heavy atoms within the unit cell. The volume of the unit cell, V , and the number of heavy atoms within it, N_x , may thus be regarded as accurately known experimental quantities.

The volume of the unit cell for fluorides of the heavy elements under consideration can with good approximation be attributed to the fluorine atoms alone with the heavy metal atoms fitting into the interstices between the anions. The volume requirement of a fluorine atom may be set at $V_F = 18 \text{ \AA}^3$ as shown by the experimental values of Table I.

TABLE I
VOLUME REQUIREMENT OF A FLUORINE ATOM

Com- pound	UF ₂	UF ₄	U ₂ F ₆	α-UF ₆	β-UF ₆	UF ₆	LaF ₃
V _F	18.1	19.4	16.9	19.0	17.0	19.3	18.2

The mean values for the volume requirement of a sodium or potassium atom as obtained from a number of known crystal structures are $V_K = 21 \text{ \AA}^3$ and $V_{Na} = 7 \text{ \AA}^3$.

For the volume of the unit cell we have

$$V = N_A V_A + N_F V_F$$

where N_A and N_F are the number of alkali atoms and the number of fluorine atoms per unit cell, and where V_A is the volume requirement of an alkali atom. The numbers N_A , N_X and N_F are not independent since the valences must be balanced. Making use of this fact it becomes possible to determine the unknown quantities N_A and N_F in terms of the experimentally known quantities V , V_F , V_A and N_X . The result is

I. Systems AF-XF₄

$$N_A = \frac{V - 4N_X V_F}{V_A + V_F} \quad N_F = \frac{V + 4N_X V_A}{V_A + V_F} \quad (2a)$$

II. Systems AF-XF₆

$$N_A = \frac{V - 3N_X V_F}{V_A + V_F} \quad N_F = \frac{V + 3N_X V_A}{V_A + V_F} \quad (2b)$$

Since the writer succeeded in determining the lattice dimensions and the number and positions of the heavy atoms in the unit cell for all the observed phases through interpretation of the X-ray diffraction patterns, the chemical formulas of all the compounds could be determined in this novel manner. The results of this method of analysis

for the KF-UF₄ and NaF-ThF₄ systems are shown in Tables II and III for purposes of illustration.

TABLE II

IDENTIFICATION OF THE PHASES IN THE KF-UF₄ SYSTEM

Phase no.	V	N _U	N _K	N _F	Deduced formula
1	951 Å ³	12	2.2 ≈ 2	50.2 ≈ 50	KU ₂ F ₂₃
2	497	6	1.7 ≈ 2	25.7 ≈ 26	KU ₂ F ₁₃
3	697	8	3.1 ≈ 4	35.1 ≈ 36	KUF ₄
4	684	6	6.5 ≈ 6	30.5 ≈ 30	KUF ₃
5	209	1.6 ≈ 4/3	2.4 ≈ 8/3	8.8 ≈ 8	α-K ₂ UF ₆
6	139	1	1.7 ≈ 2	5.7 ≈ 6	β ₁ -K ₂ UF ₆
7	149	1	2.0 ≈ 2	6.0 ≈ 6	β ₂ -K ₂ UF ₆
8	781	4	12.6 ≈ 12	28.6 ≈ 28	α-K ₂ UF ₇
9	1558	8	25.2 ≈ 24	57.2 ≈ 56	α'-K ₂ UF ₇

TABLE III

IDENTIFICATION OF THE PHASES IN THE NaF-ThF₄ SYSTEM

Phase no.	V	N _{Th}	N _{Na}	N _F	Deduced formula
1	660 Å ³	8	3.4 ≈ 4	35.4 ≈ 36	NaTh ₂ F ₉
2	119	1	1.9 ≈ 2	5.9 ≈ 6	β ₂ -Na ₂ ThF ₆
3	241	2	3.9 ≈ 4	11.9 ≈ 12	δ-Na ₂ ThF ₆
4	2054	12	47.6 ≈ 48	95.6 ≈ 96	Na ₄ ThF ₈

The results from eqs. (2) should correspond to rational stoichiometric ratios and should give values N_K and N_F which are compatible with the observed space group symmetry. As a further check one knows, of course, the gross composition of the melts from which the phases were prepared.

N_X assumes fractional values for the α-phase compounds A₂XF₆ and for the β-phase compounds AXF₄. These phases have disordered crystal structures involving A-atoms and X-atoms in structurally equivalent positions. In these instances $N_A + N_X$, rather than N_X , is experimentally determined from the intensity calculations. Thus $N_A + N_X = 4$ for α-A₂XF₆ and $N_A + N_X = 3$ for β-AXF₄.

When the A-atoms and X-atoms are regarded as structurally equivalent the formulas for α-A₂XF₆ and β-AXF₄ may be written as YF₂ where Y repre-

TABLE IV
RESULTS OF CHEMICAL ANALYSES

Compound	Theoretical	Experimental	
		Direct method	X-ray method
KU ₂ F ₉	U 69.5%	69.6%	70.7%
	F 24.9	23.4	24.8
	K 5.6	..	4.5
KTh ₂ F ₉	Th 68.8	67.0	68.7
	F 25.4	22.0	25.4
	K 5.8	..	5.9
α-K ₂ UF ₆	U 55.3	55.0	54.2
	F 26.5	26.5	26.5
	K 18.2	..	19.3
β ₁ -K ₂ UF ₆	U 55.3	59.9	57.7
	F 26.5	24.9	26.2
	K 18.2	..	16.1
β ₁ -KLaF ₄	La 54.6	52.6	54.7
	F 29.9	26.7	29.9
	K 15.5	..	15.4

sents the A-atoms as well as the X-atoms. Thus, the α - A_2XF_6 and the β - AXF_4 phases may be regarded as pseudo-difluorides, and the unit cell will contain an integral number of formula weights YF_2 . The unit cell of α - A_2XF_6 contains four molecules YF_2 and that of β - AXF_4 three molecules.

The method of analysis is remarkably accurate. This is demonstrated in Table IV where the results of this method are compared with those of the orthodox, direct method of chemical analysis for some of the phases. C. Carter and B. Holt carried out the conventional analyses.

3. The Phase Composition of the Preparations.—Tables V–X show the phase compositions of the preparations made from melts as determined by analysis of the X-ray diffraction patterns. It is seen that the two lanthanum systems are very simple ones while the uranium and thorium systems are exceptionally complex.

TABLE V

PHASE COMPOSITION OF MELTS IN THE SYSTEM KF-UF ₆			
Mole % UF ₆	Major	Phases present Minor	Trace
89	KU ₂ F ₂₃ + UF ₆		
86	KU ₂ F ₂₃	KU ₂ F ₉ + UF ₆	
83	KU ₂ F ₂₃	KU ₂ F ₉	UF ₆
80	KU ₂ F ₉ + KU ₂ F ₂₃		UF ₆ + KU ₂ F ₁₉
75	KU ₂ F ₉ + KU ₂ F ₂₃		KU ₂ F ₁₉ + UF ₆
67	KU ₂ F ₉	KU ₂ F ₂₃ + KU ₂ F ₁₉ + KUF ₅	
60	KU ₂ F ₉ + UF ₆		
50	KUF ₅		
45	KUF ₅	β_1 -K ₂ UF ₆	
40	KUF ₅ + β_1 -K ₂ UF ₆		
36	β_1 -K ₂ UF ₆	α -K ₂ UF ₆	
33 (a) ^a	β_1 -K ₂ UF ₆		
(b)	β_1 -K ₂ UF ₆	α -K ₂ UF ₆	
(c)	β_1 '-K ₂ UF ₆ ^b		
(d)	β_1 -K ₂ UF ₆		
29	β_1 -K ₂ UF ₆ + α -K ₂ UF ₆		
25 (a)	α '-K ₂ UF ₆		KF
(b)	α -K ₂ UF ₆		
22	α -K ₂ UF ₆		
20	α -K ₂ UF ₆		KF
17	α -K ₂ UF ₆	KF	
14	α -K ₂ UF ₆	KF	

^a Symbols (a), (b), (c), (d) are used to indicate different rates of cooling, a indicating the lowest rate. ^b β_1 ' - A_2XF_6 is a disordered form of β_1 - A_2XF_6 involving isomorphous replacement between A-atoms and X-atoms.

TABLE VI

PHASE COMPOSITION OF MELTS IN THE KF-ThF ₄ SYSTEM			
Mole % ThF ₄	Major	Phases present Minor	Minor
86	KTh ₂ F ₂₅		ThF ₄ + KTh ₂ F ₉
75	KTh ₂ F ₉ + KTh ₂ F ₂₅		
67	KTh ₂ F ₉		KThF ₅ + KTh ₂ F ₂₅
50	KThF ₅		
40	KThF ₅ + β_1 -K ₂ ThF ₆		
33 (a) ^a	β_1 -K ₂ ThF ₆		
(b)	β_1 -K ₂ ThF ₆	α -K ₂ ThF ₆	
(c)	β_1 '-K ₂ ThF ₆		
29	β_1 -K ₂ ThF ₆		
25	β_1 -K ₂ ThF ₆		K ₂ ThF ₆
20	K ₂ ThF ₆		
17	K ₂ ThF ₆		

TABLE VII

PHASE COMPOSITION OF MELTS IN THE KF-LaF ₃ SYSTEM			
Mole % LaF ₃	Major	Phases present Minor	Minor
67	LaF ₃ + α -KLaF ₄		β_1 -KLaF ₄
58	α -KLaF ₄		LaF ₃ + β_1 -KLaF ₄
50 (a) ^a	β_1 -KLaF ₄		
(b)	β_1 -KLaF ₄		α -KLaF ₄
33	β_1 -KLaF ₄ + KF		
25	β_1 -KLaF ₄ + KF		

TABLE VIII

PHASE COMPOSITION OF MELTS IN THE NaF-UF ₆ SYSTEM			
Mole % UF ₆	Major	Phases present Minor	Minor
67	NaUF ₆ + UF ₆		
50	NaUF ₆		
40	α -Na ₂ UF ₆		
36	α -Na ₂ UF ₆		
33 (a) ^a	γ -Na ₂ UF ₆		
(b)	γ -Na ₂ UF ₆		β_2 -Na ₂ UF ₆ + α -Na ₂ UF ₆
(c)	β_2 -Na ₂ UF ₆ + α -Na ₂ UF ₆ + γ -Na ₂ UF ₆		
31	γ -Na ₂ UF ₆		
29	Na ₃ UF ₇		
27	Na ₃ UF ₇		
25	Na ₃ UF ₇		
20	Na ₃ UF ₇		NaF

TABLE IX

PHASE COMPOSITION OF MELTS IN THE NaF-ThF ₄ SYSTEM			
Mole % ThF ₄	Major	Phases present Minor	Minor
67	NaTh ₂ F ₉		
33–67	Not investigated ^b		
33 (a) ^a	δ -Na ₂ ThF ₆		
(b)	β_2 -Na ₂ ThF ₆		
29	δ -Na ₂ ThF ₆		Na ₄ ThF ₈
25	Na ₄ ThF ₈		δ -Na ₂ ThF ₆
20	Na ₄ ThF ₈		
14	Na ₄ ThF ₈ + NaF		

^b Preliminary data indicate two new phases in this range.

TABLE X

PHASE COMPOSITION OF MELTS IN NaF-LaF ₃ SYSTEM		
Mole % LaF ₃	Major	Phases present Minor
67		β_2 -NaLaF ₄ + LaF ₃
50		β_2 -NaLaF ₄
33		β_2 -NaLaF ₄ + NaF
25		β_2 -NaLaF ₄ + NaF

The systems involving potassium were also examined by means of samples precipitated from solutions. The precipitates from lanthanum solutions all proved to consist of anhydrous lanthanum fluoride irrespective of the potassium concentration in the solution. However, some of the potassium-uranium and potassium-thorium fluorides can be prepared in the wet way.

KU₂F₉ and KTh₂F₉ are obtained as pure and anhydrous phases by precipitation from solutions containing large excess of uranium or thorium over potassium. Anhydrous KUF₅ and KThF₅ are present as pure phases in the precipitates from

formulas deduced by him with the aid of direct chemical analyses. X-Ray diffraction patterns of these preparations showed the compounds to be isomorphous with the corresponding uranium and thorium compounds.

NaPuF₄ was found in a sample which was supposed to be plutonium metal. L. Baumbach had prepared this sample.

The isomorphous compounds of neptunium and plutonium are also listed in Table XII.

Miss Anne Plettinger gave valuable aid by taking most of the numerous X-ray diffraction patterns which were required. Mr. W. C. Koehler helped by measuring some of the diffraction patterns. Miss C. Carter and Mr. B. Holt contributed to the work by carrying out direct chemical analyses for some of the phases. The loan of micro-preparations of neptunium and plutonium made by Drs. T. LaChapelle and L. B. Magnusson, H. H. Anderson and L. Baumbach is gratefully acknowledged. The writer is also indebted to Dr. R. Livingston for some pure thorium tetrafluoride.

Abstract

A large number of double fluorides have been found in the systems KF-UF₄, KF-ThF₄, KF-LaF₃, NaF-UF₄, NaF-ThF₄ and NaF-LaF₃. In addition to the terminal compounds the following phases have been observed:

In the KF-UF₄ system: KU₂F₂₆, KU₃F₁₃, KU₂F₉, KUF₆, α-K₂UF₆, β₁-K₂UF₆, β₂-K₂UF₆, α-K₃UF₇, and α'-K₃UF₇.

In the KF-ThF₄ system: KTh₂F₂₆, KTh₂F₉, KThF₆, α-K₂ThF₆, β₁-K₂ThF₆, and K₃ThF₉.

In the KF-LaF₃ system: α-KLaF₄, β₁-KLaF₄.

In the NaF-UF₄ system: NaUF₆, α-Na₂UF₆, β₂-Na₂UF₆, γ-Na₂UF₆, and Na₃UF₇.

In the NaF-ThF₄ system: NaTh₂F₉, β₂-Na₂ThF₆, δ-Na₂ThF₆, and Na₄ThF₈.

In the NaF-LaF₃ system: β₂-NaLaF₄.

Lattice dimensions are given for all the phases. Some results for isomorphous neptunium and plutonium compounds are reported.

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A Versatile Technique for X-Ray Single Crystal Structural Analysis Applied to Benzaldehyde 2,4-Dinitrophenylhydrazone and Zinc Salts of Salicylic and Benzoic Acids

BY GEORGE L. CLARK AND HUNG KAO

It is well known among crystal structure analysts that Weissenberg diffraction photographs provide distorted projections of the levels of a reciprocal lattice, from which the true reciprocal lattice, and thence the direct lattice, may be reconstructed after more or less elaborate measurement and interpretation; whereas the comparatively new precession technique devised by Buerger¹ gives X-ray diagrams which are undistorted images of the reciprocal lattice and thus easily interpreted by inspection only. Although the precession method records only a limited part of the reciprocal lattice, especially in case of *n*-levels and has some other disadvantages, it has some distinct advantages over Weissenberg methods in that it requires a less perfect crystal, shorter time of exposure and above all simpler interpretation. Moreover the precession method makes it possible to precess along two crystal axes without changing a crystal setting if the angle between the two axes is known; thus two reciprocal lattice photographs which will give all three linear constants and two angles can be obtained.

Inasmuch as new Weissenberg and precession cameras designed by Buerger and made by one instrument maker² under the same conditions of

precision were available, the crystal holders for the two cameras could be interchanged. Thus it seemed possible that a combination usage of the precession and Weissenberg cameras might provide a simpler and more dependable technique than any single method. This paper is a brief report of our first experience in using the precession camera, presented in the hope that it may be helpful in other laboratories, as well as a record of crystallographic information so obtained for benzaldehyde 2,4-dinitrophenylhydrazone, zinc salicylate trihydrate, zinc benzoate and zinc hydrogen benzoate dihydrate.

Notes on the Precession Method

A few remarks concerning our own experience on this method may be useful. The first step in crystal analysis of course is to adjust a crystallographic axis to the precession axis. The techniques are discussed in detail in Buerger's monograph. An improved technique which we have used is the pre-usage of a 57.3 mm. Weissenberg camera. Since the 57.3 mm. Weissenberg camera and the precession camera have an interchangeable adjustable crystal holder, transfer from one to the other is easily accomplished without disturbing the crystal. From the zero-level Weissenberg pattern the possible zones and the angles between them can be determined by simple inspection.

(1) M. J. Buerger, "The Photography of the Reciprocal Lattice," ASXRED Monograph No. 1, 1944.

(2) Charles Supper, Newton Centre, Mass.