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.

$NaPuF_4$ 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 $KF-UF_4$, $KF-ThF_4$, $KF-LaF_3$, $NaF-UF_4$, $NaF-ThF_4$ and $NaF-LaF_3$. In addition to the terminal compounds the following phases have been observed:

In the $KF-UF_4$ system: KU_6F_{25}, KU_3F_{13}, KU_2F_9, KUF_5, α-K_2UF_6, β_1-K_2UF_6, β_2-K_2UF_6, α-K_3UF_7, and α'-K_3UF_7.

In the $KF-ThF_4$ system: KTh_6F_{25}, KTh_2F_9, $KThF_5$, α-K_2ThF_6, β_1-K_2ThF_6, and K_5ThF_9.

In the $KF-LaF_3$ system: α-$KLaF_4$, β_1-$KLaF_4$.

In the $NaF-UF_4$ system: $NaUF_5$, α-Na_2UF_6, β_2-Na_2UF_6, γ-Na_2UF_6, and Na_3UF_7.

In the $NaF-ThF_4$ system: $NaTh_2F_9$, β_2-Na_2ThF_6, δ-Na_2ThF_6, and Na_4ThF_8.

In the $NaF-LaF_3$ system: β_2-$NaLaF_4$.

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

CHICAGO, ILLINOIS RECEIVED FEBRUARY 27, 1948

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

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 Buerger[1] 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 maker[2] 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.

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

[2] Charles Supper, Newton Centre, Mass.

One of these zone axes can be located and set parallel to the X-ray beam by several trials on the precession camera. Once it is identified any of the others can be located by turning the crystal through the angle between them followed by readjustment of the crystal. (In the cases of an orthorhombic, a tetragonal crystal or a monoclinic crystal oriented on its b-axis the other axis can be located by simply turning the crystal.) By this method even in the case where the crystal does not possess any well developed faces, it is still possible to locate its axes unambiguously. Moreover the data from the 0-layer line Weissenberg film will provide the best criterion to check whether the correct zone axis is chosen for precession.

Various methods have been discussed in the monograph for the determination of d^* (reciprocal lattice spacing) values for n-level photographs. From the information obtained from a 0-layer Weissenberg film as described above, the value of d^* for one crystallographic axis can be determined easily from the precession photograph along the other axis and *vice versa*. For example, for a monoclinic crystal whose b-axis is parallel to the axis of the crystal holder and whose β-angle is known from the Weissenberg pattern with the crystal rotating along this axis, a precession photograph is made along one axis, say the a-, and then after turning the crystal through $\beta°$ another precession photograph is made along the c-axis. The former will give the d^* value for n-level precession along the latter axis and *vice versa*.

It has been found, in the case of zinc hydrogen benzoate dihydrate, that the value of d^*, derived from precession along the c-axis with Cu Kα radiation, is so small that the annular slit of the layer-line screen will permit more than one level of the reciprocal lattice to register simultaneously, if the layer-line screen is set at the usual distance from the crystal. This will yield patterns with entirely anomalous extinctions. The difficulty can be avoided by selecting the n-level such that the layer-line screen will be as far from the crystal as possible. An alternative way is, of course, to change the X-ray radiation to one with longer wave length (for example Cr Kα radiation).

The Suggested Simple Technique for Single Crystal Structural Analysis

After considerable experience a simple procedure has been adopted by utilizing both the 57.3 mm. Weissenberg camera and precession camera, especially for needle crystals, where the orientation of the crystal along the axis other than needle axis is very difficult, if not impossible, as follows:

(1) Set the crystal on its holder so that the needle axis coincides with the horizontal axis of the crystal holder. Suppose that the needle axis is the b-axis of a monoclinic crystal. Take a rotation pattern from which the approximate value of b can be determined simply by means of a Bernal chart.

(2) Take zero- and first-layer Equi-inclination Weissenberg photographs from which the angle β^* can be accurately measured and a^* and c^* uniquely determined.

(3) Remove the crystal holder from the Weissenberg camera to the precession camera and make a zero-level photograph along one of the other axes, say the a-axis, from which b^*, c^* and α^* are determined by inspection.

(4) Turn the crystal β^* or $180°-\beta^*$ and make the zero-level precession photograph along c-axis, and thus determine a^*, b^*, γ^*. Take the n-level precession photographs using the d^* value obtained from (3).

(5) Turn the crystal back to the position (3) and make n-level photographs along a-axis using the d^* found in (4).

By these operations all lattice translations and angles of the reciprocal and hence of the direct lattice can be found. The space group can be determined by examining the extinction data from these two sets of precession photographs. This is usually enough, but additional n-layer line Weissenberg photographs along the b-axis can be made, if necessary.

The Crystal Structure of Benzaldehyde- 2,4-Dinitrophenylhydrazone

This compound was chosen as a logical extension of the work in the laboratory on the X-ray diffraction and crystallography of the 2,4-dinitrophenylhydrazones of aldehydes and ketones.[3]

The benzaldehyde derivative was prepared by the method of Shriner and Fuson.[4] Orange crystals with sharp melting point 233–4° were obtained after four recrystallizations from ethyl acetate. No polymorphism was observed in crystallization from other solvents such as glacial acetic acid. Well-defined crystals were easily obtained. The density of the crystal determined by flotation in a solution of silver nitrate was 1.54. The "ideal" density calculated from X-ray data was 1.569.

X-Ray Data.—The results obtained by using the above procedure for single crystal analysis and that obtained by the Weissenberg method are summarized as follows for comparison:

		From Precession	From Weissenberg
(1) Unit cell constants	α	90°	90°
	β	92.7° ± 0.2°	92.8° ± 0.2°
number of molecules per unit cell		4	4
a (A. U.)		12.8 ± 0.1	13.1 ± 0.1
b		6.78 ± 0.01	6.79 ± 0.01
c		14.26 ± 0.02	14.20 ± 0.05
(2) Space-group		$P2_1/c$	$P2_1/c$
Extinctions (from both):	$h0l$ appears only when $l = 2n$ $0k0$ appears only when $k = 2n$		

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[3] G. L. Clark, W. I. Kaye and T. D. Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 310 (1946).

[4] "Identification of Organic Compounds," 2nd ed., 1940.

The Crystal Structure of Zinc Salicylate Trihydrate

Because of some interest in zinc salts of salicylic (*o*-hydroxybenzoic) and benzoic acids and their complexes with boric acid as antiseptics, a determination of structure may have added significance. Zinc salicylate trihydrate is formed by mixing equal volumes of 2-molar sodium salicylate and 1-molar zinc sulfate solutions at room temperature. A white powder rapidly separates which may be recrystallized to fine single crystals. It has been claimed that the crystals are needles, but only in the first stage of crystallization was this found to be true since the crystals lost their acicular shape during growth. The composition of the crystal as zinc salicylate trihydrate, $Zn(C_7H_5O_3)_2 \cdot 3H_2O$, is verified by its powder pattern, and by chemical analysis.

For this crystal a procedure similar to that just described was used. From the Weissenberg data the following results are obtained:

$\beta = 94^\circ$
$a = 15.40 \pm 0.02$ A. U.
$b = 5.36 \pm 0.01$ A. U.
$c = 9.18 = 0.01$ A. U.

Extinctions: hkl appears only when $h + k = 2n$
$h0l$, $h = 2n$: $0k0$. $k = 2n$
Space group C2/m. C2. or Cm

From zero, first and second layer fine precession photographs around all three axes, the following data are obtained

$\beta = 93.8^\circ \pm 0.2^\circ$
$a = 15.40 \pm 0.02$ A. U.
$b = 5.37 \pm 0.01$ A. U.
$c = 9.18 \pm 0.01$ A. U.

Extinctions and space group as above.

The measured density is 1.64 from which about 2 molecules per unit cell are found. The ideal density for $n = 2$ is 1.653 g./ml.

The Crystal Structure of Zinc Benzoate

These crystals were prepared by double recrystallization from a pure commercial material, or from the product obtained by treating zinc carbonate with benzoic acid followed by slow evaporation of the solvent. Chemical analysis indicated pure anhydrous $Zn(C_6H_5COO)_2$, with a measured density of 1.54 by flotation in chloroform and carbon tetrachloride. Both equi-inclination Weissenberg and precession patterns gave concordant data as follows:

Monoclinic $\beta = 94^\circ 26'$
$a = 10.67 \pm 0.02$ A. U.
$b = 12.94 \pm 0.02$ A. U.
$c = 19.22 \pm 0.02$ A. U.

Systematic extinctions: hkl all appear
$h0l$ appears only when $l = 2n$
$0k0$ appears only when $k = 2n$

Space group $P2_1/c$

Number of molecules per unit cell 8. The "ideal" density calculated 1.546 g./ml.

The Crystal Structure of Zinc Hydrogen Benzoate Dihydrate

The compound was prepared either by adding zinc chloride to an aqueous solution containing sodium benzoate and benzoic acid or by the reaction of benzoic acid with zinc carbonate in aqueous solution. It was also obtained, as observed in this work, by the addition of benzoic acid to zinc borate which was suspended in hot water; from such solutions benzoic acid first settled out, then long colorless needles of $ZnH_2(C_6H_5COO)_4 \cdot 2H_2O$ crystallized out (for zinc found 11.17%; calculated 11.13%). The compound is soluble in ether and alcohol and slightly soluble in benzene. The crystals have about the same density as pure chloroform at 32°, 1.47 g./ml.

The usual series of equi-inclination Weissenberg and precession patterns in 0, 1 and 2-levels were made yielding the following data:

Orthorhombic, with shortest translations

$a = 5.20 \pm 0.02$ A. U.
$b = 25.4 \pm 0.02$ A. U.
$c = 40.0 \pm 0.5$ A. U.

Compounds	Crystal habits	Crystal system	Cell constants	Space group	n	"Ideal" density
Benzaldehyde 2,4-dinitrophenylhydrazone	Orange plates	Monoclinic	a 12.8 ± 0.1 A. U. b 6.79 ± 0.01 c 14.23 ± 0.02 β 92.8° ± 0.2°	$P2_1/c$	4	1.569
Zinc salicylate trihydrate	Colorless plates	Monoclinic	a 15.4 ± 0.02 b 5.36 ± 0.01 c 9.18 ± 0.01 β 94.0° ± 0.2°	C2/m or C2 or Cm	2	1.653
Zinc benzoate	Colorless plates	Monoclinic	a 10.67 ± 0.02 b 12.94 ± 0.02 c 19.22 ± 0.02 β 94.4° ± 0.2°	$P2_1/c$	8	1.546
Zinc hydrogen benzoate dihydrate	White needles	Orthorhombic	a 5.20 ± 0.02 b 25.4 ± 0.2 c 40.0 ± 0.5	F d d	8	1.47

Systematic extinctions:

hkl appears only when all odd or all even
0*kl* appears only with $k = 2n$ and $l = 2n$
*h*0*l* appears only with $h = 2n$, $l = 2n$ and $h + l = 4n$
*hk*0 appears only with $h = 2n$, $k = 2n$ and $h + k = 4n$
Space group: F d d

The number of molecules per unit cell is 8 and the "ideal" density of the crystal is 1.478 g./ml. The compound is unusually interesting because of the very small *a* spacing in comparison with *b* and *c*, probably indicating very flat molecules lying extended in the *bc* plane, also probably with hydrogen bonding. Hence this offers an excellent opportunity for a two-dimensional Fourier analysis of electron densities which is now being carried out.

Summary

1. A new simple procedure for single crystal analysis by the combination of the equi-inclination Weissenberg and the Buerger precession methods has been investigated and its application has been illustrated with practical problems. This new procedure provides a simple solution for needle crystals the orientation of which, along the crystallographic axes other than needle axis, is extraordinarily difficult.

2. Determinations were made of crystal habits, densities, lattice constants and probable space-groups of four compounds, for which no previous X-ray and crystallographical data are available, as tabulated on the preceding page.

URBANA, ILLINOIS RECEIVED FEBRUARY 9, 1948

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Contents at High Temperatures of Vanadium Dichloride and Vanadium Trichloride[1]

BY E. G. KING[2]

In continuation of a program of study of the thermodynamic properties of vanadium compounds, high-temperature heat contents of vanadium dichloride and vanadium trichloride were measured. No previous similar values exist for these substances, but low temperature heat capacity and entropy data have been reported by Shomate.[3]

Materials

The samples used in this work were portions of the materials prepared for previous low temperature heat capacity measurements, and the methods of preparation and the analyses were described by Shomate.[3] Before the present measurements were begun, both compounds were given a preliminary heating in vacuum, the dichloride to 850° and the trichloride to 150°.

Measurements and Results

The high temperature heat content measurements were made by the "dropping" method with previously described[4,5] apparatus. Frequent calibrations of the furnace thermocouple at the gold point were made by the method described by Southard.[4]

The samples were contained in platinum–rhodium alloy capsules. Two capsules were employed for the dichloride, containing, respectively, 8.9608 and 8.6643 g. (corrected to vacuum) of sample. These capsules were sealed by platinum welding after replacing air in the pore space by helium. One capsule, containing 7.4429 g. (corrected to vacuum) of sample was used for the trichloride. It was sealed by gold soldering, after the pore space was filled with helium. Corrections for the capsules were made by means of separate measurements of the platinum–rhodium alloy and the known heat contents of gold and platinum. These corrections amounted to 25% of the total measured heats for the dichloride and 28% for the trichloride.

The experimental results, expressed in defined calories[6] (1 cal. = 4.1833 int. joules), are in Table

TABLE I

HIGH-TEMPERATURE HEAT CONTENT OF VCl_2
(Mol. wt. = 121.86)

T. °K.	$H_T - H_{298.16}$, cal./mole	*T*, °K.	$H_T - H_{298.16}$, cal./mole
339.9	760	875.9	10.730
389.0	1670	971.3	12,620
393.9	1745	1029.5	13,850
471.7	3125	1072.7	14,640
570.4	4895	1172.9	16,660
673.8	6830	1272.5	18.740
773.8	8740		

HIGH-TEMPERATURE HEAT CONTENT OF VCl_3
(Mol. wt. = 157.32)

T. °K.	$H_T - H_{298.16}$, cal./mole	*T*. °K.	$H_T - H_{298.16}$, cal./mole
343.1	1070	704.9	9,875
400.3	2405	803.8	12,420
502.2	4775	902.5	14.870
601.9	7225		

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(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Chemist, Pacific Experiment Station, Bureau of Mines.

(3) Shomate, THIS JOURNAL, **69**, 220 (1947).

(4) Southard, *ibid.*, **63**, 3142 (1941).

(5) Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper*, 686, 1946, 34 pp.

(6) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).